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(54) Method of forming abrasion-resistant coating layer.

(57) A method of forming an abrasion resistant coating layer comprising spray coating material obtained by mixing, melting, cooling and pulverizing at least molybdenum or molybdenum alloy and Cr_2O_3 and then spraying the same to the surface of a member.

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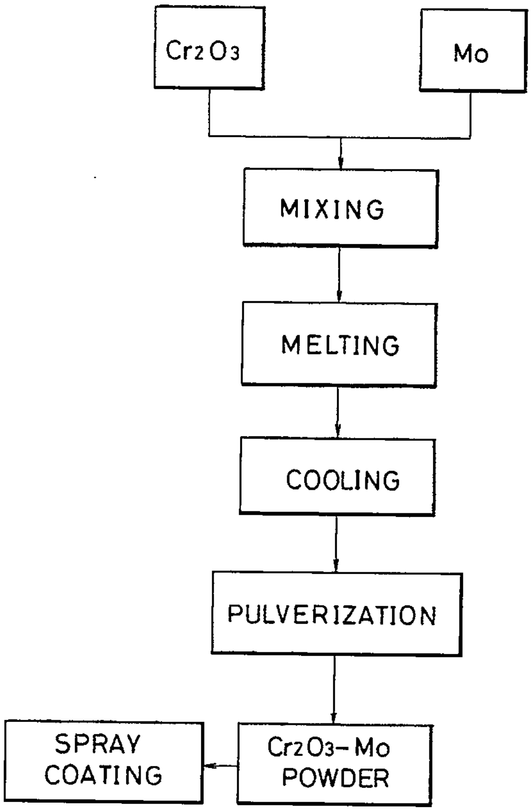
FIG.1


Cr_2O_3
Mo
MIXING
MELTING
COOLING
PULVERIZATION
Cr_2O_3-Mo POWDER
SPRAY COATING

METHOD OF FORMING ABRASION-RESISTANT COATING LAYER

FIELD OF THE INVENTION AND RELATED ART STATEMENT

The present invention concerns a method of forming an abrasion resistant coating layer and, more in particular, it relates to a method of forming a coating layer having high lubricant retainability and excellent abrasion resistance.

It is necessary that mechanical parts or constituent materials for various apparatus have sufficient mechanical strength, as well as abrasion resistance, corrosion resistance, etc. depending on the purpose of use, but it is difficult to provide a single component material with two or more of necessary properties altogether. For example, those materials of high abrasion resistance are often poor the toughness.

In view of the above, various surface treating methods have been developed for coating the surface of members with high abrasion resistant material.

As the surface treatment, there have been known various methods such as plating, enamel coating, vapor deposition, spray coating and build-up welding. Among them, spray coating process makes possible to form coating layer of various metals, ceramics or composite materials thereof, because the molten metal, ceramics, and others collide against the surface of substrate at a high speed and a coating layer is formed on the surface of members by the process. Then, by spray coating a metal, for instance, desirable property such as corrosion resistance, heat resistance and electroconductivity can be provided.

When a hard metal for example, is spray coated to the surface of a member, the abrasion resistance can be improved.

However, when the coatings were used as the sliding component, the surface must not be excessively smooth to keep the scuffing resistance property. If the surfaces is extremely smooth, the lubricant retainability at the sliding surfaces is lowered tending to cause lack of the lubricant and led to scuffing.

In a case of ceramics spray coating, the abrasion resistance can be improved due to the high hardness of the coating layer. However, if a member is a sliding member, the sliding property is inevitably reduced since the roughness at the surface of the coating layer is high. In addition, ceramic coating layer of high hardness may possibly injure the mating material. Further, since the fracture toughness of the ceramics is low, the brittle fracture occurs on the friction surface, follows a problem that abrasion can not be reduced sufficiently.

In order to overcome such a problem, the present applicant has already found a process of forming an abrasion resistant coating layer comprising Mo (molybdenum) or Mo alloy and Cr_2O_3 in a specific blending ratio by spray coating and previously filed a patent application regarding this finding (Japanese Patent Application Sho 61-157111, hereinafter referred to as "prior application").

For forming a coating layer, a spray coating gun 1 as shown in Fig. 3 is usually employed and spray coating material is supplied from a spray coating material supply port 2 and jetted in a flame or plasma 4 onto the surface of a substrate 3 to form the coating layer.

The spray coating gun 1 is moved relative to the plate surface of the substrate 3 as shown in Fig. 4. Specifically, Fig. 4 shows a trace of a center of the working spray coating gun (center of the plasma) projected on the plate surface of the substrate 3. As shown in the figure, the spray coating gun is reciprocated leftward and lightward from a starting point A for spray coating and, simultaneously, displaced little by little downwardly at each of the turning points on both ends. Then, after reaching the lowermost end of the substrate 3, the gun is returned to the starting point A for spray coating. Such procedures of the spray coating gun are usually repeated by an appropriate number of cycles to form required coating thickness.

By the method of the prior application, an abrasion resistant coating layer excellent both in the lubricant retainability and the sliding property, can be formed. But, in a case of forming a spray coating layer using a powder mixture of a Mo or Mo alloy powder and a Cr_2O_3 powder as the spray coating material, there is the following problem.

When a powder of Mo or Mo alloy, for instance, Mo powder and a Cr_2O_3 powder are merely mixed as a powder mixture and spray coated by the spray coating method as shown in Fig. 3 and Fig. 4, Cr_2O_3 particles of a relatively low specific gravity of 5.2 in the powder mixture are carried on the flame or plasma on the side nearer to supply port 2 for the spray coating material, whereas Mo particles of relatively high specific gravity of 10.2 are caused to fly on the side far from the supply port 2 of the spray coating gun 1. Accordingly, in the flame or plasma 4 from the spray coating gun 1, the area above the center line constitutes a flying range 4a enriched with Cr_2O_3 particles, while the lower area below the center line constituted a flying range 4b enriched with Mo particles.

Therefore, in a case of moving the spray coating gun as shown in Fig. 4 thereby gradually laminating the spray coating layer as shown in Fig. 4, the spray coating layer 5 thus formed comprises the Cr_2O_3-enriched layer 5a and the Mo-enriched layer 5b stacked one above the other and it is impossible to form a Cr_2O_3-Mo composite material coating layer in which Mo and Cr_2O_3 are finely dispersed.

If tensile strain should occur in the direction of the thickness of such a coating layer in which Mo and Cr_2O_3 are locallized in a layerous form, since fracture is caused in the Cr_2O_3 layer with small fracture strain, the fracture strain over the entire coating layer is small. Further, the layerous portion of high Cr_2O_3 content causes the reduction of fracture toughness for the entire coating layer. Further, in the coating layer where Mo and Cr_2O_3 are locallized in the layerous form, the abrasion resistance and sliding property are changed greatly depending on whether the Mo layer or the Cr_2O_3 layer is exposed to the surface. Accordingly, excellent property of Cr_2O_3-Mo composite material can not fully be attained and it is difficult to obtain excellent abrasion resistance and sliding property.

By mixing Mo or Mo alloy and Cr_2O_3, followed by melting them, Mo and Cr_2O_3 can be dispersed extremely finely. Accordingly, a powder obtained by cooling to solidify the molten mixture and then pulverizing them can provide Cr_2O_3-Mo composite material particles in which respective particles are finely dispersed therein.

Therefore, according to the method of the present invention using the Cr_2O_3-Mo composite material particles finely dispersed to each other as the spray coating material, since Mo and Cr_2O_3 are present being dispersed extremely finely, a spray coating layer of high fracture strain against tensile strain in any of the directions can be formed. Further, Mo of high toughness is finely dispersed to hinder the propergation of cracks and form a spray coating layer of high fracture toughness.

The spray coating layer formed by the method according to the present invention is a coatinglayer of composite material comprising Mo as high melting point metal and Cr_2O_3 as ceramics of high hardness. Accordingly, the coating layer is excellent having both of the high toughness of Mo and heat resistance, high hardness and chemical stability of Cr_2O_3. Great toughness and high hardness thus combined can remarkably improve the abrasion resistance of the coating layers.

The coating layer formed in accordance with the present invention has a structure in which a Mo phase is dispersed into a Cr_2O_3 matrix phase. When the surface of the coating layer is in sliding contact with other member, the Mo phase hardness lower than Cr_2O_3 is abraded to form a plurality of fine pits at the surface of the coating layer. The pits function as a retainer of the lubricant, remarkably improve the lubricant supply and improve the abrasion resistance at the surface of the member.

OBJECT AND SUMMARY OF THE INVENTION

An object of the present invention is to provide a method capable of preventing separate flying of Mo or Mo alloy particles and Cr_2O_3 particles during spray coating and forming a coating layer of Cr_2O_3-Mo composite material coating layer having satisfactory abrasion resistance and sliding property together.

Another object of the present invention is to provide a method of forming a coating layer of Cr_2O_3-Mo composite material capable of greatly improving the endurance of sliding members, etc. using a lubricant.

The method of forming an abrasion resistant coating layer according to the present invention has a feature in that spray coating material obtained by mixing, melting, cooling and then pulverizing at least Mo or Mo alloy and Cr_2O_3 to the surface of a member.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a systematic diagram illustrating a method of practicing the present invention;

Fig. 2 is a graph showing preferred values for the contents of Mo and Cr_2O_3 in a spray coating layer formed in accordance with the present invention;

Fig. 3 is an explanatory view for the spray coating method;

Fig. 4 is an explanatory view for the scanning method of a spray coating gun;

Fig. 5 is a cross sectional view of a coating layer formed by a conventional method;

Fig. 6 is a cross sectional view showing an arc melting furnace used in Example 1;

Fig. 7 is a chart for X-ray diffractiometry of Cr_2O_3-24%Mo composite material obtained in Example 1;

Fig. 8 is a perspective view of test specimens prepared in Example 2 and Comparative Example 2;

Fig. 9 is a front elevational view of them;

Fig. 10 is a cross sectional view for explaining the test method in Example 2 and Comparative Example 2; and

Fig. 11 is a graph illustrating the results of Example 2 and Comparative Example 2.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is to be described more in details referring to the drawings.

Fig. 1 is a systematic diagram illustrating a method of practicing the present invention.

In the present invention, a Mo or Mo alloy powder, a Cr_2O_3 powder and, optionally, other powder are at first mixed at a predetermined ratio and the resultant powder mixture is melted.

There is no particular restriction for the melting method but arc melting is suitable. Upon melting, it is preferred to apply heating under an inert gas atmosphere such as of Ar gas for preventing degeneration of the starting material such as oxidation of Mo upon melting under heating. In addition, it is also possible to employ a heat melting method by means of electron beams under vacuum of less than 10^{-1} Torr.

Melting may be conducted at any temperature so long as the powder mixture can be melted and, usually, it is conducted at a temperature higher than the melting point of Mo or Mo alloy. By the melting, the powder mixture is formed into a state where Mo, Cr_2O_3, etc. are finely dispersed and mixed to each other.

Accordingly, solidified products obtained by cooling after melting the powder mixture constitute an ingot of Cr_2O_3-Mo series composite material in which Mo, Cr_2O_3, etc. are finely dispersed.

The resultant ingot of Cr_2O_3-Mo system composite material is then pulverized and sieved using appropriate means. For example, the ingot is coarsely pulverized by using a hammer mill, etc. and then finely pulverized by a ball mill, etc. and then sieved.

In the present invention, since the Cr_2O_3-Mo system composite material powder obtained by the pulverization and sieving is used as the spray coating material, the grain size is adjusted such that it is suitable to spray coating, that is, about from 1 to 100 μm, preferably, from 10 to 44 μm.

As a method of spray coating the resultant Cr_2O_3-Mo series composite material powder, it is possibled to employ usual spray coating method such as plasma spray coating, flame spray coating, etc.

In the method of the present invention, the Cr_2O_3-Mo system composite material powder, as the starting material, may be spray coated to the surface of a member and, subsequently, laser beams may be irradiated further to the surface of the spray-coated layer thus formed for promoting melting of the coating layer. Irradiation of laser beams is suitable to a case where the melting of starting material is insufficient but it also has an effect of increasing the density of the spray coating layer even in a case where sufficiently melted powder is spray coated. Further, it has an effect of melting also the mating interface between the coating layer and the substrate thereby increasing the bonding strength and enabling to form the coating layer to all kinds of substrates.

Furthermore, it is extremely effective to form an appropriate bonding layer previously to the surface of the member so as to improve the bondability between the member and the spray coating layer.

According to the method of the present invention, coating layer can be formed to the surface of members of any kind of materials with no particular restriction. Further, the thickness of the coating layer formed can be varied optionally by changing conditions for spray coating such as a spray coating time.

Description will now be made to the ingredient composition for the spray coating layer formed in accordance with the present invention. In the description, "%" means "% by weight".

The spray coating layer formed in the present invention preferably has the following relationship:

$X = 60 \sim 90$
$Y = 0.10 \times X \sim 0.45 \times X$
$X + Y \leq 100$
$(X + Y + Z = 100)$

where
X (%) represents the content of Cr_2O_3,
Y (%) represents the content of Mo and
Z (%) represents the total content of other ingredients.

In a diagram showing the correlationship the blending ratio between Cr_2O_3 and Mo in Fig. 2, the foregoing relationship is represented by a region surrounded with the following lines:
$X = 60$
$X = 90$
$Y = 0.10X$
$Y = 0.45\,X$
$X + Y = 100$,
that is, a region surrounded with points a, b, c, d and e.

If Cr_2O_3 is not greater than 60%, the ratio of Cr_2O_3 and Mo in the eutectic texture is reduced, failing to obtain a sufficient effect of improving the mechanical property by compositing the materials, by which the abrasion resistance, etc. of the coating layer is deteriorated. On the other hand, if Cr_2O_3 exceeds 90%, the amount of Mo is relatively reduced even if Mo occupies all the portion of the balance. Thus, the ratio in the eutectic texture is also insufficient to obtain an aimed composite effect thereby deteriorating the toughness of the coating layer.

If Mo is not greater than 10% of Cr_2O_3 ($Y < 0.10 \times X$), since Mo is insufficient, the ratio in the eutectic texture is reduced failing to obtain a sufficient effect. If Mo exceeds 45% relative to Cr_2O_3, ($Y > 0.45 \times X$), phase separation into Cr_2O_3-enriched molten liquid and Mo-enriched molten liquid occurs during melting and the solidified texture is also separated into two phases, that is, a phase comprising Cr_2O_3 as the matrix and a phase comprising Mo as a matrix. Therefore a Cr_2O_3-Mo system composite material in which the ingredients are finely dispersed can't be obtained.

In the present invention, content of other ingredients than Cr_2O_3 and Mo is defined as below 34% in view of the preferred range described above (60% of Cr_2O_3 and 6% (60 x 0.10) of Mo). As the ingredients other than Cr_2O_3 and Mo, there can be mentioned, for example, the following ingredients (1) - (4).

(1) A slight amount of impurity contained in the starting Cr_2O_3, for example, SiO_2, TiO_2 and Fe_2O_3.

(2) A slight amount of impurity contained in the starting Mo, for example, Fe and Al.

(3) Alloying element in a case of using Mo alloy as the starting material and a slight amount of impurity, for example, Fe, Al, Ni, Cr, Co and C.

Fe is inexpensive and capable of reducing the cost of the Mo alloy but, since excess Fe will deteriorate the abrasion resistance and the melting point of the coating layer, it is preferred that Fe is not greater than 30%, particularly, not greater than 20%.

Al can refine the metal texture and improve the corrosion resistance thereof but, since excess amount of Al will reduce the corrosion resistance and lower the melting point of the coating layer, it is preferably not greater than 10%, more preferably, not greater than 7%.

Ni is effective for reinforcing the substrate but excess amount of Ni tends to cause different textures. Accordingly, Ni is preferably not greater than 10% and, particularly, not greater than 7%.

Cr improves the corrosion resistance of the substrate but it easily tends to form carbides and excess content thereof tends to deteriorate the toughness of the metal texture. Accordingly, Cr is preferably not greater than 15%, particularly preferably, not greater than 10%.

Co has an effect of reinforcing the substrate but, since excess Co will lower the melting point of the substrate, it is preferably not greater than 10% and, particularly preferably, not greater than 7%.

C has a function of improving the scuffing resistance and the abrasion resistance of the substrate (4) Ingredients separately admixed in addition to Mo or Mo alloy and Cr_2O_3 in the production step of the spray coating material. In this case, the following (a) or (b) can be mentioned as the additive.

(a) The ingredient reactive neither with Cr_2O_3 nor with Mo during melting, not deteriorating the mechanical property such as abrasion resistance of the spray coating layer and having an effect of improving the ratio of material deposited as the coating layer among the spray coating material used (deposition efficiency), etc. For example, Al_2O_3, SiO_2, Fe_2O_3.

(b) Ingredient reactive with Cr_2O_3 and/or Mo during melting but not deteriorating the mechanical property of the abrasion resistance of the spray coating layer with the reaction product and having an effect of improving the deposition efficiency, etc.

They are, for instance, TiO_2, Y_2O_3, as well as R_2O_3 type oxides (R represents rare earth element) of rare earth elements such as La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu.

In the present invention, when a Mo alloy is used as the starting material, it is preferred that the Mo alloy contains not greater than 30% of Fe, not greater than 10% of Al, not greater than 10% of Ni, not greater than 15% of Cr, not greater than 10% of Co, not greater than 3% of C. but, since excess amount of C increases the deposition amount of the carbide and deteriorating the strength of the substrate itself, it is preferably not greater than 3%.

With the method of forming the abrasion resistance coating layer according to the present invention, it is possible to easily form a coating layer of high performance comprising Cr_2O_3 and Mo finely dispersed therein having satisfactory lubricant-retainability, excellent both in abrasion resistance and scuffing resistance and also excellent in mechanical property onto the surface of substrates made of any kind of materials.

According to the present invention, endurance of sliding members, etc. using lubricant can be improved remarkably.

The present invention will now be described referring to examples and comparative examples.

Example 1

A Cr_2O_3 powder and a Mo powder were mixed to obtain a powder mixture of a composition comprising 76%Cr_2O_3 - 24%Mo and a powder mixture 10 was melted in an arc melting furnace 11 shown in Fig. 6. Upon melting, a valve V_1 was at first opened to evacuate the inside to 1 x 10^{-4} Torr by means of a vacuum pump 13. Then, the valve V_1 is closed and another valve V_2 was opened to introduce an Ar gas at 99.99% purity to increase the pressure in a melting chamber 12 to 760 Torr. Under this state, a voltage was applied between a tungsten electrode (negative electrode) 14 and a water-cooled copper crucible (positive electrode) 15 in a melting chamber 12 (16 represents an inlet and 17 represents an exit of coolants) and arc discharge was conducted to melt the powder mixture 10 by the heat of the arc.

Subsequently, the arc discharge was interrupted and molten product was cooled and solidified.

When the cross section of obtained solidified product was examined by an optical microscope, white phase was dispersed in a gray matrix. As a result of X-ray diffraction analysis on the solidified product, a pattern as shown in Fig. 7 was obtained to confirm that the solidified product was composed of Cr_2O_3 and Mo. When overall estimation was made including the result of EPMA analysis, it has been found that the gray matrix portion was composed of Cr_2O_3, the white matrix phase was Mo and the obtained solidified product was Cr_2O_3 - 24%Mo composite material in which proeutectic Mo of a relatively large structure and Mo of relatively small structure formed by the eutectic reaction with Cr_2O_3 were finely dispersed.

Then, the obtained solidified product was coarsely pulverized by using a hammer mill, finely pulverized in a ball mill using an alumina pot and alumina balls and then sieved to obtain a powder of a grain size of 10 to 44 um. When the cross section of the resultant particulate grains was observed by way of an optical microscope. It was confirmed that the respective grains were Cr_2O_3 - Mo composite material particles in which Mo was finely dispersed in the Cr_2O_3 matrix.

Then, the resultant Cr_2O_3-Mo composite material powder was plasma spray coated to the surface of a substrate made of SUS 430 to form a coating layer of 300 um thickness.

The conditions for spray coating are as shown below :

Conditions for Spray coating:

Spray coating device : Low pressure plasma spray coating device
Pressure of atmosphere : 100~120 Torr.
Amount of power supplied : 1.5 kg/hr

When the cross section of the coating layer thus formed was observed under an optical microscope, it was confirmed that a coating layer was formed in which Mo was finely dispersed in the Cr_2O_3 matrix.

Further, after grinding the surface of the substrate thus formed with the coating layer to a minimum degree, two test specimens each of 10 mm width and 100 mm length were cut out, which were subjected to 4-point bending test with the coated side being inside such that the tensile strength was caused in the direction of the thickness of the coating layer. Then, at an instance the coating layer was destructed, the compressive strain in the longitudinal direction of the test specimen resulted at the outermost surface of the coating layer was measured. The results are shown in Table 1.

Comparative Example 1

A coating layer was formed in the same procedures as those in Example 1 except for using a powder mixture of Cr_2O_3 - 24%Mo prepared by merely mixing a Cr_2O_3 powder and a Mo powder as the spray coating material.

When the cross section of the resultant coating layer was observed under an optical microscope, it was confirmed that the coating layer had a laminated structure in which white Mo layers and gray Cr_2O_3 layers were alternately laminated with respect to the direction along the thickness of the coating layer.

Further, the result of measurement for the compressive strain in the same manner as in Example 1 for the resultant materials are shown in Table 1.

From Table-1, it is apparent that the coating layer formed by the method according to the present invention shows extremely great compressive strain resistance and is excellent in mechanical property.

Table - 1

Example	No.	Spray coating material	Compressive strain ($\times 10^{-6}$)
Example 1	1	Composite material powder of Cr_2O_3-Mo	10530
	2		10300
Comparative Example 1	3	Mixed powder of Cr_2O_3-Mo	4200
	4		3600

Example 2

Cr_2O_3-Mo composite material particles prepared in the same procedures as those in Example 1 were spray-coated to the surface of a pin-type test specimen 21 and a disc-type test specimen 22 made of SUS 403 shown in Fig. 8 by the same method as in Example 1.

After grinding the surface of the resultant pin-type specimen (rotation side) 21 and the disc-type specimen (fixing side) 22 on the side of sliding movement, they were set so as to be applied with the rotational force R and vertical load W as shown in Fig. 9 and the abrasion amount was measured by using a device as shown in Fig. 10. In Fig. 10, are shown a belt 23, a shaft 24, a motor 25, a coolant oil circulating pipe 26, a lubricant 27 and air cylinder 28. The experiment conditions in this case are as shown in Table-2. Results are shown in Fig. 11.

Table-2

Area of contact	59 mm^2
Sliding direction	uni-direction
Vertical load	4300N
Sliding speed	1.5 m/s
Total frictional distance	390 km
Lubricant	SAE#20 diesel engine oil
Temperature	160°C
Measured items	load, speed, temperature, frictional force, abrasion amount and surface state

Comparative Example 2

Test specimen was prepared in the same procedures as those in Example 2 except for using a powder mixture of Cr_2O_3 + 24%Mo only by mixing a Cr_2O_3 powder and a Mo powder. The resultant test specimen was measured for the abrasion amount in the same way as in Example 2. The results are shown in Fig. 11-(a) and (b).

From Fig. 11, it is apparent that the coating film formed according to the method of the present invention is much more excellent in the abrasion resistance.

Claims

1. A method of forming an abrasion resistant coating layer comprising the following steps:
   a step of mixing molybdenum or molybdenum alloy with Cr_2O_3,
   a step of melting a resultant mixture,
   a step of cooling a molten product,
   a step of pulverizing an ingot obtained by cooling, and,
   a step of spray coating of powder obtained from the pulverization to the surface of a member.

2. A method as defined in claim 1, wherein the melting is conducted in an inert gas atmosphere by using an arc melting method.

3. A method as defined in claim 1, wherein the melting is conducted at a temperature higher than the melting point of molybdenum or molybdenum alloy.

4. A method as defined in claim 1, wherein the grain size of the powder is from 1 to 100 µm.

5. A method as defined in claim 1, wherein the grain size of the powder is from 10 to 44 µm.

6. A method as defined in claim 1, wherein the spray coating method is a plasma spray coating or flame spray coating method.

7. A method as defined in claim 1, wherein the spray coating method is a low pressure plasma spray coating carried out under the atmosphere pressure from 50 to 300 Torr.

8. A method as defined in claim 1, wherein the spray coating material is spray-coated to the surface of a member and, subsequently, laser beams are irradiated on the surface of the thus formed spray-coating layer.

9. A method as defined in claim 1, wherein a bonding layer is formed prior to the spray-coating of an abrasion resistant coating layer to the surface of the member.

10. A method as defined in claim 1, wherein a molybdenum or molybdenum alloy are mixed with Cr_2O_3.

11. A method as defined in claim 10, wherein the molybdenum alloy comprises not greater than 30% by weight of Fe, not greater than 10% by weight of Al, not greater than 10% by weight of Ni, not greater than 15% by weight of Cr, not greater than 10% by weight of Co and not greater than 3% by weight of C.

12. A method as defined in claim 11, wherein the molybdenum alloy comprises not greater than 20% by weight of Fe, not greater than 7% by weight of Al, not greater than 7% by weight of Ni, not greater than 10% by weight of Cr, not greater than 7% by weight of Co and not greater than 3% by weight of C.

13. A method as defined in claim 1, wherein the composition of the spray coating layer formed is represented by a relationship:

$$X = 60 \sim 90$$
$$Y = 0.10 \times X = 0.45 \times X$$
$$X+Y \leqq 100$$
$$(X+Y+Z = 100)$$

wherein X (%) represents the content of Cr_2O_3, Y (wt%) represents Mo content, Z (wt%) represents the total content of other ingredients.

14. A method as defined in claim 13, wherein the total content Z of other ingredients than Cr_2O_3 and Mo is not greater than 34% by weight.

15. A method as defined in claim 13, wherein the other ingredients than Cr_2O_3 and Mo is one of the followings ① - ④ :
① a slight amount of impurity contained in the starting Cr_2O_3,
② a slight amount of impurity contained in the starting Mo,
③ an alloying element in a case of using a Mo alloy as the starting material and a slight amount of impurity,
④ ingredients separately admix in addition to Mo or Mo alloy and Cr_2O_3 in the production step of the spray coating material.

16. A method as defined in claim 15, wherein the additives ④ comprise the following (a) or (b) :
(a) an ingredient reactive neither with Cr_2O_3 nor with Mo during melting, not deteriorating the mechanical property such as abrasion resistance of the spray coating layer and having an effect of improving the ratio of material deposited as the coating layer among the spray coating material used (deposition efficiency), etc.
(b) an ingredient reactive with Cr_2O_3 and/or Mo during melting but not deteriorating the mechanical property of the abrasion resistance of the spray coating layer with the reaction product and having an effect of improving the deposition efficiency, etc.

17. A method as defined in claim 16, wherein the additive (a) is Al_2O_3, SiO_2 or Fe_2O_3.

18. A method as defined in claim 16, where the additives (b) is TiO_2, Y_2O_3 or an R_2O_3 type oxide (where R represents a rare earth element) of rare earth elements.

FIG. 1

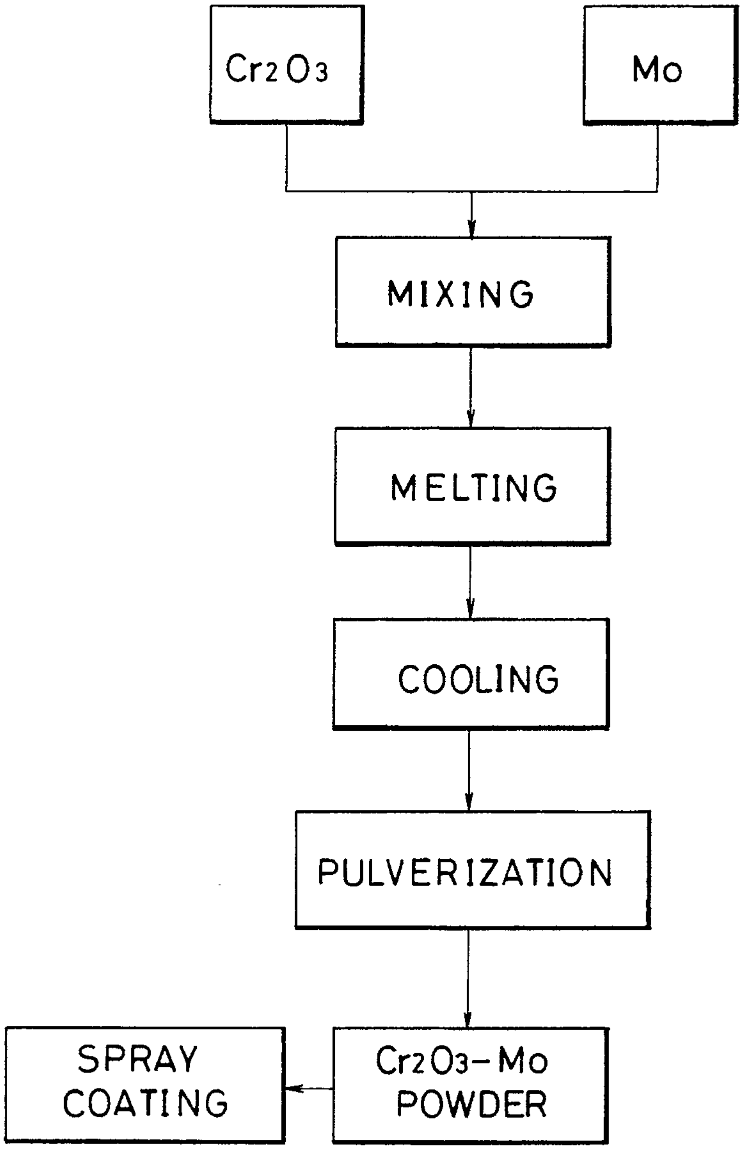

Cr_2O_3
Mo
MIXING
MELTING
COOLING
PULVERIZATION
Cr_2O_3-Mo POWDER
SPRAY COATING

FIG.2

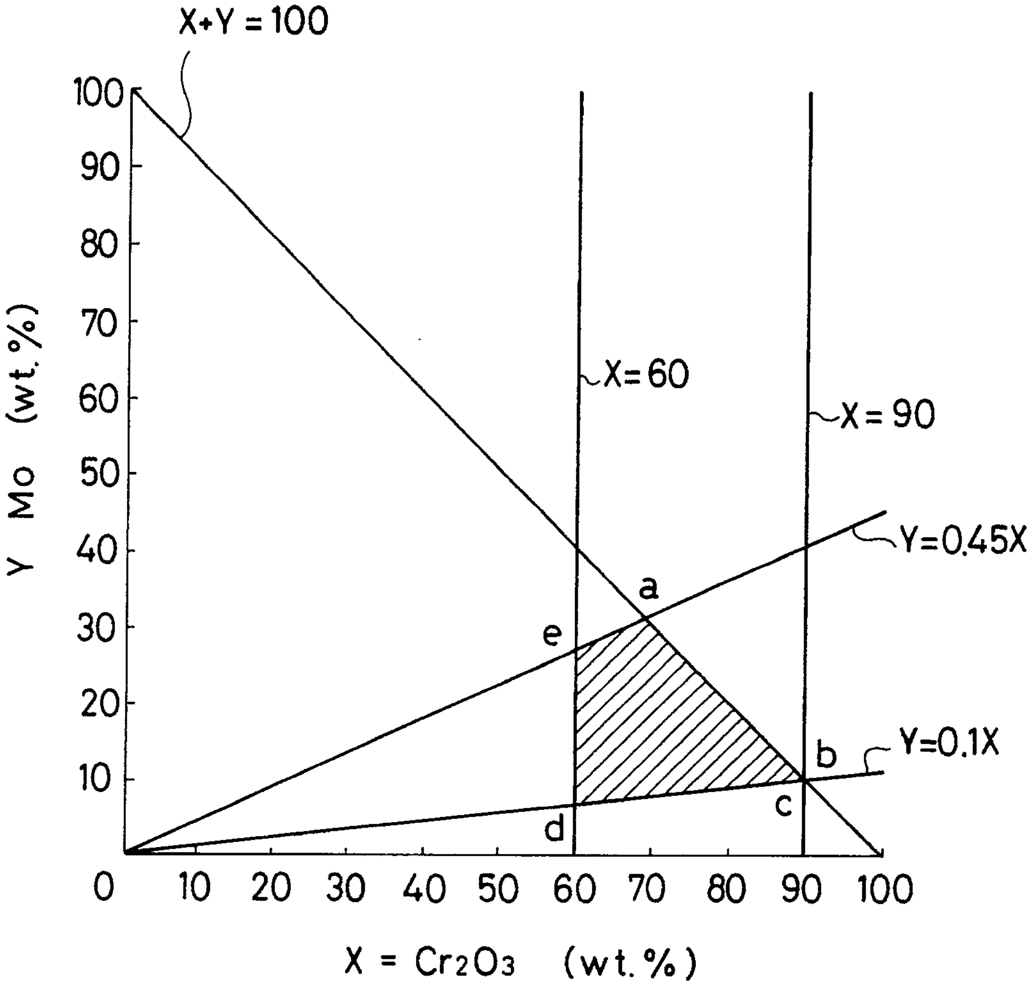

X+Y = 100
100
90
80
70
60
50
40
30
20
10
0
Y Mo (wt.%)
X=60
X = 90
Y=0.45X
Y=0.1X
a
b
c
d
e
10
20
30
40
50
60
70
80
90
100
X = Cr2O3 (wt.%)

FIG.3

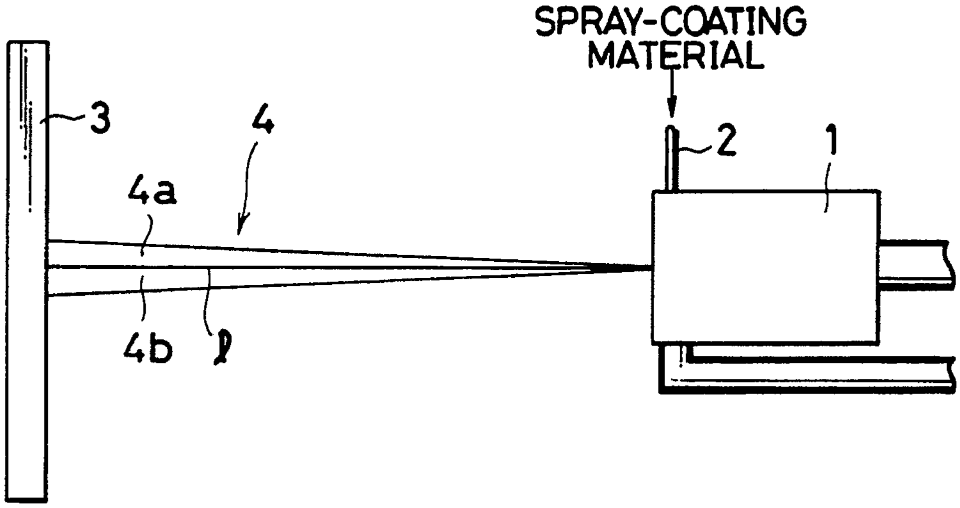


FIG.4

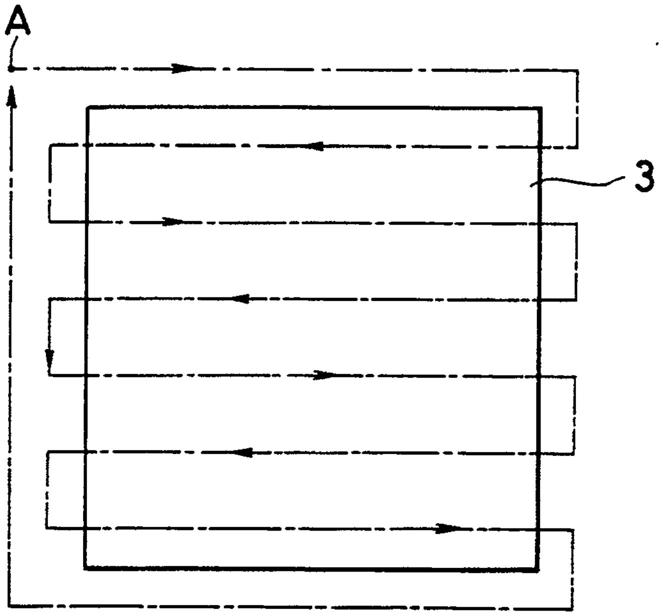


FIG.5

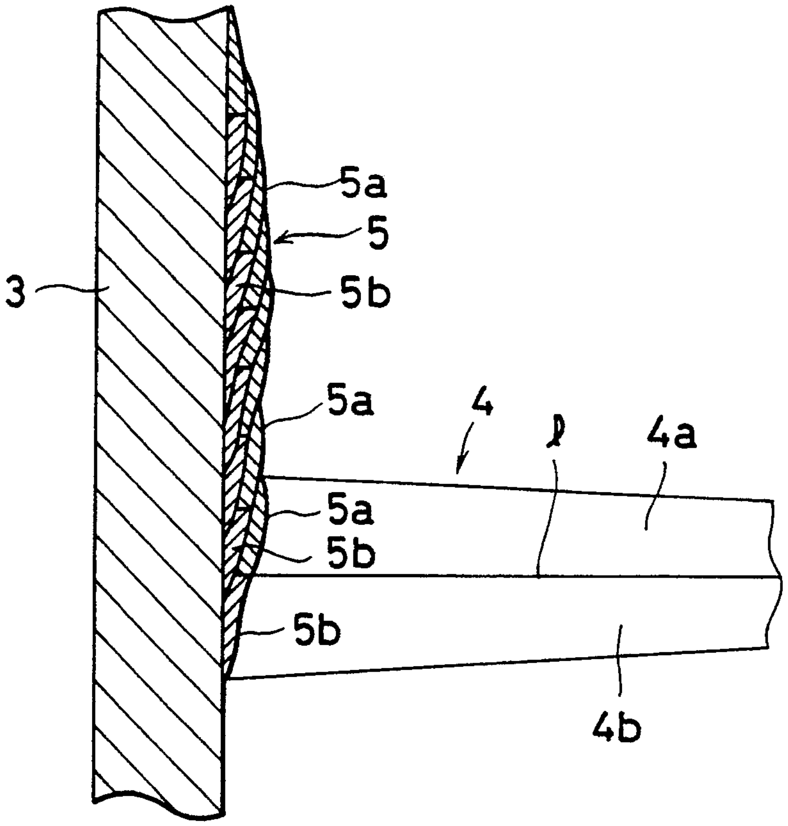


FIG.6

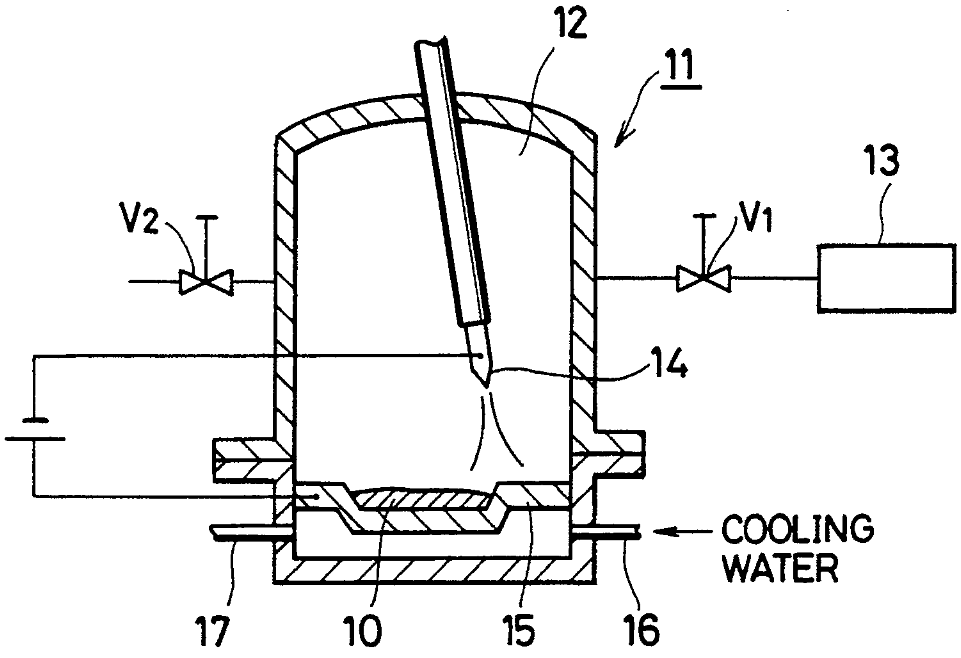


FIG. 7

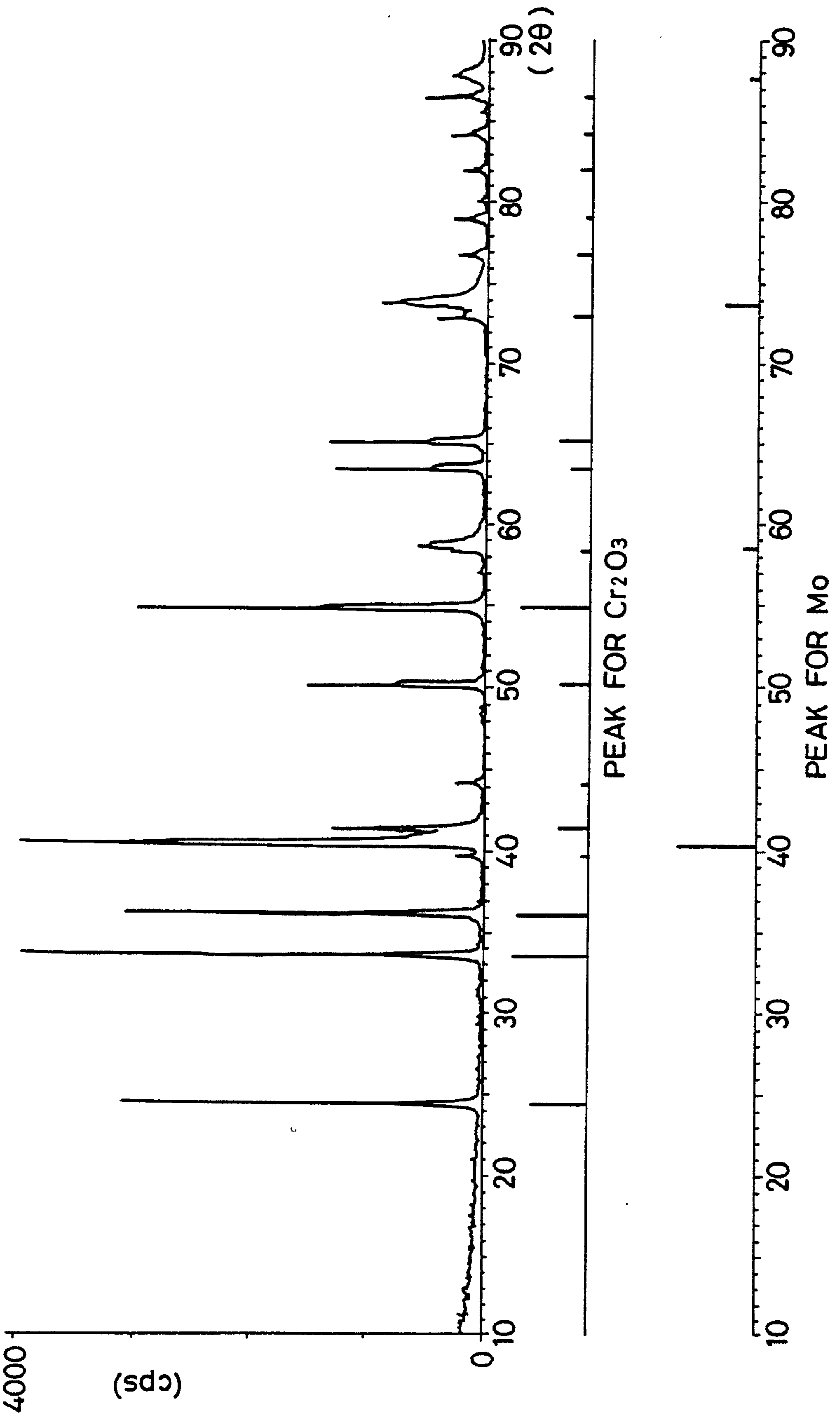

4000
(cps)
0
10
20
30
40
50
60
70
80
90
(2θ)
PEAK FOR Cr_2O_3
10
20
30
40
50
60
70
80
90
PEAK FOR Mo

FIG.8

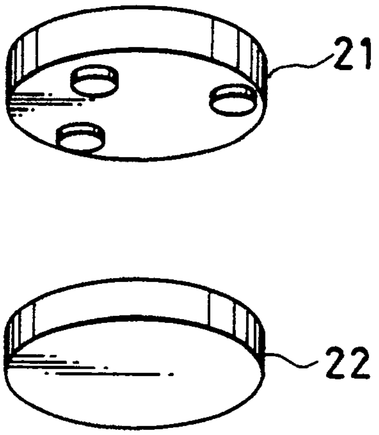


FIG.9

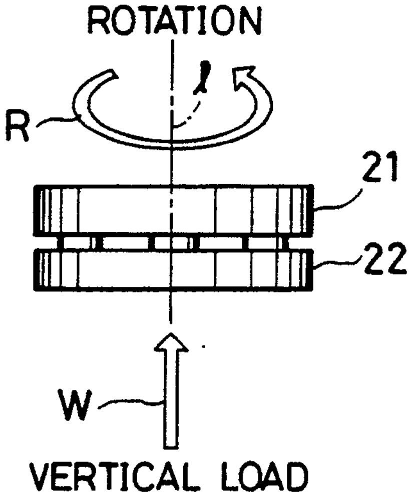


FIG.10

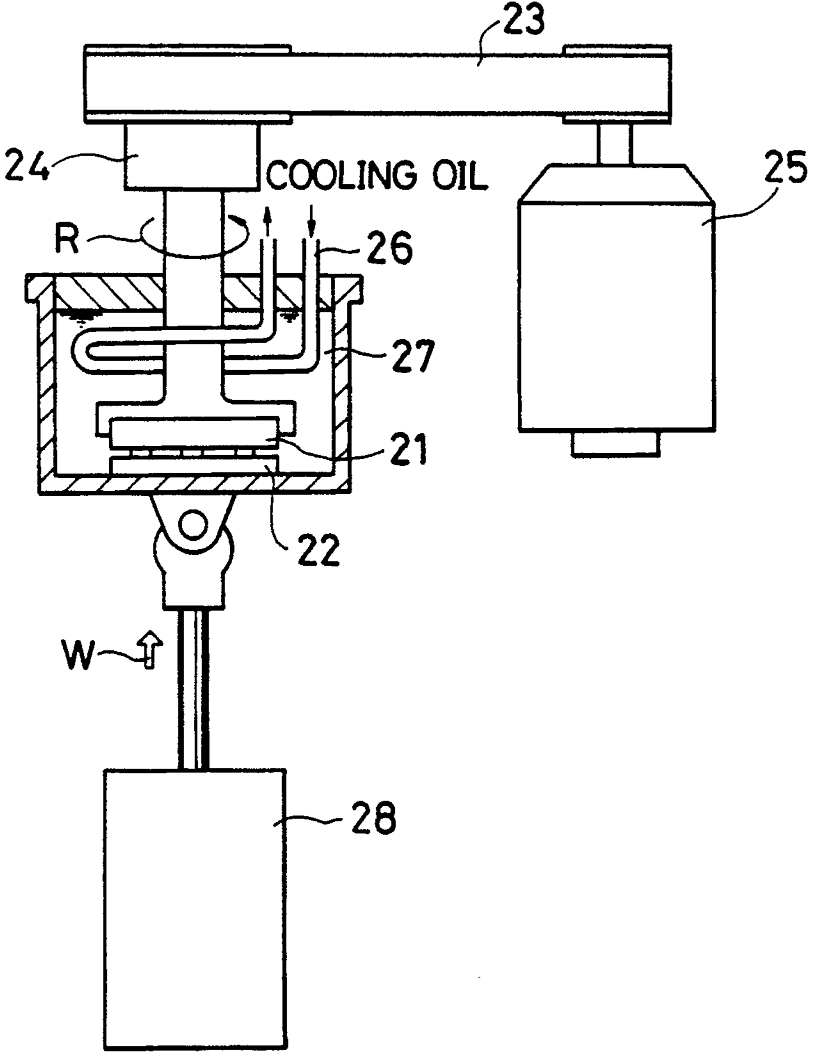
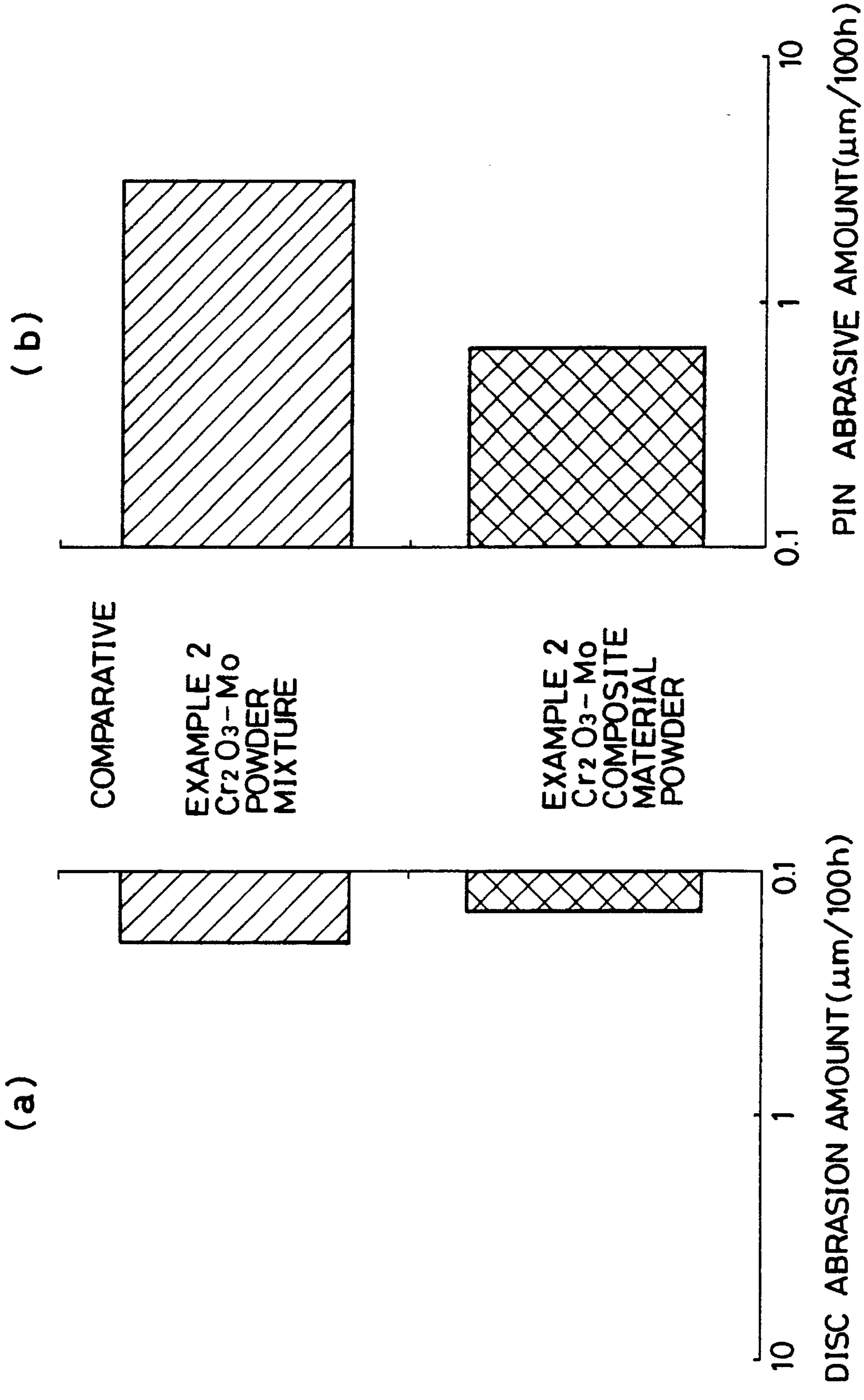


FIG.11


(a)
(b)
COMPARATIVE
EXAMPLE 2
Cr2O3-Mo
POWDER
MIXTURE
EXAMPLE 2
Cr2O3-Mo
COMPOSITE
MATERIAL
POWDER
DISC ABRASION AMOUNT (μm/100h)
10
1
0.1
PIN ABRASIVE AMOUNT (μm/100h)
0.1
1
10

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 90 10 3062

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 219 (C-506)[3066], 22nd June 1988; & JP-A-63 14 851 (TECH. RES. ASSOC. HIGHLY RELIAB. MARINE PROPUL. PLANT) 22-01-1988 * Abstract * ---	1	C 23 C 4/06
A	* Abstract * ---	4,5,6, 10,11, 12,13	
Y	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 118 (C-167)[1263], 21st May 1983; & JP-A-58 37 170 (SHOWA DENKO) 04-03-1983 * Abstract * ---	1	
E	PATENT ABSTRACTS OF JAPAN, vol. 14, no. 242 (C-721)[4185], 23rd May 1990; & JP-A-2 61 050 (TECH. RES. ASSOC. HIGHLY RELIAB. MARINE PROPUL. PLANT) 01-03-1990 * Abstract * -----	1,3,4,5 ,6,10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C 23 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02-10-1990	ELSEN D.B.A.

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