OPIC
OFFICE DE LA PROPRIÉTÉ INTELLECTUELLE DU CANADA

CIPO
CANADIAN INTELLECTUAL PROPERTY OFFICE

(12) (19) (CA) Brevet-Patent

(11) (21) (C) 2,078,369

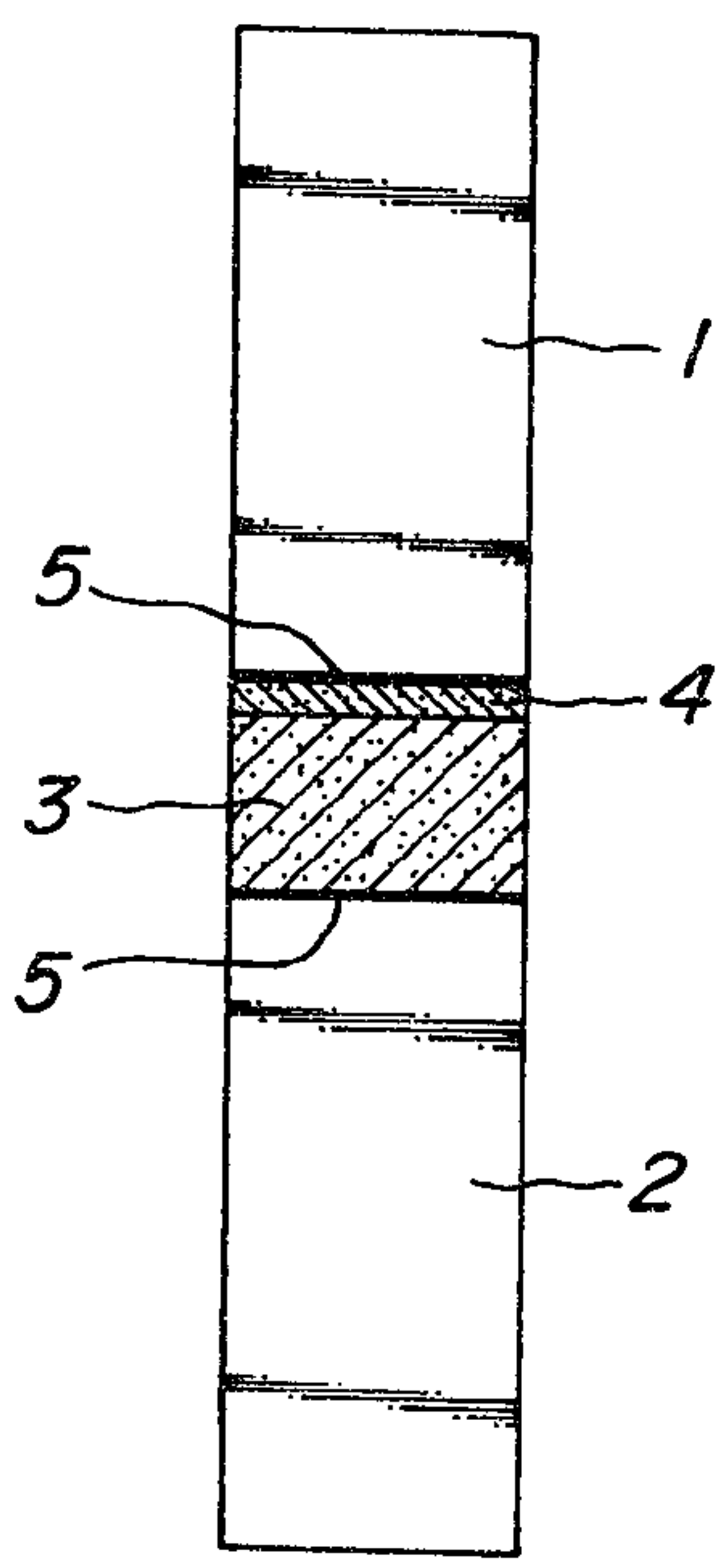
(22) 1992/09/16
(43) 1993/03/18
(45) 2001/05/29

(72) Harada, Yoshio, JP
(72) Takeuchi, Junichi, JP
(72) Okunishi, Shigeki, JP
(72) Tojo, Tetsuro, JP
(72) Hiraiwa, Jiro, JP
(72) Kuroda, Koji, JP
(73) Tocalo Co., Ltd., JP
(73) Toyo Tanso Co., Ltd., JP

(51) Int.Cl.^{5} C23C 4/08
(30) 1991/09/17 (3-262,566) JP

(54) **ELEMENT DE CARBONE A REVETEMENT METALLIQUE APPLIQUE PAR VAPORISATION**

(54) **CARBON MEMBER HAVING A METAL SPRAY COATED**



(57) A carbon member having an excellent bonding property is provided at its surface with a metal spray coating layer, and comprises a carbon substrate and a spray coating layer made from at least one metal selected from Cr, Ti, V, W, Mo, Zr, Nb and Ta or an alloy thereof, in which the coating layer has a ratio of linear expansion coefficient to carbon of 0.73-1.44 and a large chemical affinity to carbon at its interface.

ABSTRACT OF THE DISCLOSURE

A carbon member having an excellent bonding property is provided at its surface with a metal spray coating layer, and comprises a carbon substrate and a spray coating layer made from at least one metal selected from Cr, Ti, V, W, Mo, Zr, Nb and Ta or an alloy thereof, in which the coating layer has a ratio of linear expansion coefficient to carbon of 0.73-1.44 and a large chemical affinity to carbon at its interface.

70756-11

CARBON MEMBER HAVING A METAL SPRAY COATING

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a carbon member provided at its surface with a metal spray coating having an excellent adhesion property, and more particularly to carbon members suitable for use in various rolls made from sintered carbon, metal or vitreous crucibles, various cells, electrodes for electrolysis, structural members for flying objects, heating bodies and sport and leisure goods such as tennis racket, golf club, fishing rods and the like.

Disclosure of the Related Art

The carbon products are light in the weight, excellent in the thermal stability, excellent in thermal and electrical conductivities though they are non-metal, and have mechanical strengths under high temperature environment higher than those of iron steel in the fiber-shaped products, so that they are widely used in up-to-date industrial fields such as chemistry, fiber, high polymer, metal refining, ceramics and the like.

However, the carbon products are poor in the wear resistance and low in the bonding force to metals, so that it is required to eliminate these drawbacks by combining with the other materials.

As the conventional countermeasure for

overcoming the above drawbacks in the carbon products, carbon has hitherto been combined with different materials such as polymers, metals or the like. Lately, there is noticed metal coating formed by electroplating process, chemical plating process, physical vapor deposition process (PVD), chemical vapor deposition process (CVD), spraying process or the like. Up to the present, however, the electroplating process, chemical plating process, PVD process and CVD process are critical in accordance with the shape and size of the product, and also the resulting metal coating layer is relatively thin and can not sufficiently develop the functions as the metal coating layer.

In the method of forming the metal coating layer by the spraying process, the restriction in accordance with the shape and size of the product is less significant and also an optional metal can more freely be thickened as compared with other methods for the formation of the metal coating layer. For instance, the method described in Japanese Unexamined Patent Publication (Kokai) No. 60-221591 published November 6, 1985 has taken notice of such advantageous and proposed a method of forming a metal layer onto a contact surface of a current collecting member of a carbon electrode by the spraying process. In this conventional technique, at least one of Sn, Pb, Zn, Cu, Ag, Al, Ni, Fe, stainless steel, brass, bronze, monel metal and the like is used as a spraying material and spray-coated by an electric type spraying process to form a carbon electrode. In this technique, however, when using plasma spraying process or detonation flames spraying process, the carbon product is undesirably oxidized or broken by a spraying heat source.

In the method of spraying metal onto a surface of a carbon member through the electric arc spraying process described in Japanese Unexamined Patent Publication (Kokai) No. 60-221591 published on November 6, 1985, there are problems that (1) the spraying material is restricted to a soft metal capable of being worked to a wire and hence a metal suitable for the joining to carbon may not be used, and (2) the joining strength of the spraying metal recommended by the conventional technique to carbon is weak, and (3) the coating work speed is slow and the operation efficiency is poor because of the electric arc spraying process.

SUMMARY OF THE INVENTION

It is, therefore, an object of the invention to establish a technique effective for obtaining carbon products having a strong bonding strength between metal spray coating layer and carbon material as a substrate and developing excellent composite functions without causing the above problems.

The inventors have made various studies in order to achieve the above object and found that the considerable effect of solving the above problems is obtained when the surface of the carbon product is preliminarily subjected to a blast treatment and then sprayed with a metal having a linear expansion coefficient near that of carbon and a strong chemical affinity to carbon or an alloy thereof or a mixture with another metal, alloy, ceramic or the like. As a result, the invention has been accomplished.

According to the invention, there is provided of a carbon member having at its surface with a metal spray coating layer having an excellent bonding property. More specifically, the carbon member comprises a carbon substrate previously subjected to a blast treatment and a spray coating layer formed on a surface thereof and made of at least one metal selected from the group consisting of Cr, Ti, V, W, Mo, and Nb or an alloy thereof. The coating has a ratio of linear expansion coefficient to carbon of 0.73-1.44 and a large chemical affinity to carbon at its interface.

In a preferred embodiment of the invention, the metal spray coating layer is further provided at its surface with a spray coating of a metal having a ratio of a linear expansion coefficient of more than 1.44 or a non-metallic compound having a ratio of linear expansion coefficient of less than 0.73, or the carbon member is provided at its surface with a metal coating layer formed by adding Ni, Al, Cu, Co or iron alloy having a ratio of linear expansion coefficient of not more than 1.85 to the metal or alloy to be sprayed and spraying at a mixed state or alloyed state.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described with respect to the accompanying drawings, wherein:

Fig. 1 is a sectional view showing a method for measuring a bonding strength of a metal spray coating layer formed on a sintered carbon substrate; and

Fig. 2 is a graph showing a relation between apparent ratio of linear expansion coefficient and bonding strength of metal coating layer when Cr powder is mixed with Ni powder or Cu powder at an optional ratio and applied onto a sintered carbon substrate by an atmospheric plasma spraying process.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the invention, the reason why a material of spraying metal to be applied onto a surface of a carbon substrate is restricted to Cr, Ti, V, N, Mo, Zr, Nb, Ta and an alloy thereof is due to the fact that the linear expansion coefficient of these metals or alloy is within a range of 4.5 to 8.9 x 10^{-6}/°C (room temperature to 100°C) and is near that of the carbon substrate (4.2 to 6.5 x 10^{-6}/°C: room temperature to 100°C).

In general, when different materials are joined to each other, if there is a difference in the linear expansion coefficient between both the materials, shearing stress is caused at the joint face in accordance with the temperature change or the like in use, and if such a stress exceeds the joining strength, both the materials are peeled off from each other.

As the spraying metal used in the invention, at least one metal or alloy having a linear expansion coefficient of $4.5 \times 10^{-6}/°C$ to $8.9 \times 10^{-6}/°C$ is used. These metals and alloys are characterized by having a small difference to the linear expansion coefficient of carbon substrate.

A ratio of the linear expansion coefficient of the metal to linear expansion coefficient of carbon substrate ($6.2 \times 10^{-6}/°C$), i.e linear expansion coefficient ratio (metal/carbon) is within a range of 0.73-1.44 as seen from Table 1.

Table 1 ($\times 10^{-6}/°C$, room temperature to 100°C)

Metal	Cr	Ti	V	W	Mo	Zr	Nb	Ta
Linear expansion coefficient	6.5	8.9	8.3	4.5	5.1	5.0	7.2	6.5
Linear expansion coefficient ratio	1.05	1.44	1.34	0.73	0.82	0.81	1.16	1.05

Therefore, if two or more of these metals are mixed or alloyed for use in the spraying materials, the linear expansion coefficient of the mixture or alloy is sufficient to be within a range of 0.45-1.85 x 10^{-6}/°C, preferably 0.73-1.44 x 10^{-6}/°C.

Although a metal or alloy having a linear expansion coefficient of more than 1.59 such as Ni, Al, Cu, Fe alloy (stainless steel) or the like is not a spraying material according to the invention, it may be mixed with the above spraying material (Cr, Ti, etc.) for the spray coating. In the latter case, the ratio of the linear expansion coefficient of the metal or alloy mixture to the linear expansion coefficient of the carbon substrate should be not more than 1.85.

The peeling phenomena at the joint portion due to the thermal expansion difference can be prevented as long as the above linear expansion coefficient ratio is maintained.

In the spraying metal or alloy according to the invention, it is required to have an excellent chemical affinity to carbon. That is, fine particles of the metal, alloy or the like fly toward the surface to be coated at a molten state during the spraying and collide with the surface of the carbon substrate to form a coating layer. In this case, it has been found that the metal or alloy takes a lamination structure physically bonded to the substrate and also is bonded thereto through strong chemical affinity.

In general, it is known that the intensity of chemical affinity between metal and carbon has the following order, from which it is apparent that all of the metals according to the invention have strong affinity.

Nb > Ti > V > W > Mo > Cr > Mn > Fe > Ni > Co > Si

Moreover, the metals and alloys according to the invention have a side that they are easily oxidized by oxygen under a high temperature spraying environment. However, the resulting oxides are low in the sublimation temperature (for example, sublimation temperature of each oxide MO_3: 795°C, WO_3: 1000°C, Nb_2O_5, Ta_2O_5: not lower than 1370°C), and evaporate very easily in the spraying heat source such as plasma, combustion gas or the like. Therefore, when they collide with the carbon substrate, the oxide film formed on the surface of the metal particle becomes fine and hence the bonding strength of the coating layer is improved without obstructing the chemical affinity to carbon. Moreover, a slight amount of oxide film retained without evaporation is microscopically removed by reduction reaction.

In the carbon member according to the invention, after the spray coating layer of the above metal or alloy is formed, a metal having a linear expansion coefficient of more than 1.85 such as Ni, Al, Cu, Ca or the like may be sprayed thereon to form a multilayer-like coating layer.

Alternatively, ceramics such as Al_2O_3, ZrO_2, TiO_2, Cr_2O_3, WC, TiC, Cr_3C_2 and the like or cermet material thereof, which have a linear expansion coefficient smaller than 0.73, may be sprayed to form a multi-layer like coating layer.

According to the invention, many kinds of the metal, alloy, ceramics and the like may be coated onto the surface of the carbon substrate. In this meaning, the invention is expected to be applied to various industrial fields and is considerably large in the industrial merit.

In the invention, the thickness of the metal spray coating is desirable to be 0.05-5 mm on the surface of the carbon substrate. When the thickness is less than 0.05 mm, the effect of the metal coating layer can not sufficiently be developed, while when it exceeds 5 mm, the operation takes a long time and the amount of metal consumed becomes large and disadvantageous in the economical reasons.

If the material having a linear expansion coefficient larger than the above defined range or the material having a linear expansion coefficient smaller than the above defined range is sprayed to form a multi-layer like coatings, the thickness of the metal spray coating as an under layer may be thinned.

In the production of the metal spray coating layer obtained by spraying the metal or alloy according to the method of the invention, plasma, combustion gas flame, explosion energy or the like may be used as a spraying heat source. Further, the spraying may be conducted in atmosphere or an argon gas environment under a low pressure as a spraying atmosphere.

According to such a spraying method, the coating metal or alloy may be rendered into a linear or powdery form, so that metals suitable for the joining to carbon such as metals of Cr or the like not capable of working into the linear form and metals of Nb, Ta, W hardly working into the linear form or very high in the cost even in the working can be used freely.

In the invention, the metal spraying material of powdery state may be used, so that different metals may be mixed at an optional mixing ratio to form a metal spray coating layer for various applications.

Moreover, when such spraying powdery materials passed through a high temperature plasma flame even at the mixed state, the powdery materials are rendered into a molten state containing a large amount of metal completely alloyed through metallurgical reaction and adhered to the surface of the carbon substrate, which largely contributes to improve the bonding strength of the coating layer according to the invention.

As mentioned above, the metal spray coating layer having an excellent bonding property is formed on the surface of the carbon substrate.

The following examples are given in illustration of the invention and are not intended as limitations thereof.

Example 1

A high density carbon sintered body of a discontinuous layer structure (width 50 x length 100 x thickness 10 mm) was used as a test mother material. It was first subjected to a blasting treatment with Al_2O_3 (# 60) and further at the surface thereof to an electric arc spraying process, a powdery spraying process using oxygen·acetylene combustion flame as a heat source (flame spraying), an atmospheric plasma spraying process mainly using argon gas (atmospheric plasma spraying), or a spraying process in which plasma as a heat source is used in an atmosphere adjusted to 100-200 mbar with argon gas after the removal of air (low-pressure plasma spraying), whereby various spraying materials shown in table 2 were spray-coated at a thickness of 150 μm. Thereafter, a circular specimen of 25 mm in diameter was cut out from a carbon sintered body provided with the resulting metal spray coating and subjected to a method of measuring bonding strength as shown in Fig. 1 to measure the bonding property between the metal spray coating layer and carbon substrate. In Fig. 1, numerals 1, 2 are fixing jigs of carbon steel, numeral 3 a sintered carbon body, numeral 4 a metal spray coating layer, and numeral 5 a joint portion with a synthetic resin adhesive.

The measurement of the bonding property was carried out by providing two carbon steel (SS400) jigs of 25 mm in diameter and 80 mm in length, applying a thermosetting epoxy resin to each end portion of the jigs, pushing the carbon specimen provided with the metal spray coating layer onto the resin surfaces between the jigs, and balking the resin through heating at 150·C for 90 minutes.

The measured results on the bonding strength of the metal spray coating layer in accordance with the spraying material are shown in Table 2.

Table 2

	No.	Coating metal	Ratio of linear expansion coefficient	Spraying process				peeling
				arc spraying	flame spraying	atmosphere plasma spraying	low-pressure plasma spraying	
Acceptable Example	1	Cr	1.05	-	470	470	470	○
	2	Ti	1.44	350	320	335	405	○
	3	V	1.34	-	320	350	450	○
	4	W	0.73	-	-	405	430	○
	5	Mo	0.82	310	-	380	420	○
	6	Zr	0.81	-	280	380	405	○
	7	Nb	1.16	-	-	390	420	○
	8	Ta	1.05	-	-	470	470	○
Comparative Example	9	Al	3.80	55	35	18	20	×
	10	Co	2.02	65	40	58	60	×
	11	Fe	1.95	140	130	145	180	×
	12	Ni	2.15	35	38	42	51	×
	13	Cu	2.74	28	25	25	20	×
	14	Zn	5.00	35	41	20	20	×
	15	Stainless steel	2.58	30	41	28	22	×

[Note] - : not conducted
○ : no peeling
× : peeling occurred

As seen from the results of Table 2, the bonding strength in all of the acceptable examples exceeded 300 kgf/cm², while the bonding strength in the metal spray coating layer as a comparative example was very low and the peeling was caused at a bonding strength of less than 200 kgf/cm². Furthermore, when the peeled portion was observed by means of an optical microscope, the peeling was almost caused at an interface between the metal spray coating layer and the carbon substrate.

In the metal spray coating layers having a very small bonding strength (Nos. 9, 12, 13, 15), when the section of the spray coated portion in these layers before the tensile test or immediately after the spraying was observed by means of an optical microscope, the metal spray coating layer was at a state just before the peeling from the carbon substrate, or the interface between the metal spray coating layer and the carbon substrate was completely peeled though the abnormal appearance was not observed.

On the contrary, all of the metal spray coating layers according to the invention (Nos. 1-8) showed a bonding strength of not less than 300 kgf/cm². Furthermore, the breaking was observed in the vicinity of the central portion of the carbon substrate, but the interface between the metal spray coating layer and the carbon substrate showed a good bonding property. As seen from this result, the bonding strength of the metal spray coating layer according to the invention became larger than the tensile strength of the carbon substrate itself (470 kgf/cm^2).

Among the above spraying processes, a linear metal was used in the arc spraying process, but metal wire of Cr, V, W, Nb, Ta or the like was not commercially available (which could not be produced technically or economically), so that each of these metals was used in form of powder, from which the metal spray coating layer was formed by the other spraying process.

As the spraying process according to the invention, it has been found that the low-pressure spraying process shows a best bonding property, but the excellent bonding strength was provided even in the atmosphere spraying process and other spraying processes. That is, as seen from the above test, the bonding property is largely influenced by the kind of the spraying metal rather than the kind of the spraying process.

Example 2

Onto the same carbon substrate as in Example 1 was formed a metal spray coating layer of 150 μ m in thickness by mixing two or more metal powders at a mixing ratio as shown in Table 3 and then spraying the resulting mixture through atmosphere plasma spraying process, and thereafter the bonding strength of the metal spray coating layer was measured by the same method as in Example 1.

The measured results are shown in Table 3. As seen from Table 3, all of the metal spray coating layers in the comparative examples showed a bonding strength of not more than 40 kgf/cm^2, while all of the metal spray coating layers according to the invention were sound and excellent in the bonding strength though the substantially neighborhood of the central portion of the carbon substrate was broken likewise Example 1. From these results, it has been found that the metal spray coating layer according to the invention has a strong bonding strength even if the metals are used alone or in admixture.

Table 3

	No.	Spraying metals (weight ratio)	Bonding strength (kgf/cm^2)
Acceptable Example	1	Cr (80) -Ti (20)	385
	2	Cr (60) -Mo (40)	395
	3	Nb (80) -Ta (20)	405
	4	Cr (60) -Ta (20) -Nb (20)	420
	5	Cr (40) -W (10) -Nb (30) -Ta (20)	410
Conparative Example	6	Ni (80) -Cu (20)	40
	7	Co (40) -Ni (40) -Fe (20)	38
	8	Cu (80) -Zn (15) -Al (5)	27

Example 3

In this example, Ni or Cu powder unsuitable as a metal material according to the invention was mixed with Cr powder suitable as a metal material according to the invention at an optional mixing ratio to form a mixed spraying material, which was sprayed through atmosphere plasma spraying process to form a metal spray coating layer. The bonding strength of the resulting metal spray coating layer was measured by the same method as in Example 1.

In Fig. 2 is shown a relation between the linear expansion coefficient ratio of metal spray coating layer having a different mixing ratio to carbon substrate and the bonding strength of metal spray coating layer, wherein an arrow shows a measured value of bonding strength when the central portion of the carbon substrate is broken, and an arrow portion shows the average bonding strength of the metal spray coating layer higher than the measured value. Furthermore, each mark shows the bonding strength of the metal spray coating layer formed by adding Ni powder or Cu powder to Cr powder.

As seen from the results of Fig. 2, when Cr as a metal suitable for the invention is mixed with 10-99 wt% of Ni or 15-99 wt% of Cu as a metal unsuitable for the invention, if the mixing ratio is small, the high bonding strength is obtained.

On the other hand, the bonding strength tends to lower as the linear expansion coefficient ratio increases together with the high mixing ratio of Ni or Cu. That is, the linear expansion coefficient ratio of the metal spray coating layer to the carbon substrate is critical to be 1.85, so that it has been confirmed that the metal spray coating layer made from the alloy having the mixing ratio of Cr/Ni or Cu lower than the above value shows a high bonding strength.

As mentioned above, the metal spray coating layer made from the metal or alloy having a linear expansion coefficient ratio to carbon of 0.73-1.44, or from a mixture with another material having a linear expansion coefficient ratio of not more than 1.85 has a bonding strength to the sintered carbon substrate stronger than the bonding strength of carbon particle. Therefore, according to the invention, the joining property of the carbon substrate to abrasion-resistant metallic member, which has not been attained in the conventional technique, can be improved while maintaining the properties of the carbon substrate. Furthermore, according to the invention, it is possible to produce carbon members coated with various ceramics, and the formation of the ceramic insulation coating is easy together with the improvement of the appearance, so that the invention develops large effects on the improvement of the properties as a carbon product and the enlargement of applications.

70756-11

CLAIMS:

1. A carbon member comprising, a carbon substrate having a surface previously subjected to a blast treatment, and a spray coating layer formed on the surface, the spray coating layer being made of at least one metal selected from the group consisting of Cr, Ti, V, W, Mo, and Nb or an alloy thereof, and having a ratio formed by dividing the linear expansion coefficient of the spray coating layer by the linear expansion coefficient of the carbon substrate of from 0.73 to 1.44 within the temperature range of from room temperature to 100°C and a chemical affinity to carbon at its interface of at least 280 kgf/cm^2.

2. A carbon member according to claim 1, wherein the spray coating layer is further provided on its surface with a spray coating of a metal having a ratio formed by dividing the linear expansion coefficient of the further metal spray coating by the linear expansion coefficient of the carbon substrate of more than 1.44 within the temperature range specified in claim 1.

3. A carbon member according to claim 2, wherein the metal of the further spray coating is Ni, Al, Cu, Co or iron alloy.

4. A carbon member according to claim 1, wherein the spray coating layer is further provided on its surface with a spray coating of a non-metallic compound having a ratio formed by dividing the linear expansion coefficient of the further non-metallic spray coating by the linear expansion coefficient of the carbon substrate of less than 0.73 within the temperature range specified in claim 1.

5. A carbon member according to claim 4, wherein the non-metallic compound is Al_2O_3, ZrO_2, TiO_2, Cr_2O_3, WC, TiC, Cr_3C_2 or a cermet material thereof.

6. A carbon member according to any one of claims 1 to 5, wherein the spray coating layer made of at least one metal of Cr, Ti, V, W, Mo and Nb is made of a mixture or alloy of the metal with at least one of Ni, Al, Cu, Co or iron alloy and has a ratio of linear expansion coefficient to carbon of not more than 1.85 within the temperature range specified in claim 1.

7. A carbon member according to any one of claims 1 to 6, wherein the metal spray coating layer formed on the carbon substrate has a thickness of 0.05-5 mm.

8. A carbon member according to any one of claims 1 to 7 wherein blast treatment of the carbon member is an alumina blast treatment.

9. A carbon member according to any one of claims 1 to 8 wherein the bonding strength of the metal spray coating layer is 300-470 kgf/cm^2.

10. A carbon member according to any one of claims 1 to 9, wherein the spray coating layer of at least one metal of Cr, Ti, V, W, Mo and Nb is formed by an electric arc spraying process.

11. A carbon member according to any one of claims 1 to 9, wherein the spray coating layer of at least one metal of Cr, Ti, V, W, Mo and Nb is formed by a powder spraying process using an oxygen/acetylene combustion flame as a heat source.

12. A carbon member according to any one of claims 1 to 9, wherein the spray coating layer of at least one metal of Cr, Ti, V, W, Mo and Nb is formed by an atmospheric plasma spraying process using an argon gas.

70756-11

13. A carbon member according to any one of claims 1 to 9, wherein the spray coating layer of at least one metal of Cr, Ti, V, W, Mo and Nb is formed by a spraying process in which plasma is used as a heat source in an atmospheric adjusted to 100-200 mbar with an argon gas after removal of air.

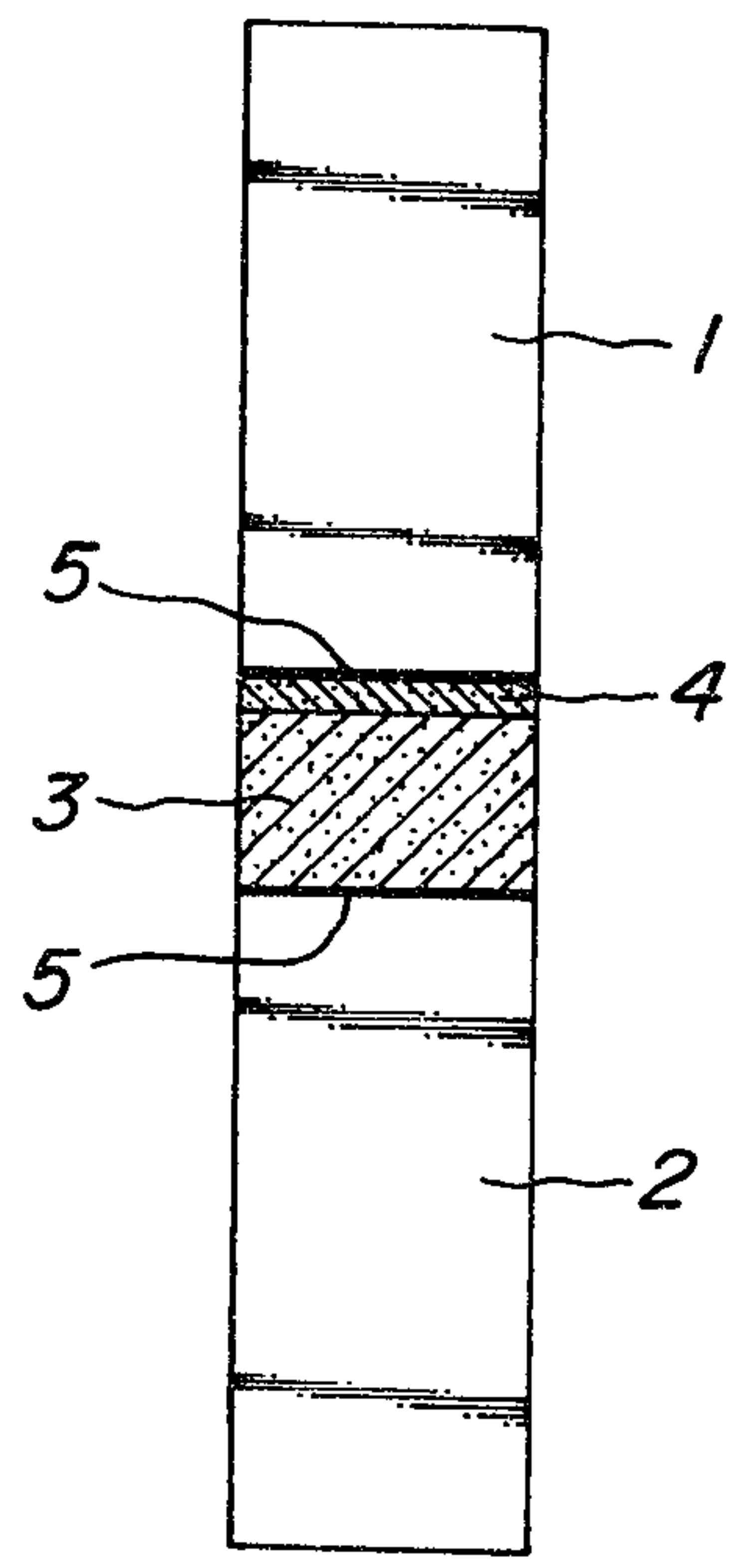
SMART & BIGGAR

OTTAWA, CANADA

PATENT AGENTS

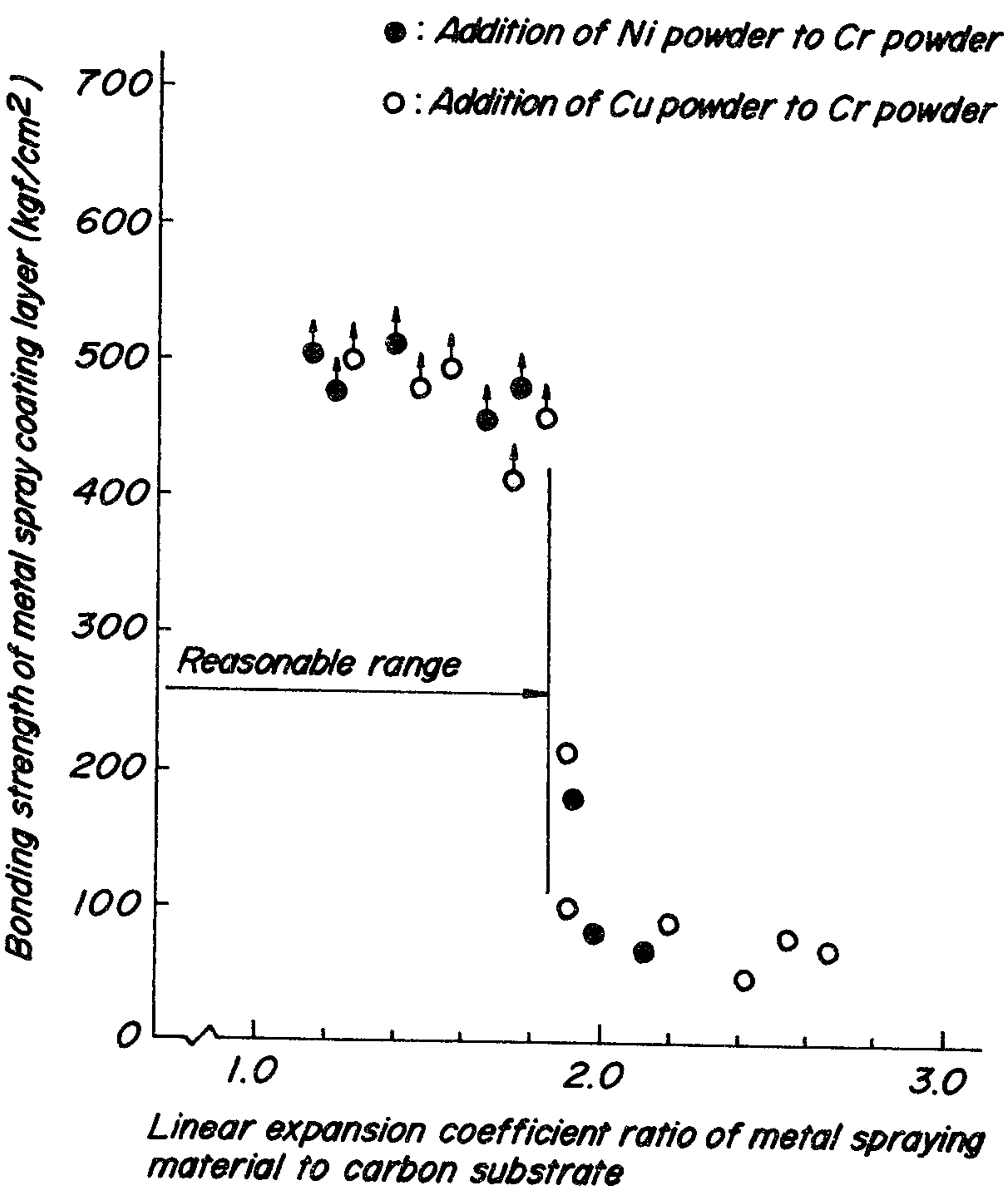
2078369

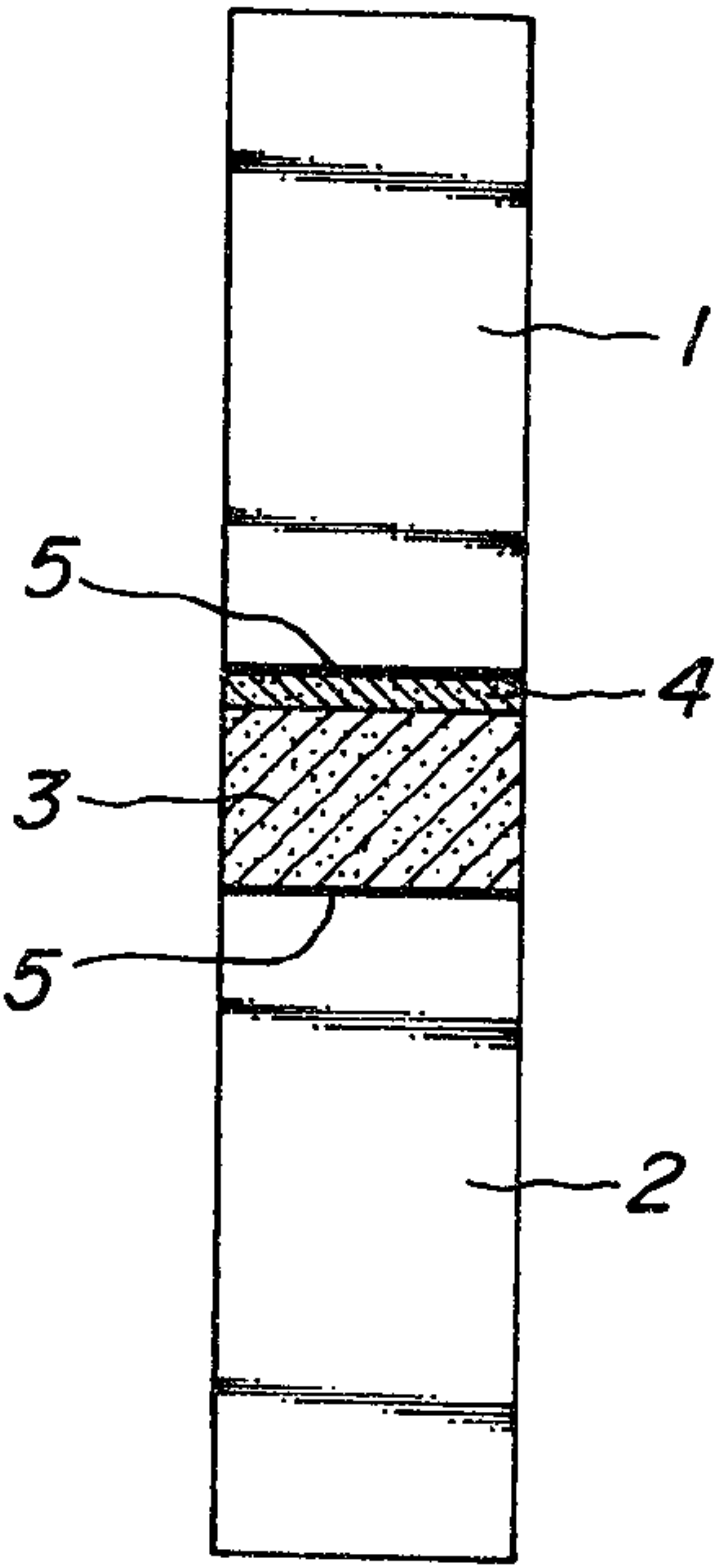
FIG_1



2078369

FIG_2




1
5
4
3
5
2