

[Document Name] DESCRIPTION

[Title of Invention] POWDER FOR FORMING THERMAL SPRAYING LAYER, CERMET LAYER, CERMET COATING MATERIAL, AND METHOD OF MANUFACTURING
5 CERMET COATING MATERIAL

[Technical Field]

[0001]

10 The present invention relates to a powder for forming a thermal spraying layer, a cermet layer, a cermet coating material, and a method of manufacturing a cermet coating material.

[Background Art]

[0002]

15 To improve surface properties of a base material such as metal, there has been used a process of forming a coating on the base material using a spray (thermal spray) method in which an alloy powder or the like is sprayed to the surface of the base material. Such a spray method is widely applied to various kinds of members because the spray method can be carried out relatively easily. In particular, the spray method is used as an effective approach in various industrial fields when it is necessary to impart corrosion resistance and/or wear
20 resistance partially to a surface of a base material.

[0003]

In general, a Ni-based self-fluxing alloy, a Co-based stellite alloy or the like is used as an alloy powder material for forming a coating on a base material using the spray method because such materials allow the coating to exhibit good interfacial adhesion to the base
25 material. In particular, it is known that the interfacial adhesion of the Ni-based self-fluxing alloy to the base material can be further enhanced by heating, after forming a thermal spraying layer via thermal spraying, the thermal spraying layer to perform a fusing treatment (melting treatment) so that the thermal spraying layer is molten to thermally diffuse into the base material. However, while the Ni-based self-fluxing alloy and the Co-based stellite alloy
30 exhibit good interfacial adhesion to the base material, the corrosion resistance and wear resistance of the thermal spraying layer are insufficient, which may be problematic.

[0004]

To overcome the above, for example, Patent Document 1 discloses a technique of using a cermet material that contains a Mo_2NiB_2 -type composite boride as the powder material

to be used for the spray method, thereby improving the corrosion resistance and wear resistance.

[Prior Art Document]

[Patent Document]

5 [0005]

[Patent Document 1] JP 2009-68052 A

[Summary of Invention]

[Problems to be solved by Invention]

10 [0006]

According to the technique as described in the above Patent Document 1, however, while the Mo_2NiB_2 -type composite boride to be the cermet layer exhibits good corrosion resistance and wear resistance, the interfacial adhesion to the base material may possibly be poor compared to the above-described Ni-based self-fluxing alloy. To enhance the interfacial
15 adhesion to the base material, there may also be used a method of performing the fusing treatment for the cermet layer which comprises the Mo_2NiB_2 -type composite boride, but in this case the heating temperature may have to be a higher temperature than $1,200^\circ\text{C}$ which is a melting temperature of the cermet layer. There is therefore a concern that the base material deforms and the properties deteriorate due to the excessive heat.

20 [0007]

In addition, there has conventionally been another problem in that, when a cermet coating material formed with the cermet layer is used as a member of a resin molding machine or the like, if cracks and delamination occur in the cermet layer, broken pieces of the cermet layer are mixed in the resin, which may cause contamination of the resin and malfunction of
25 the resin molding machine. Therefore, such broken pieces of the cermet layer mixed in the resin may have to be removed in an additional step. For example, when the broken pieces of the cermet layer mixed in the resin have a magnetic property, it is possible to easily collect the broken pieces using a magnet, and the contamination of the resin and the malfunction of the resin molding machine can thereby be prevented. In the technique as described in the above
30 Patent Document 1, however, the cermet layer to be formed has a poor magnetic property. Therefore, such a collecting method using a magnet cannot be applied, and the broken pieces of the cermet layer are difficult to be picked out from the resin, which may lead to deterioration in the quality of resin molded products to be obtained and a poor production yield.

[0008]

The present invention has been created in view of such actual circumstances, and an object of the present invention is to provide a powder for forming a cermet layer which has a magnetic property and is excellent in the corrosion resistance and wear resistance and to which a fusing treatment can be carried out at a relatively low temperature to enhance the interfacial adhesion to a base material. Another object of the present invention is to provide a cermet layer and a cermet coating material which are obtained using such a powder for forming a thermal spraying layer. Still another object of the present invention is to provide a method of manufacturing such a cermet coating material.

[Means for solving problems]

[0009]

The present inventors have found that the above objects can be achieved by using a powder that contains a $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride and has a specific composition range, as a powder for forming a cermet layer. The inventors have thus accomplished the present invention.

[0010]

That is, according to an aspect of the present invention, there is provided a powder for forming a thermal spraying layer. The powder comprises a $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride. The powder is characterized by having a composition of 5.5-6.5 wt% of B, 48.8-57.7 wt% of Mo, 1.8-2.5 wt% of Si, 6.0-10.0 wt% of Cr, 1.0-3.0 wt% of V, 6.0-10.0 wt% of Fe, and 17.0 wt% or more of Ni.

[0011]

According to another aspect of the present invention, there is provided a cermet layer formed by thermally spraying the above powder for forming a thermal spraying layer. The cermet layer is characterized by comprising 55.0-75.0 wt% of a hard phase and the balance of a binder phase, wherein the hard phase comprises the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride, and the binder phase comprises a Ni-based alloy as a main component.

[0012]

According to still another aspect of the present invention, there is provided a cermet coating material comprising a base material and the above cermet layer formed on the base material.

According to an embodiment of the present invention, there may be provided a cermet coating material comprising a diffusion layer formed by performing a melting treatment to heat the above cermet layer at 1,000-1,150°C so that the base material and the cermet layer are

thermally diffused to each other.

[0013]

According to an embodiment of the present invention, the above base material may preferably be alloy steel, carbon steel or stainless steel in any of the above cermet coating materials.

[0014]

According to a further aspect of the present invention, there is provided a method of manufacturing a cermet coating material. The method comprises a step of spraying a powder for forming a thermal spraying layer onto a base material thereby to form a cermet layer on the base material. The powder comprises a $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride. The method is characterized by the following features. The powder has a composition of 5.5-6.5 wt% of B, 48.8-57.7 wt% of Mo, 1.8-2.5 wt% of Si, 6.0-10.0 wt% of Cr, 1.0-3.0 wt% of V, 6.0-10.0 wt% of Fe, and 17.0 wt% or more of Ni. The cermet layer comprises 55.0-75.0 wt% of a hard phase and the balance of a binder phase. The hard phase comprises the $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride. The binder phase comprises a Ni-based alloy as a main component.

[0015]

The method of manufacturing a cermet coating material according to the present invention may preferably further comprise a step of performing a melting treatment to heat the cermet layer at 1,000-1,150°C after forming the cermet layer on the base material.

[Effect of Invention]

[0016]

According to the present invention, there can be provided a powder for forming a cermet layer which has a magnetic property and is excellent in the corrosion resistance and wear resistance and to which a fusing treatment can be carried out at a relatively low temperature to enhance the interfacial adhesion to the base material. The present invention can also provide a cermet layer and a cermet coating material which are obtained using such a powder for forming a thermal spraying layer, and a method of manufacturing such a cermet coating material.

[Brief Description of Drawings]

[0017]

[FIG. 1] FIG. 1 is a set of diagrams illustrating evaluation results of wear resistance of cermet layers in examples and comparative examples.

[FIG. 2] FIG. 2 is a view illustrating a test piece for measuring an interfacial adhesion force of a cermet layer.

[FIG. 3] FIG. 3 is a set of diagrams illustrating evaluation results of interfacial adhesion of cermet layers in examples and comparative examples.

5

[Mode(s) for Carrying out the Invention]

[0018]

<Powder for forming thermal spraying layer>

10 A powder for forming a thermal spraying layer according to the present invention will first be described.

The powder for forming a thermal spraying layer according to the present invention is an alloy powder for forming a cermet layer on a base material by thermal spraying, and comprises a $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride. The powder is characterized by having a composition of 5.5-6.5 wt% of B, 48.8-57.7 wt% of Mo, 1.8-2.5 wt% of Si, 6.0-10.0 wt% of Cr, 1.0-3.0 wt% of V, 6.0-10.0 wt% of Fe, and 17.0 wt% or more of Ni.

15 [0019]

According to the present invention, the powder for forming a thermal spraying layer contains the $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride and the composition is within the above range thereby to exhibit advantageous effects as below. That is, first, when a cermet layer is formed by thermally spraying the powder for forming a thermal spraying layer according to the present invention to the base material, the obtained cermet layer can be excellent in the corrosion resistance and wear resistance owing to the action of the $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride which exhibits good corrosion resistance and wear resistance. In addition, the obtained cermet layer can have a lowered melting temperature because Si acts to reduce the eutectic point. This allows the heating temperature to be more lowered when a fusing treatment is performed for the cermet layer, which has been formed by thermally spraying the powder for forming a thermal spraying layer according to the present invention to the base material, to have an enhanced interfacial adhesion to the base material. According to the present invention, therefore, when the fusing treatment is performed for the obtained cermet layer, it is possible to thermally diffuse the cermet layer into the base material to form a diffusion layer while preventing deformation of the base material and deterioration in the properties due to heat, thereby to effectively enhance the interfacial adhesion between the base material and the cermet layer.

25 [0020]

Moreover, according to the present invention, a certain amount of Fe is contained in the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride which constitutes the powder for forming a thermal spraying layer, so that the cermet layer to be obtained has a magnetic property. In particular, according to the present invention, the content of Fe in the composite boride is within the above range thereby to allow the cermet layer to have an appropriate magnetic property. Therefore, when a cermet coating material obtained by thermally spraying the powder for forming a thermal spraying layer to the base material is used as a member of a resin molding machine or the like, even if cracks and delamination occur in the cermet layer and broken pieces of the cermet layer are mixed in the resin, it is possible to easily collect the broken pieces using a magnet. This allows to prevent the contamination of resin produced by the resin molding machine and the malfunction of the resin molding machine.

[0021]

According to the present invention, the cermet layer can be formed by thermally spraying the above-described powder for forming a thermal spraying layer of the present invention to the base material. The obtained cermet layer ordinarily contains the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride, and may be formed of hard phases that contribute to the hardness (wear resistance) of the cermet layer and binder phases that form matrices for binding such hard phases.

[0022]

Descriptions will then be directed to the action of each element contained in the powder for forming a thermal spraying layer according to the present invention.

[0023]

B (boron) is an element that, when incorporated in the cermet layer, is for forming the composite boride to be the hard phases in the cermet layer. The content ratio of B is within the above range thereby to allow the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride to be appropriately formed in the cermet layer, so that the cermet layer obtained can be excellent in the wear resistance and strength. If the content ratio of B is unduly low, the amount of formation of the composite boride may be reduced to possibly deteriorate the wear resistance of the cermet layer to be obtained. If, on the other hand, the content ratio of B is unduly high, the amount of formation of the composite boride may increase so that the contact ratio between the hard phases increases in the cermet layer obtained. This may result in deterioration of the mechanical strength.

[0024]

Mo (molybdenum) is an element that, like B, when incorporated in the cermet layer, is

for forming the composite boride to be the hard phases in the cermet layer. In addition, when incorporated in the cermet layer, a part of Mo dissolves in the binder phases in the cermet layer thereby to have an effect of enhancing the corrosion resistance. Unduly low content ratio of Mo may possibly deteriorate the wear resistance and corrosion resistance of the cermet layer to be obtained. On the other hand, unduly high content ratio of Mo may cause third phases to be formed when Mo is incorporated in the cermet layer, and the mechanical strength will deteriorate. In the present invention, a part of Mo of the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride may be substituted by other element, such as W, Nb, Zr, Ti, Ta and Hf, when incorporated in the cermet layer.

[0025]

Ni (nickel) is an element that, like B and Mo, when incorporated in the cermet layer, is for forming the composite boride to be the hard phases in the cermet layer. Ni is also a primary element that, when incorporated in the cermet layer, forms a Ni-based alloy to be the binder phases in the cermet layer, and contributes to the excellent corrosion resistance. In the present invention, a part of Ni of the composite boride in the cermet layer obtained may be substituted by other element, such as Cr, V and Fe, as will be described later. Examples of the Ni-based alloy which constitutes the binder phases when incorporated in the cermet layer may include, but are not particularly limited to, an alloy of Ni and at least one kind of metal selected from Co, Cr, Mo, W, Fe, Mn, and V.

[0026]

Cr (chrome), when incorporated in the cermet layer, substitutes for and dissolves into Ni in the composite boride to be the hard phases in the cermet layer, and has an effect of stabilizing the crystal structure of the composite boride to tetragonal structure. The added Cr, when incorporated in the cermet layer, dissolves also into the binder phases in the cermet layer thereby to considerably enhance the corrosion resistance, wear resistance, high-temperature properties and mechanical properties. If the Cr content is unduly large, boride such as Cr_5B_3 may be formed in the cermet layer obtained, so that the mechanical strength will be deteriorated.

[0027]

Fe (iron) is an element that, when incorporated in the cermet layer, is for forming the composite boride by substituting for and dissolving into Ni in the composite boride to be the hard phases in the cermet layer. A part of Fe, when incorporated in the cermet layer, dissolves also into the binder phases in the cermet layer. According to the present invention, Fe is contained thereby to be able to impart a magnetic property to the cermet layer obtained.

In particular, by setting the content ratio of Fe within the above range, the magnetic property imparted to the cermet layer can be appropriately adjusted. If the content ratio of Fe is unduly low, there cannot be sufficiently obtained the effect of imparting the magnetic property to the cermet layer obtained, while on the other hand if the content ratio of Fe is unduly high, the hardness of the cermet layer obtained deteriorates, which may result in poor wear resistance.

[0028]

V (vanadium), when incorporated in the cermet layer, substitutes for and dissolves into Ni in the composite boride to be the hard phases in the cermet layer, and has an effect of stabilizing the crystal structure of the composite boride to tetragonal structure. A part of V, when incorporated in the cermet layer, dissolves also into the binder phases in the cermet layer to enhance the wear resistance. As described above, according to the present invention, Fe is contained in the powder for forming a thermal spraying layer thereby to be able to impart a magnetic property to the cermet layer obtained, but the content ratio of Fe is increased to impart the magnetic property, the hardness of the cermet layer obtained tends to deteriorate. For this reason, according to the present invention, V is contained in the powder for forming a thermal spraying layer, and the content of Fe and the content of V in the powder for forming a thermal spraying layer are balanced thereby to enhance the hardness while imparting the magnetic property to the cermet layer obtained. If the content of V is unduly small, the effect of adding V may be difficult to be obtained, while on the other hand if the content of V is unduly large, boride such as VB may be formed in the cermet layer obtained, so that the mechanical strength will be deteriorated.

[0029]

Si (silicon) is an element that, when incorporated in the cermet layer, constitutes the binder phases in the cermet layer, and has an effect of lowering the melting temperature of the cermet layer obtained. If the content ratio of Si is unduly low, there cannot be sufficiently obtained the effect of lowering the melting temperature of the cermet layer obtained, and there is a concern that the base material deforms and the properties deteriorate due to the excessive heat when the fusing treatment is performed at the melting temperature of the cermet layer. If, on the other hand, the content ratio of Si is unduly high, in addition to the disadvantage that there cannot be obtained the effect of lowering the melting temperature of the cermet layer obtained, the content of silicide increases to possibly deteriorate the properties such as toughness.

[0030]

Each element contained in the powder for forming a thermal spraying layer acts in the above manner.

[0031]

In the powder for forming a thermal spraying layer according to the present invention, the content ratio of Fe is sufficient if it is within a range of 6.0-10.0 wt% as described above, but may preferably be within a range of 6.0-8.0 wt%. By setting the content ratio of Fe within the above range in the powder for forming a thermal spraying layer, an appropriate magnetic property can be imparted to the cermet layer obtained. If the content ratio of Fe is unduly low in the powder for forming a thermal spraying layer, a sufficient magnetic property cannot be imparted to the cermet layer obtained. If the content ratio of Fe is unduly high, the hardness of the cermet layer obtained will be deteriorated.

[0032]

In the powder for forming a thermal spraying layer according to the present invention, the content ratio of V is sufficient if it is within a range of 1.0-3.0 wt% as described above, but may preferably be within a range of 1.0-2.0 wt%. By setting the content ratio of V within the above range in the powder for forming a thermal spraying layer, the hardness of the cermet layer obtained can be appropriately enhanced. As described above, according to the present invention, Fe and V are contained in the powder for forming a thermal spraying layer thereby to allow for both imparting the magnetic property to and enhancing the hardness of the cermet layer obtained. It is preferred in this case that the content ratio of V is adjusted depending on the content ratio of Fe.

[0033]

In the powder for forming a thermal spraying layer according to the present invention, the content ratio of Si is sufficient if it is within a range of 1.8-2.5 wt% as described above. By setting the content ratio of Si within the above range in the powder for forming a thermal spraying layer, the cermet layer obtained can have a lowered melting temperature, and it is possible to lower the heating temperature necessary when the fusing treatment is performed for the cermet layer.

[0034]

As can be understood, the powder for forming a thermal spraying layer according to the present invention may contain elements that are unavoidably mixed therein, to an extent that does not inhibit the effect of imparting the magnetic property to the cermet layer obtained, the effect of enhancing the hardness, and the effect of lowering the melting temperature of the cermet layer.

[0035]

<Base material>

The base material to which the powder for forming a thermal spraying layer according to the present invention is sprayed is not particularly limited, and various kinds of metal materials can be used as the base material. Considering that the material strength is excellent, preferred examples of the base material include alloy steel, carbon steel, stainless steel, tool steel, and powder high-speed steel, among which the alloy steel, carbon steel and stainless steel may preferably be used because the hardness is relatively low and the formation of the thermal spraying layer is thus easy.

[0036]

<Cermet layer>

The cermet layer according to the present invention is obtained by thermally spraying the above-described powder for forming a thermal spraying layer to the base material, and has the hard phases which comprise the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride. The balance comprises the binder phases which include a Ni-based alloy as the main component.

[0037]

Here, the hard phases in the cermet layer are phases that contribute to the hardness of the cermet layer, i.e., the wear resistance.

[0038]

The content ratio of the hard phases in the cermet layer may preferably be 55.0-75.0 wt%, more preferably 65.0-75.0 wt%, and further preferably 70.0-75.0 wt%. By setting the content ratio of the hard phases within the above range, it is possible to enhance the corrosion resistance and wear resistance of the cermet coating material obtained. If the content ratio of the hard phases is unduly low, the cermet layer will be excessively soft to deteriorate the wear resistance. If the content ratio of the hard phases is unduly high, the dispersibility of the hard phases will be considerably poor to deteriorate the strength. The content ratio of the hard phases in the cermet layer can be controlled, for example, by adjusting the content ratio of Mo and B in the powder for forming the cermet layer.

[0039]

The binder phases in the cermet layer are phases that are to form matrices for binding the hard phases.

[0040]

The binder phases in the cermet layer comprise a Ni-based alloy as the main component. Such a Ni-based alloy is formed of Ni that is contained in the above powder for

forming a thermal spraying layer. Examples of the Ni-based alloy include, but are not particularly limited to, an alloy of Ni and at least one kind of metal selected from Co, Cr, Mo, W, Fe, Mn, and V.

[0041]

5 According to the present invention, since the cermet layer is formed using the above powder for forming a thermal spraying layer, the content ratios of Fe and V in the cermet layer are ordinarily the same as those in the powder for forming a thermal spraying layer, i.e., Fe: 6.0-10.0 wt%, and V: 1.0-3.0 wt%. Therefore, in the cermet layer according to the present invention, Fe and V act in the above-described manner thereby to allow for both imparting the
10 magnetic property and enhancing the hardness. Here, Fe and V contained in the cermet layer may be included in either of the hard phases or the binder phases in the cermet layer, or may also be included both in the hard phases and in the binder phases.

[0042]

 The hardness of the cermet layer may preferably be 1,200 or more, and more
15 preferably 1,250 or more, as the Vickers hardness (HV). By setting the Vickers hardness of the cermet layer within the above range, it is possible to impart excellent wear resistance to the cermet layer.

[0043]

 Moreover, since the cermet layer according to the present invention is formed using
20 the above powder for forming a thermal spraying layer, the content ratio of Si in the cermet layer is ordinarily the same as that in the powder for forming a thermal spraying layer, i.e., Si: 1.8-2.5 wt%. Therefore, in the cermet layer according to the present invention, Si acts in the above-described manner thereby to allow the heating temperature to be a relatively low temperature when the fusing treatment is performed. Here, Si contained in the cermet layer
25 may be included in either of the hard phases or the binder phases in the cermet layer, or may also be included both in the hard phases and in the binder phases.

[0044]

 As a cermet layer formed on a base material, there has conventionally been used a cermet layer that contains a Mo_2NiB_2 -type composite boride as the component of hard phases.
30 However, the cermet layer which contains such a Mo_2NiB_2 -type composite boride is problematic because the interfacial adhesion to the base material may be poor. To enhance the interfacial adhesion between the cermet layer and the base material, there may also be used a method of performing the fusing treatment after the cermet layer is formed on the base material. In this case, however, the heating temperature for performing the fusing treatment

may have to be a higher temperature than 1,200°C because the cermet layer which contains the Mo₂NiB₂-type composite boride may ordinarily have a melting temperature of 1,200°C or higher. There is therefore a concern that the base material deforms and the properties deteriorate due to the excessive heat.

5 [0045]

In contrast, the cermet layer according to the present invention is configured such that Si is contained in the cermet layer which contains the Mo₂(Ni, Cr, V, Fe)B₂-type composite boride, thereby to lower the melting temperature. Therefore, the fusing treatment can be performed at a low temperature, and the cermet layer can thus be thermally diffused into the
10 base material to form a diffusion layer thereby to effectively enhance the interfacial adhesion between the base material and the cermet layer while preventing the deformation of the base material and the deterioration in the properties.

[0046]

The melting temperature of the cermet layer according to the present invention can be
15 controlled, for example, by varying the content ratio of Si in the binder phases. The melting temperature may preferably be 1,000-1,150°C, and more preferably 1,000-1,100°C.

[0047]

When the fusing treatment is performed for the cermet layer according to the present invention, the heating temperature during the fusing treatment can be set depending on the
20 melting temperature of the cermet layer. The heating temperature may preferably be 1,000-1,150°C, and more preferably 1,000-1,100°C. According to the present invention, the heating temperature in the fusing treatment may be set within the above range thereby to effectively prevent the deformation of the base material and the deterioration in the properties due to heat when the fusing treatment is performed for the cermet layer. The heating time
25 when performing the fusing treatment is not particularly limited, but may appropriately be set depending on the thickness of the cermet layer and other factors.

[0048]

<Cermet coating material>

The cermet coating material according to the present invention can be obtained by
30 forming the above-described cermet layer on the base material. The cermet coating material according to the present invention thus comprises the base material and the cermet layer formed on the base material. The cermet coating material according to the present invention may further comprise a diffusion layer in addition to the above. The diffusion layer can be formed by thermally diffusing the base material and the cermet layer into each other. That is,

the diffusion layer can be formed by performing the fusing treatment for the cermet layer of the cermet coating material under the above-described conditions so that the base material and the cermet layer are thermally diffused into each other.

[0049]

5 <Method of manufacturing cermet coating material>

A method of manufacturing the cermet coating material according to the present invention will then be described.

[0050]

10 First, a raw material powder is prepared for manufacturing the powder for forming a thermal spraying layer. As the raw material powder, there may be prepared a powder having a mixing ratio of 5.5-6.5 wt% of B, 48.8-57.7 wt% of Mo, 1.8-2.5 wt% of Si, 6.0-10.0 wt% of Cr, 1.0-3.0 wt% of V, 6.0-10.0 wt% of Fe, and 17.0 wt% or more of Ni.

[0051]

15 Next, the prepared raw material powder is processed into the powder for forming a thermal spraying layer. Any method can be employed as the method of processing the raw material powder into the powder for forming a thermal spraying layer as long as the method is designed such that the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride is formed from the raw material powder. For example, there may be mentioned a method in which: a binder and an organic solvent are added to the raw material powder; they are mixed and crushed using a
20 crusher such as a ball mill; the raw material powder after being mixed and crushed is granulated using a spray dryer; and the granulated powder is sintered and then classified. Through this method, there can be obtained the powder for forming a thermal spraying layer according to the present invention, containing the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride and having a composition of 5.5-6.5 wt% of B, 48.8-57.7 wt% of Mo, 1.8-2.5 wt% of Si,
25 6.0-10.0 wt% of Cr, 1.0-3.0 wt% of V, 6.0-10.0 wt% of Fe, and 17.0 wt% or more of Ni. As can be understood, the powder for forming a thermal spraying layer according to the present invention may contain elements that are unavoidably mixed therein, to an extent that does not inhibit the effect of lowering the melting temperature of the cermet layer obtained.

[0052]

30 When the mixing and crushing are performed using a ball mill and the like, the particle diameter of the raw material powder after being mixed and crushed is not particularly limited. Any particle diameter can be employed as long as a reaction of forming the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride progresses appropriately when the raw material powder after being mixed and crushed is granulated and sintered.

[0053]

Conditions when performing the sintering may fall under a scope that allows the reaction of forming the $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride to progress appropriately. For example, there may be employed conditions of a temperature of 1,000-1,150°C, a sintering
5 time of 30-90 minutes, and a rate of temperature rise of 0.5-60°C/min.

[0054]

In view of making it easy to perform thermal spray, the size of the powder to be manufactured for forming a thermal spraying layer may preferably be 10-200 μm , and more preferably 32-150 μm , as a particle diameter.

[0055]

Subsequently, the powder for forming a thermal spraying layer is sprayed to the base material using a spray method to form the cermet layer. Through this method, according to the present invention, there can be manufactured a cermet coating material that is formed such that the base material is coated with the cermet layer. As the spray method, there can be
15 employed any of flame spray and high velocity flame spray which are less likely to give thermal effect when the cermet layer is formed. Among them, the high velocity flame spray is preferred because the spray velocity of the powder for forming a thermal spraying layer is high and a dense film can be formed.

[0056]

The thickness of the cermet layer to be formed may preferably be 0.05-2.0 mm, and more preferably 0.2-1.0 mm. If the thickness of the cermet layer to be formed is less than 0.05 mm, pores may remain in the cermet layer to trigger delamination of the cermet layer from the base material, and the wear resistance tends to deteriorate because the cermet layer is thin. If, in contrast, the thickness of the cermet layer to be formed is larger than 2.0 mm, the
25 residual stress will be large due to heat at the time of forming the cermet layer, and the interfacial adhesion between the cermet layer and the base material tends to be poor.

[0057]

In such a manner as described above, the cermet coating material is manufactured using the powder for forming a thermal spraying layer according to the present invention.

[0058]

It is preferred in the present invention to further perform a fusing treatment for the cermet coating material thus manufactured. By performing the fusing treatment for the cermet coating material, the cermet layer thermally diffuses into the base material to form a diffusion layer, so that the interfacial adhesion between the base material and the cermet layer

can be enhanced. A method of the fusing treatment is not particularly limited. For example, there can be employed a method such as through heating by a flame torch using acetylene as a fuel and oxygen, high-frequency induction heating, heating by an atmosphere furnace, or heating by a vacuum furnace. Considering that the cermet layer can stably be thermally
5 diffused, it is preferred to use the method of heating by a vacuum furnace. The heating temperature when performing the fusing treatment is the same as that in the above-described conditions.

[0059]

According to the present invention, the powder for forming a thermal spraying layer
10 contains the $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride and has a composition of 5.5-6.5 wt% of B, 48.8-57.7 wt% of Mo, 1.8-2.5 wt% of Si, 6.0-10.0 wt% of Cr, 1.0-3.0 wt% of V, 6.0-10.0 wt% of Fe, and 17.0 wt% or more of Ni, and it is thereby possible to form, through thermal spray, a cermet layer which is excellent in the corrosion resistance and wear resistance.

[0060]

15 In addition, according to the cermet coating material of the present invention obtained using such a powder for forming a thermal spraying layer, the heating temperature can be a relatively low temperature when the fusing treatment is performed. Therefore, it is possible to thermally diffuse the cermet layer into the base material to form a diffusion layer while preventing deformation of the base material and deterioration in the properties due to heat,
20 thereby to effectively enhance the interfacial adhesion between the base material and the cermet layer. Moreover, the cermet coating material of the present invention is excellent in the productivity because the heating temperature can be a relatively low temperature when performing the fusing treatment. Furthermore, through the fusing treatment, the cermet coating material of the present invention acquires excellent interfacial adhesion between the
25 base material and the cermet layer, and can have durability capable of withstanding a high load. Therefore, when the cermet coating material is used as an expendable member, the exchange frequency can be reduced. Consequently, the disposal amount of expendable members can be reduced to contribute to the environmental conservation.

[0061]

30 In addition, the cermet coating material of the present invention obtained using such a powder for forming a thermal spraying layer has a magnetic property owing to the action of Fe contained in the cermet layer. Therefore, when the cermet coating material is used as a member of a resin molding machine or the like, even if cracks and delamination occur in the cermet layer and broken pieces of the cermet layer are mixed in the resin, it is possible to

easily collect the broken pieces using a magnet because the broken pieces of the cermet layer have a magnetic property. This allows to prevent the contamination of resin produced by the resin molding machine and the malfunction of the resin molding machine.

[0062]

5 In particular, when an insulating resin is used as a resin to be molded by a resin molding machine, if the broken pieces of the cermet layer are mixed in the insulating resin, the insulation property of the resin will be deteriorated due to the conductivity of metals contained in the broken pieces. In contrast, according to the present invention, since the broken pieces of the cermet layer mixed in the resin can be easily collected using a magnet, the insulating
10 resin to be molded can maintain the insulation property, thus having good quality, and the production yield can also be improved.

[Examples]

[0063]

Hereinafter, the present invention will be more specifically described with reference to
15 examples, but the present invention is not limited to these examples.

[0064]

«Example 1»

After a raw material was prepared by mixing 6.0 wt% of B, 53.25 wt% of Mo, 2.0 wt% of V, 8.0 wt% of Fe, 8.0 wt% of Cr, 2.5 wt% of Si, and 20.25 wt% of Ni, 5 weight parts of
20 paraffin was added to 100 weight parts of the raw material, and wet-crushing of 25 hours using a vibration ball mill was performed for the paraffin and the raw material in acetone to prepare a crushed powder. The prepared crushed powder was then dried at 150°C for 18 hours under a nitrogen atmosphere. Subsequently, the dried crushed powder was mixed with acetone with a weight ratio of 1:1, and granulated using a spray drier. The granulated powder was
25 maintained at 1,150°C in vacuum for 1 hour to be sintered, and then classified to prepare a powder for forming a thermal spraying layer, containing a $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride.

[0065]

Thereafter, measurement of the melting temperature was conducted for the prepared
30 powder for forming a thermal spraying layer. Specifically, the measurement of the melting temperature was performed such that the powder for forming a thermal spraying layer was crushed to have a particle diameter of 10-300 μm and the melting temperature was measured using a differential thermal analyzer (model number: TG8120, available from Rigaku Corporation). Results are listed in Table 1.

[0066]

Subsequently, a steel sheet of SUS304 was prepared as a nonmagnetic base material, and the prepared powder for forming a thermal spraying layer was sprayed to the prepared base material using a high velocity flame spraying machine (model number: JP8000, available from TAFE Incorporated) thereby to obtain a cermet coating material formed such that the base material was coated with a cermet sprayed layer. The formation of the cermet layer was performed under the conditions of a spray distance (distance between the base material and a spray gun) of 300 mm, a kerosene fuel amount of 5.5 gph, and an oxygen flow rate of 1,900 scfh. Further, a fusing treatment was performed for the obtained cermet coating material in a vacuum furnace under the conditions of a heating temperature of 1,150°C and a heating time of 60 minutes.

[0067]

Thereafter, for the cermet coating material to which the fusing treatment was performed, presence or absence of the magnetic property in the cermet layer was evaluated by confirming whether the cermet layer was attracted by the magnetic force of a magnet (ferrite magnet) when the magnet was moved to come close to the cermet layer at the surface. Results are listed in Table 1.

[0068]

Furthermore, for the cermet coating material to which the fusing treatment was performed, the Vickers hardness (HV) of the cermet layer at the surface was measured using a Vickers hardness tester (model number: MVK-G2, available from Akashi Seisakusho). Results are listed in Table 1.

[0069]

«Examples 2-12»

Powders for forming a thermal spraying layer and cermet coating materials were obtained in the same manner as that for Example 1 except that each mixing ratio of V, Fe, Cr, Si and Ni in the raw material was changed as listed in Table 1, and evaluations were performed in the same manner. Results are listed in Table 1.

[0070]

[Table 1]

Table 1

	Material composition [wt%]	B [wt%]	Mo [wt%]	V [wt%]	Fe [wt%]	Cr [wt%]	Si [wt%]	Ni [wt%]	Melting temperature [°C]	Magnetic property	Hardness [HV]
Example 1	6B-53.25Mo-2V-8Fe-8Cr-2.5Si-bal.Ni	6.0	53.25	2.0	8.0	8.0	2.5	20.25	1141	Present	1240
Example 2	6B-53.25Mo-2V-9Fe-8Cr-2.5Si-bal.Ni	6.0	53.25	2.0	9.0	8.0	2.5	19.25	1143	Present	1250
Example 3	6B-53.25Mo-2V-7Fe-9Cr-2.5Si-bal.Ni	6.0	53.25	2.0	7.0	9.0	2.5	20.25	1144	Present	1280
Example 4	6B-53.25Mo-3V-6Fe-9Cr-2.5Si-bal.Ni	6.0	53.25	3.0	6.0	9.0	2.5	20.25	1093	Present	1300
Example 5	6B-53.25Mo-3V-7Fe-8Cr-2.5Si-bal.Ni	6.0	53.25	3.0	7.0	8.0	2.5	20.25	1044	Present	1340
Example 6	6B-53.25Mo-2V-8Fe-8Cr-1.8Si-bal.Ni	6.0	53.25	2.0	8.0	8.0	1.8	20.95	1140	Present	1250
Example 7	6B-53.25Mo-2V-8Fe-8Cr-2.0Si-bal.Ni	6.0	53.25	2.0	8.0	8.0	2.0	20.75	1130	Present	1260
Example 8	6B-53.25Mo-1V-6Fe-9Cr-2.0Si-bal.Ni	6.0	53.25	1.0	6.0	9.0	2.0	22.75	1080	Present	1290
Example 9	6B-53.25Mo-1V-6Fe-9Cr-1.8Si-bal.Ni	6.0	53.25	1.0	6.0	9.0	1.8	22.95	1122	Present	1250
Example 10	6B-53.25Mo-1V-6Fe-10Cr-2.2Si-bal.Ni	6.0	53.25	1.0	6.0	10.0	2.2	21.55	1080	Present	1263
Example 11	6B-53.25Mo-2V-6Fe-8Cr-1.8Si-bal.Ni	6.0	53.25	2.0	6.0	8.0	1.8	22.95	1148	Present	1275
Example 12	6B-53.25Mo-2V-6Fe-10Cr-2.5Si-bal.Ni	6.0	53.25	2.0	6.0	10.0	2.5	20.25	1130	Present	1250

[0071]

«Comparative Examples 1-23»

Powders for forming a thermal spraying layer and cermet coating materials were obtained in the same manner as that for Example 1 except that each mixing ratio of B, Mo, V, Fe, Cr, Si and Ni in the raw material was changed as listed in Table 2, and evaluations were performed in the same manner. Results are listed in Table 2. In Table 2 and in Table 3 to be described later, values of the melting temperature of higher than 1,150°C are shown with gray background in the measurement results of the melting temperature. Evaluation results of absence of the magnetic property are also shown with gray background in the evaluation results of presence or absence of the magnetic property. Values of the hardness of less than 1,200 HV are also shown with gray background in the measurement results of the Vickers hardness of the cermet layer.

[0072]

[Table 2]

Table 2

	Material composition [wt%]	B [wt%]	Mo [wt%]	V [wt%]	Fe [wt%]	Cr [wt%]	Si [wt%]	Ni [wt%]	Melting temperature [°C]	Magnetic property	Hardness [HV]
Comparative Example 1	6B-53.25Mo-40.75Ni	6.0	53.25	-	-	-	-	40.75	1250	Present	887
Comparative Example 2	6B-53.25Mo-3Si-37.75Ni	6.0	53.25	-	-	-	3.0	37.75	1198	Present	1075
Comparative Example 3	6B-53.25Mo-5V-5Fe-bal.Ni	6.0	53.25	5.0	5.0	-	-	30.75	1240	Absent	1090
Comparative Example 4	5.5B-48.81Mo-5V-5Fe-bal.Ni	5.5	48.81	5.0	5.0	-	-	35.69	1238	Absent	933
Comparative Example 5	5.5B-48.81Mo-9V-5Fe-bal.Ni	5.5	48.81	9.0	5.0	-	-	31.69	1236	Absent	1090
Comparative Example 6	5.5B-48.81Mo-5V-9Fe-bal.Ni	5.5	48.81	5.0	9.0	-	-	31.69	1224	Present	920
Comparative Example 7	5.5B-48.81Mo-9Fe-5Cr-bal.Ni	5.5	48.81	-	9.0	5.0	-	31.69	1228	Present	870
Comparative Example 8	6B-53.25Mo-5Fe-bal.Ni	6.0	53.25	-	5.0	-	-	35.75	1230	Present	833
Comparative Example 9	6B-53.25Mo-10Fe-bal.Ni	6.0	53.25	-	10.0	-	-	30.75	1238	Present	805
Comparative Example 10	5.5B-48.81Mo-bal.Ni	5.5	48.81	-	-	-	-	45.69	1238	Present	627
Comparative Example 11	5.5B-48.81Mo-7.5V-10Fe-bal.Ni	5.5	48.81	7.5	10.0	-	-	28.19	1242	Present	832
Comparative Example 12	5.7B-50.29Mo-5V-9Fe-bal.Ni	5.7	50.29	5.0	9.0	-	-	30.01	1238	Present	847
Comparative Example 13	5.7B-50.59Mo-7.5V-10Fe-bal.Ni	5.7	50.59	7.5	10.0	-	-	26.21	1233	Present	867
Comparative Example 14	6B-53.25Mo-5V-9Fe-bal.Ni	6.0	53.25	5.0	9.0	-	-	26.75	1200	Present	960
Comparative Example 15	6B-53.25Mo-10V-10Fe-1Si-bal.Ni	6.0	53.25	10.0	10.0	-	1.0	19.75	1198	Present	1125
Comparative Example 16	6B-53.25Mo-10V-10Fe-2Si-bal.Ni	6.0	53.25	10.0	10.0	-	2.0	18.75	1168	Present	1238
Comparative Example 17	6B-53.25Mo-10V-7Fe-1Si-bal.Ni	6.0	53.25	10.0	7.0	-	1.0	22.75	1188	Present	1175
Comparative Example 18	6B-53.25Mo-10V-8Fe-1Si-bal.Ni	6.0	53.25	10.0	8.0	-	1.0	21.75	1178	Present	1163
Comparative Example 19	6B-53.25Mo-10V-10Fe-3Si-bal.Ni	6.0	53.25	10.0	10.0	-	3.0	17.75	1166	Present	1312
Comparative Example 20	5.5B-48.81Mo-7.5V-7.5Fe-bal.Ni	5.5	48.81	7.5	7.5	-	-	30.69	1220	Present	1263
Comparative Example 21	5.7B-50.59Mo-10V-10Fe-bal.Ni	5.7	50.59	10.0	10.0	-	-	23.71	1231	Present	927
Comparative Example 22	5.7B-50.59Mo-7.5V-7.5Fe-bal.Ni	5.7	50.59	7.5	7.5	-	-	28.71	1221	Present	900
Comparative Example 23	6B-53.25Mo-10V-10Fe-bal.Ni	6.0	53.25	10.0	10.0	-	-	20.75	1224	Present	940

[0073]

«Comparative Examples 24-44»

5 Powders for forming a thermal spraying layer and cermet coating materials were obtained in the same manner as that for Example 1 except that each mixing ratio of B, Mo, V, Fe, Cr, Si and Ni in the raw material was changed as listed in Table 3, and evaluations were performed in the same manner. Results are listed in Table 3.

[0074]

[Table 3]

Table 3

	Material composition [wt%]	B [wt%]	Mo [wt%]	V [wt%]	Fe [wt%]	Cr [wt%]	Si [wt%]	Ni [wt%]	Melting temperature [°C]	Magnetic property	Hardness [HV]
Comparative Example 24	6B-53.25Mo-10V-9Fe-1.3Si-bal.Ni	6.0	53.25	10.0	9.0	-	1.3	20.45	1182	Present	1175
Comparative Example 25	6B-53.25Mo-10V-10Fe-1.3Si-bal.Ni	6.0	53.25	10.0	10.0	-	1.3	19.45	1178	Present	1250
Comparative Example 26	6B-53.25Mo-10V-9Fe-1.5Si-bal.Ni	6.0	53.25	10.0	9.0	-	1.5	20.25	1167	Present	1200
Comparative Example 27	6B-53.25Mo-10V-10Fe-1.5Si-bal.Ni	6.0	53.25	10.0	10.0	-	1.5	19.25	1172	Present	1213
Comparative Example 28	6B-53.25Mo-10V-11Fe-1.7Si-bal.Ni	6.0	53.25	10.0	11.0	-	1.7	18.05	1162	Present	1260
Comparative Example 29	6B-53.25Mo-10V-11Fe-1.5Si-bal.Ni	6.0	53.25	10.0	11.0	-	1.5	18.25	1182	Present	1163
Comparative Example 30	6B-53.25Mo-10V-11Fe-1.2Si-bal.Ni	6.1	54.14	10.0	11.0	-	1.2	17.56	1191	Present	1187
Comparative Example 31	6B-53.25Mo-10V-11Fe-1.6Si-bal.Ni	6.0	53.25	10.0	11.0	-	1.6	18.15	1178	Present	1263
Comparative Example 32	6B-53.25Mo-10V-11Fe-1.3Si-bal.Ni	6.0	53.25	10.0	11.0	-	1.3	18.45	1220	Present	1183
Comparative Example 33	6B-53.25Mo-7V-11Fe-3Cr-1.7Si-bal.Ni	6.0	53.25	7.0	11.0	3.0	1.7	18.05	1176	Present	1225
Comparative Example 34	6B-53.25Mo-8V-11Fe-2Cr-1.7Si-bal.Ni	6.0	53.25	8.0	11.0	2.0	1.7	18.05	1169	Present	1233
Comparative Example 35	6B-53.25Mo-9V-11Fe-1Cr-1.7Si-bal.Ni	6.0	53.25	9.0	11.0	1.0	1.7	18.05	1190	Present	1275
Comparative Example 36	6B-53.25Mo-6.5V-11Fe-3.5Cr-1.7Si-bal.Ni	6.0	53.25	6.5	11.0	3.5	1.7	18.05	1179	Present	1283
Comparative Example 37	6B-53.25Mo-6.11V-11Fe-3.9Cr-1.7Si-bal.Ni	6.0	53.25	6.1	11.0	3.9	1.7	18.06	1168	Present	1312
Comparative Example 38	6B-53.25Mo-5V-11Fe-5Cr-1.7Si-bal.Ni	6.0	53.25	5.0	11.0	5.0	1.7	18.05	1157	Present	1275
Comparative Example 39	6B-53.25Mo-6Fe-10Cr-1.8Si-bal.Ni	6.0	53.25	-	6.0	10.0	1.8	22.95	1112	Present	1180
Comparative Example 40	6B-53.25Mo-2V-8Fe-8Cr-1.5Si-bal.Ni	6.0	53.25	2.0	8.0	8.0	1.5	21.25	1167	Present	1225
Comparative Example 41	6B-53.25Mo-2V-8Fe-8Cr-1.3Si-bal.Ni	6.0	53.25	2.0	8.0	8.0	1.3	21.45	1176	Present	1200
Comparative Example 42	6B-53.25Mo-2V-8Fe-8Cr-1.1Si-bal.Ni	6.0	53.25	2.0	8.0	8.0	1.1	21.63	1191	Present	1183
Comparative Example 43	6B-53.25Mo-4V-9Fe-6Cr-2.5Si-bal.Ni	6.0	53.25	4.0	9.0	6.0	2.5	19.25	1153	Present	1312
Comparative Example 44	6B-53.25Mo-6Fe-10Cr-2.0Si-bal.Ni	6.0	53.25	0.0	6.0	10.0	2.0	22.75	1080	Present	1190

[0075]

The wear resistance of the cermet layer at the surface was then evaluated using the cermet layer of the above-described Example 6. More specifically, evaluation of the wear resistance was performed using a method ("Ogoshi" wear test) of pressing a rotating ring member against the cermet coating material of Example 6 to form a wear trace on the surface of the cermet coating material and measuring the volume of the wear trace. As the ring member to be pressed against the cermet coating material, three kinds of materials were used, i.e., martensite-based stainless steel (SUS440C, Vickers hardness at surface: 650 HV), cermet sintered compact A (product number: KH-C50, available from Toyo Kohan Co., Ltd., Vickers hardness at surface: 1,150 HV), and cermet sintered compact B (product number: KH-N51, available from Toyo Kohan Co., Ltd., Vickers hardness at surface: 1,280 HV). Test conditions were a final load of 19.8 kg and a sliding distance of 200 m, and evaluations were performed under three kinds of conditions of a sliding speed, i.e., 0.2, 0.9 and 4.21 m/s. FIG. 1(A) to FIG. 1(C) show the measurement results of the volumes (wear volumes) of wear traces formed on the surfaces of the cermet coating materials. FIG. 1(A), FIG. 1(B) and FIG. 1(C) show the results, respectively, when the martensite-based stainless steel was used as the ring member, when the above cermet sintered compact A was used as the ring member, and when the above cermet sintered compact B was used as the ring member.

[0076]

«Comparative Examples 45-47»

For comparison with the cermet coating material of Example 6, alumina sintered compact (Comparative Example 45), WC-based self-fluxing alloy having a content ratio of WC of 50 wt% (Comparative Example 46) and a cermet sintered compact A as used for the above ring member (Comparative Example 47) were prepared, and the wear resistance was evaluated in the same manner as that for the above-described Example 6. Results are shown in FIG. 1(A) to FIG. 1(C).

[0077]

Next, the interfacial adhesion was evaluated when the powder for forming a thermal spraying layer was sprayed to a steel material using the powder for forming a thermal spraying layer of the above-described Example 6. Specifically, a test piece 100 was prepared as a base material to undergo thermal spray, comprising a steel material (SKD11) and having a shape as illustrated in FIG. 2. The test piece 100 of the shape as illustrated in FIG. 2 has: both ends (a stationary part 10 and a rotating part 30 in FIG. 2) each having a cylindrical shape of a diameter of 20 mm; and a center part (a part 20 to be formed with a cermet layer in FIG. 2)

having a cylindrical shape of a diameter of 10 mm. The powder for forming a thermal spraying layer of Example 6 prepared as the above was then sprayed to a part of the surface of the prepared test piece 100, i.e., the part 20 to be formed with a cermet layer in FIG. 2, using a high velocity flame spraying machine (JP-5000 available from TAFE Incorporated) thereby to form a cermet layer on the part 20 to be formed with a cermet layer. The formation of the cermet layer was performed under the conditions of a spray distance of 300 mm, a kerosene fuel amount of 6 gph, and an oxygen flow rate of 1,850 scfh. Thereafter, a fusing treatment was performed for the test piece 100 formed with the cermet layer in a vacuum furnace under the conditions of a heating temperature of 1,100°C and a heating time of 60 minutes, and a cermet coating material was thus obtained as illustrated in FIG. 2.

[0078]

For the cermet coating material obtained in the above-described manner as illustrated in FIG. 2, evaluation of the interfacial adhesion was conducted. More specifically, evaluation of the interfacial adhesion was performed such that a torsion tester (UET-300 available from SHIMADZU CORPORATION) was used to rotate the rotating part 30 of the test piece 100 to apply a torsional torque to the cermet coating material while fixing the stationary part 10, and it was observed whether cracks and delamination occurred in the cermet layer under the conditions of three kinds of target values of the torsional torque, i.e., 200 N·m, 300 N·m and 400 N·m. In this evaluation, the criteria below were used. Results are listed in Table 4 and shown in FIG. 3(A) to FIG. 3(C). FIG. 3(A), FIG. 3(B) and FIG. 3(C) are photographs each showing the cermet coating material of Example 6 when performing evaluation at a torsional torque value of 196 N·m, a torsional torque value of 294 N·m and a torsional torque value of 401 N·m, respectively.

○: Cracks and delamination were not confirmed in the cermet layer.

×: Cracks and delamination occurred in the cermet layer.

[0079]

«Comparative Example 48»

A powder for forming a thermal spraying layer of WC-12%Co was sprayed to a steel material (SKD11) having the shape as shown in FIG. 2 under the conditions of a spray distance of 380 mm, a kerosene fuel amount of 6 gph, and an oxygen flow rate of 2,100 scfh thereby to prepare a cermet coating material, and the interfacial adhesion was evaluated when the target value of the torsional torque was 200 N·m in the same manner as that for the above-described Example 6. Results are listed in Table 4 and shown in FIG. 3(D). FIG. 3(D) is a photograph showing the cermet coating material of Comparative Example 48 when performing evaluation

at a torsional torque value of 191 N·m.

[0080]

[Table 4]

Table 4

	Torsional torque [N·m]	Interfacial adhesion
Example 6	196	○
	294	○
	401	○
Comparative Example 48	191	×

[0081]

As listed in Table 1, in all of the powders for forming a thermal spraying layer of Examples 1-12, which each contain a $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride and have a composition of 5.5-6.5 wt% of B, 48.8-57.7 wt% of Mo, 1.8-2.5 wt% of Si, 6.0-10.0 wt% of Cr, 1.0-3.0 wt% of V, 6.0-10.0 wt% of Fe, and 17.0 wt% or more of Ni, the melting temperature is 1,000-1,150°C. It can therefore be evaluated that the powders for forming a thermal spraying layer of Examples 1-12 can reduce the heating temperature for thermally diffusing the cermet layer when the fusing treatment is performed after the powder has become the cermet layer via the thermal spray, thus resulting in advantages that the deformation of the base material and the deterioration in the properties are prevented from occurring and the interfacial adhesion to the base material is excellent. In particular, as listed in Table 4 and shown in FIG. 3(A) to FIG. 3(C), the powder for forming a thermal spraying layer of Example 6 can be evaluated to provide excellent interfacial adhesion to the base material because cracks and delamination do not occur in the cermet layer even when a torsional torque is applied after the powder has become the cermet layer via the thermal spray.

[0082]

Moreover, as listed in Table 1, all of the powders for forming a thermal spraying layer of Examples 1-12 have magnet properties. Therefore, when the cermet coating material obtained using such a powder for forming a thermal spraying layer is utilized as a member of a resin molding machine or the like, even if cracks and delamination in the cermet layer occur, it is possible to easily collect the broken pieces of the cermet layer using a magnet, and the contamination of the resin produced by the resin molding machine and the malfunction of the resin molding machine can thereby be prevented.

[0083]

Furthermore, as listed in Table 1, all of the cermet coating materials obtained using the powders for forming a thermal spraying layer of Examples 1-12 exhibit high values of the Vickers hardness of not less than 1,200 HV, and can thus be evaluated to have excellent wear resistance. In particular, as shown in FIG. 1(A) to FIG. 1(C), the cermet coating material obtained using the powder for forming a thermal spraying layer of Example 6 has a very small wear volume of the wear trace when the "Ogoshi" wear test is performed. Also from this result, it can be evaluated that the wear resistance is excellent.

[0084]

In contrast, as listed in Tables 2 and 3, in the powders for forming a thermal spraying layer of Comparative Examples 1-44, in which the content ratio of each element falls outside

the specific range according to the present invention, the melting temperature exceeds 1,150°C, or magnetic property is not possessed, or the Vickers hardness is less than 1,200 HV. With regard to evaluation results of the comparative examples listed in Tables 2 and 3, values of the melting temperature of higher than 1,150°C, indication of absence of the magnetic property, and values of the hardness of less than 1,200 HV, are shown with gray background.

[0085]

Among the comparative examples, comparative examples of which the melting temperature exceeds 1,150°C require the heating temperature for thermally diffusing the cermet layer to be set at a temperature higher than 1,150°C when the fusing treatment is performed after the obtained powder for forming a thermal spraying layer is sprayed to the base material to provide the cermet coating material. It can therefore be evaluated that the fusing treatment causes the deformation of the base material and the deterioration in the properties.

[0086]

The comparative examples include those having no magnetic property. When the powder for forming a thermal spraying layer obtained in those comparative examples is sprayed to the base material to provide the cermet coating material, and the cermet coating material is used as a member of a resin molding machine or the like, if the broken pieces caused by cracks and delamination in the cermet layer are mixed in the resin, the broken pieces cannot be collected using a magnet because the broken pieces mixed therein have no magnetic property. This may cause contamination of the resin and malfunction of the resin molding machine, which appear to lead to deterioration in the quality of resin molded products to be obtained and a poor production yield. It should be noted that the cermet coating materials of Comparative Examples 1, 2 and 10 do not contain Fe as listed in Tables 2 and 3, but the results show that they have magnetic properties. This is due to the action of Ni. That is, despite the poorer magnetic property of Ni compared to Fe, the large content of Ni allows the obtained cermet coating material to exhibit magnetic property to a certain extent.

[0087]

Among the comparative examples, comparative examples of which the Vickers hardness is less than 1,200 HV can be evaluated to have poor wear resistance because the obtained cermet coating layer have low hardness.

[Document Name] CLAIMS

[Claim 1]

5 A powder for forming a thermal spraying layer comprising a $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride, wherein

the powder has a composition of 5.5-6.5 wt% of B, 48.8-57.7 wt% of Mo, 1.8-2.5 wt% of Si, 6.0-10.0 wt% of Cr, 1.0-3.0 wt% of V, 6.0-10.0 wt% of Fe, and 17.0 wt% or more of Ni.

[Claim 2]

10 A cermet layer formed by thermally spraying the powder according to claim 1, wherein the cermet layer comprises 55.0-75.0 wt% of a hard phase and the balance of a binder phase, the hard phase comprising the $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride, the binder phase comprising a Ni-based alloy as a main component.

15 [Claim 3]

A cermet coating material comprising:

a base material and

a layer formed on the base material, the layer being the cermet layer according to claim

2.

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[Claim 4]

The cermet coating material according to claim 3, comprising a diffusion layer formed by performing a melting treatment to heat the cermet layer at 1,000-1,150°C so that the base material and the cermet layer are thermally diffused to each other.

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[Claim 5]

The cermet coating material according to claim 3 or 4, wherein the base material is alloy steel, carbon steel or stainless steel.

30 [Claim 6]

A method of manufacturing a cermet coating material comprising:

thermally spraying a powder for forming a cermet layer on a base material, the powder comprising a $\text{Mo}_2(\text{Ni}, \text{Cr}, \text{V}, \text{Fe})\text{B}_2$ -type composite boride,

the powder having a composition of 5.5-6.5 wt% of B, 48.8-57.7 wt% of Mo, 1.8-2.5

wt% of Si, 6.0-10.0 wt% of Cr, 1.0-3.0 wt% of V, 6.0-10.0 wt% of Fe, and 17.0 wt% or more of Ni,

the cermet layer comprising 55.0-75.0 wt% of a hard phase and the balance of a binder phase, the hard phase comprising the $\text{Mo}_2(\text{Ni, Cr, V, Fe})\text{B}_2$ -type composite boride, the binder
5 phase comprising a Ni-based alloy as a main component.

[Claim 7]

The method of manufacturing a cermet coating material according to claim 6, further comprising:

10 performing a melting treatment to heat the cermet layer at 1,000-1,150°C after forming the cermet layer on the base material.