(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 853 135 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
15.07.1998 Bulletin 1998/29

(21) Application number: **96914423.7**

(22) Date of filing: **24.05.1996**

(51) Int. Cl.[6]: **C23C 4/18**

(86) International application number:
PCT/JP96/01383

(87) International publication number:
WO 97/45566 (04.12.1997 Gazette 1997/52)

(84) Designated Contracting States:
BE DE FR GB IT

(71) Applicant:
NIPPON STEEL HARDFACING CO., LTD.
Tokyo 103 (JP)

(72) Inventors:
- **SATO, Takao**
  Chita-shi, Aichi 478 (JP)
- **MIGITA, Atsushi**
  Kitakyushu-shi, Fukuoka 802 (JP)
- **TARUMI, Kiyohiro**
  Kitakyushu-shi, Fukuoka 802 (JP)

(74) Representative: **Kyle, Diana**
Elkington and Fife
Prospect House
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)

(54) METHOD OF STRENGTHENING SPRAYED COATING

(57) A method for strengthening flame sprayed films which seals and makes minute the inner portions of such films, wherein, at a stage of flame spray film formation at which the flame sprayed film formed has reached its final thickness or less, sealing treatment is conducted using a sealant with respect to the flame sprayed film which is formed, and after the sealant has been completely dried and solidified, the flame sprayed film formation is continued, and wherein, where necessary, these processes may be repeated. It is possible to achieve an increase in the resistance to abrasion, corrosion resistance, and thermal resistance of the flame sprayed film, and thus to achieve a lengthening of the useful life of manufactured parts.

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Description

Technical Field

The present invention relates to a strengthening method for flame sprayed films which are formed by conducting flame spraying of metal, cermet, or ceramics in order to provide resistance to abrasion, corrosion resistance, thermal resistance, and the like, so that structural parts may be provided with a long service life.

Background Art

The formation or a flame sprayed film by conducting flame spraying of metal, cermet, or ceramics has been commonly used with respect to various types of structural parts for industrial use as a method for improving the surface of such structural parts.

Conventionally, when sealing treatment was necessary for flame sprayed films formed on the surface of structural parts, sealing treatment was conducted after the completion of a flame sprayed film having a target thickness.

Accordingly, in the case of the standard sealing treatment described above, penetration of the sealant into the film was approximately 2 - 5 μm from the surface in the case of films having a high density, and a sealant layer of at most 20 μm was formed in films having good permeability, so that incomplete sealing was conducted at depths of 5 μm or greater.

For this reason, there was a problem in that when the surface layer of a structural part having a flame sprayed film formed thereon was degraded or abraded during the use of the part, the effect of the sealing treatment declined, and the useful life of the structural part was shortened.

Sealing treatment was also conducted at reduced pressures in an attempt to increase the permeation of the sealant; however, there was an increase in cost, and there was a limit in permeability in the case of minute flame sprayed films, so that the minuteness of the interior portion of the film was insufficient.

The present invention solves the problems described above present in the conventional technologies; it has as an object thereof to provide a strengthening method for flame sprayed films which increases the minuteness of minute flame sprayed films in the interior thereof, by means of sealing treatment, and strengthens these films, and exhibits superior resistance to peeling.

As a result of diligent investigation in order to attain the above object, the present inventors discovered that it is effective, during the course of forming the flame sprayed film, to carry out sealing treatment in which the sealant is completely solidified; the present invention was completed on the basis of this discovery.

Disclosure of the Invention

The present invention, which is based on this discovery, has as an essential point thereof a strengthening method for flame sprayed films which functions by means of sealing and making minute the interior portion of the film, in which, at a stage of flame sprayed film formation at which the thickness of the film is at the final thickness or less during the formation of the flame sprayed film, sealing treatment is conducted using a sealant with respect to the flame sprayed film which is formed, and after the sealant has been completely dried and solidified, flame sprayed film formation is continued; the present invention also has as an essential point thereof a strengthening method for flame sprayed films in which the inner portion of the film is sealed and made minute, in which the flame sprayed film formation process and the sealing process described above are repeated in an alternating fashion, or in which either or both of heating and brushing are conducted after sealing treatment.

Furthermore, the resent invention also has as an essential point thereof a strengthening method for flame sprayed films in which the inner portion of the film is sealed and made minute, in which the uppermost portion of the film is finished and sealing treatment is conducted with respect to the flame sprayed layer; furthermore, the use of a sealant which produces, after sealing treatment and within the flame sprayed film, one of Cr_2O_3, SiO_2, Al_2O_3, ZrO_2, CrB_2, WB, Mo_2B, SiC, TiC, VC, Cr_7C_3, and NbC, or produces the presence of or a mixture of two or more of the above, or the formation of a flame sprayed film having a different flame sprayed film material after the sealing treatment, or the carrying out of sealing treatment within a vessel at high temperatures and pressures, are included in the present invention.

The structure and function of the present invention will now be explained.

In the present invention, after the formation of a flame sprayed layer having an appropriate thickness, sealing treatment is conducted using a sealant which produces oxides, borides, or carbides, or the co-presence or a mixture of two or more of these, within the flame sprayed film after sealing treatment, or using a sealant such as a metal alkoxide alcohol or the like, and this is then sufficiently dried. Furthermore, where necessary, the sealing-treated surface may be heated to 100°C or more, and a sealant solid may be formed.

After this, a process is again carried out which forms a flame sprayed film of the same material or a different material; prior to flame spraying, the surface is subjected to light brushing, and this is effective in removing excess solids. Furthermore, the sealant may be made into a stable compound by means of heat treatment. In this way, it is possible to seal and make the flame sprayed film minute to the deep layers thereof, by means of again conducting flame spraying after sealing

treatment.

By means of repeating the processes described above, it is possible to sufficiently conduct the sealing treatment of thick flame sprayed films over the entirety of the of the film thickness thereof. Furthermore, depending on the intended purpose, the thickness of the portion subjected to sealing treatment may be appropriately set.

The present invention eliminates the problem present in the conventional flame sprayed film subjected to sealing treatment, that is to say, that the sealing treated layer is too thin, and it is thus possible to effect an enormous increase in the service life of structural parts on which flame sprayed films are formed.

The concentration and type of the sealants employed in the present invention are determined in accordance with the use to which the flame sprayed film is to be put, and in accordance with the relationship between the sealing treatment time and the thickness of the flame sprayed film. Chromic acid system sealants or sealants comprising metal alkoxide alcohol or the like are commonly employed; however, if sealant components are to be employed which exhibit heat and abrasion resistance as well as strong adherence with the flame sprayed film, the sealant composition is not restricted to oxide systems, and boride systems or carbide systems, or a mixture thereof, may be employed.

With respect to flame sprayed films to which sealing treatment is applied, the application of such treatment is effective in the case of ceramic films or cermets having a comparatively high porosity; however, it is possible to apply such treatment to metal flame sprayed films as a means for creating a cermet. In such a case, solids created by the sealant are dispersed within the metal layer, and thereby, it is possible to form a cermet film. Furthermore, where necessary in such cases, it is possible to further increase the minuteness of the flame sprayed film by applying heat treatment as a final treatment.

Best Mode for Carrying Out the Invention

The present invention will be explained in detail using embodiments in which the method of the present invention is applied to the manufacture of structural components chiefly employed in steel production lines; however, the present invention is in no way restricted to such uses.

Embodiment 1

Rollers for use in molten zinc plating baths were treated using the method of the present invention. Cermet or ceramic flame spraying was applied to the surface of rollers used in molten zinc plating baths for thin steel plates.

First, high speed gas flame spraying was conducted with respect to the untreated roller surface so as to form a boride - WC system cermet having a film thickness of 70 μm, and then a chromic acid solution (with a Cr_2O_3 concentration of 30%) or a Si alkoxide alcohol sealant, or both, were applied to the film which was formed, this was sufficiently dried, and then a two pass boride - WC system cermet flame spraying or a Cr_2O_3 system ceramic flame spraying, or both, were conducted (for a thickness of approximately 20 μm). Furthermore, to this were applied the chromic acid solution or the Si alkoxide alcohol sealant, or both, and this was baked at a temperature of 400°C.

In this case, a sealing treated layer was obtained which had a thickness more than two times that of the conventional example, in which the thickness of the sealing treated layer reached 40 μm and only sealing treatment was conducted as the final finishing. Under actual operating conditions of the roller, the useful service life was 50 days when only one of the chromic acid solution and the Si alkoxide alcohol sealant was employed, while the useful service life was 60 days when both were applied.

Furthermore, the useful service life was 50 days when one or the other of the boride - WC system cermet flame spraying and the Cr_2O_3 system ceramic flame spraying was employed as the flame spraying of the upper layer.

When both flame sprayings were employed, the useful service life was unchanged, at 50 days, in the case of a standard zinc aluminum bath (0.2% Al); however, when a 2 - 3% aluminum - zinc bath was employed, it was determined that the use of both flame sprayings was clearly more effective than the use of either one alone.

The useful service life of a conventional roller under actual operating conditions is 30 days, so that it can be seen that these results represent a great improvement.

It is thought that this is because, when conventional sealing treatment is employed, the sealed surface layer is abraded in a short time and degrades quickly.

Furthermore, when a sealing treatment identical to that of the previous process is conducted prior to conducting the final one pass flame spraying of the flame spraying process, the density of the sealing layer is increased, the amount of molten zinc deposited on the surface of the roller decreases, and the corrosion process of the flame sprayed film is greatly decreased, and the quality of the steel plates which pass through is greatly improved. In this case, the useful service life of a roller used in the molten zinc plating bath is further extended and may be 50 days or more.

Embodiment 2

The present invention was applied to the production of a hearth roller.

MCrAlY system cermet flame sprayed rollers are chiefly employed as hearth rollers in continuous annealing furnaces and as appealing furnace hearth rollers in continuous zinc plating lines. It is commonly known that

such rollers which have been subjected to sealing treatment using a chromic acid solution (Cr_2O_3 concentration of 30%) on the surface thereof after the formation of the flame spraying layer have superior resistance to buildup. However, when the surface thereof is abraded, the resistance to buildup becomes somewhat poorer after approximately two years, depending on the amount of use.

In accordance with the present invention, when flame spraying MCrAlY system cermet onto an untreated roller, the flame spraying is halted with the final one pass remaining, sealing treatment is conducted using the chromic acid solution used in the first embodiment, this is lightly baked at 200°C, and then the final flame spraying pass is conducted to a thickness of 15 μm, whereupon sealing treatment is conducted using the solution described above, and this is then baked in a furnace at 400°C. It was confirmed that as a result of this, the thickness of the sealing layer is increased, the density of the flame sprayed film also increases, and the resistance to buildup does not decline even if the surface thereof is abraded somewhat.

Embodiment 3

The present invention was applied to the production of brush up bridle rollers which are employed in acidic solutions.

Conventionally, brush up bridle rollers which were employed in a 5% sulfuric acid solution at 80°C were produced in which a surface film on which a WC - NiCr system cermet was flame sprayed was subjected to sealing treatment using a Si alkoxide alcohol sealant (containing 15% Si), and an increase in roller life was achieved.

However, during the course of use of the roller, the effects of the sealing treatment were eliminated as the surface film was abraded as a result of brushing, so that the useful life span was approximately 1 - 2 years.

In contrast, applying the method of the present invention, when the WC - NiCr cermet was flame sprayed onto the untreated roller, the flame spraying was halted with the final two passes remaining (30 μm) and sealing treatment using Si alkoxide alcohol sealant described above was conducted, the surface thereof was baked at 200°C, the final two passes of flame spraying were carried out, and then sealing treatment was again conducted using the same sealant. As a result, the useful life of the roller increased to 3 - 5 years.

Embodiment 4

The method of the present invention was applied to the production of piston rods for internal combustion engines.

Normally, in order to increase the resistance to abrasion of the piston rods of internal combustion engines, flame spraying of a chromium oxide ceramic is conducted with respect to those portions of the piston rods which are subjected to rubbing.

In contrast, applying the method of the present invention, ceramic flame spraying was first conducted to only half of the total thickness of the flame sprayed film (30 μm) with respect to the portions of the piston rods subjected to rubbing, and than sealing treatment was conducted using a chromic acid solution (containing 30% Cr_2O_3), and after baking the surface at a temperature of 200°C, the remaining half of the film thickness was flame sprayed, sealing treatment was again conducted, and this was completely baked in a furnace in a temperature of 400°C.

As a result, the useful life of the piston rods was lengthened by 1.5 times with respect to that of the conventional articles.

Embodiment 5

The method of the present invention was applied to the production of continuous casting molds.

In order to increase resistance to abrasion and resistance to thermal cracking, continuous casting molds are commonly subjected to the flame spraying of a Ni - Cr system self melting alloy after Ni plating base layer treatment.

In contrast, applying the method of the present invention, after subjecting the surface of the casting mold to Ni plating base layer treatment, during the flame spraying of a Ni - Cr system self melting alloy or a cermet, the flame spraying was halted before the final two passes (50 μm), a chromic acid solution (containing 30% Cr_2O_3) was applied, and this was sufficiently dried, whereupon the final two flame spraying passes were conducted. After this, the solution described above was again applied, and heat treatment was finally conducted at 400°C. As a result of this treatment, the resistance to thermal cracking and resistance to corrosion were increased, and in actual operation, the life span increased by two times in comparison with convention molds.

Embodiment 6

The method of the present invention was applied to the production of table rollers for heat stretching plants.

The table rollers of heat stretching plants require resistance to abrasion, resistance to seizure, and resistance to slippage; conventionally, rollers produced by carrying out self melting alloy flame spraying on a high-Cr cast iron system casting roller were employed. Here, the method of the present invention was applied, and in the process of conducting NiCr - WC system self melting alloy or cermet flame spraying onto an untreated roller, the flame spraying was halted before the final two passes (50 μm), a chromic acid solution (containing

30% Cr_2O_3) was applied and sufficiently dried, and than the final two passes of flame spraying were conducted. Furthermore, the same solution was applied onto this, and heat treatment was finally conducted at a temperature of 400°C.

It was confirmed that the table roller which resulted had abrasion resistance which was more than 20 times greater than that of conventional high-Cr cast iron system casting rollers, and it was confirmed under actual conditions of use that even in the corrosive environment in which cooling water was employed, which could not be employed in the case in which only NiCr - WC system cermet flame spraying was carried out, there was no peeling of the flame sprayed layer.

Embodiment 7

The method of the present invention was applied to the production of a corrosive environment liner.

Conventionally, high-Cr cast iron system tinkered liners, cermet or self melting alloy flame sprayed liners were employed as abrasion resistant liners used in corrosive environments in which water or salt water was employed; however, the tinkered liner showed problems with lose of abrasion resistance, while cermet flame sprayed liners tended to show corrosion over long periods of use.

Here, the method of the present invention was applied to an untreated liner, and during the flame spraying of a NiCr - WC system cermet, the flame spraying was interrupted with the final two passes (20 μm) remaining. A chromic acid solution (containing 30% Cr_2O_3) was applied and sufficiently dried, and then the final two passes of flame spraying were carried out. Furthermore, the same solution was applied on top of this, and heat treatment was finally conducted at a temperature of 400°C.

As a result, the life span of the line increased more than three times under actual conditions of use in comparison with the conventional high-Cr cast iron system tinkered liner.

Embodiment 8

The method of the present invention was applied to the production of paper making rollers for a paper making plant.

Commonly, in order to increase the resistance to abrasion of paper making rollers, WC system cermet flame spraying was conducted with respect to the surface of the untreated roller. In such cases, because corrosive fluids involving sulfuric acid are employed, sealing treatment is necessary in order to provide corrosion resistance.

Here, the method of the present invention was applied to an untreated roller, so that first, cermet flame spraying was conducted so as to produce only half of the total thickness of the flame sprayed film (100 μm), sealing treatment was next conducted by applying a chromic acid solution (containing 30% Cr_2O_3) on this, the surface was baked at a temperature of 200°C, and then the remainder of the flame spraying was conducted, sealing treatment was again conducted using the solution described above, and finally baking was conducted in a furnace at a temperature of 400°C.

As a result, the surface life of the paper making roller was lengthened by 1.5 times in comparison with rollers produced by the conventional method.

Industrial Applicability

The present invention is as described above, so that the resistance to abrasion, resistance to corrosion, thermal resistance, and the like are improved in comparison with flame sprayed films subjected to conventional sealing treatments, and the useful service life of manufactured parts is increased, so that the present invention is highly useful in industry.

Claims

1. A strengthening method for flame sprayed films which seals and makes minute the inner portions of such films, wherein, at a stage of flame sprayed film formation at which the flame sprayed film which is formed has attained a final thickness or less, sealing treatment is conducted using a sealant with respect to the flame sprayed film which is formed, and after the sealant has been completely dried and solidified, flame sprayed film formation is continued.

2. A strengthening method for flame sprayed films which seals and makes minute the inner portions of such films in accordance with claim 1, wherein a flame sprayed formation process and the sealing treatment are repeatedly conducted in an alternating manner.

3. A strengthening method for flame sprayed films which seals and makes minute the inner portions of such films in accordance with claim 1 or claim 2, wherein, before or after sealing treatment, a flame sprayed film is formed of a different flame sprayed film material.

4. A strengthening method for flame sprayed films which seals and makes minute the inner portions of such films in accordance with claim 1, claim 2, or claim 3, wherein, after sealing treatment, one or both of heating and brushing are conducted.

5. A strengthening method for flame sprayed films which seals and makes minute the inner portions of such films in accordance with one of claims 1 - 4, wherein the uppermost finishing flame sprayed

layer is subjected to sealing treatment.

6. A strengthening method for flame sprayed films which seals and makes minute the inner portions of such films in accordance with one of claims 1 - 5, wherein a sealant is employed which produces within the flame sprayed film, after sealing treatment, one of Cr_2O_3, SiO_2, Al_2O_3, ZrO_2, CrB_2, WB, Mo_2B, SiC, TiC, VC, Cr_7C_3, and NbC, or the co-presence or a mixture of two or more of the above.

7. A strengthening method for flame sprayed films which seals and makes minute the inner portions of such films in accordance with one of claims 1 - 6, wherein sealing treatment is conducted in a high temperature and high pressure vessel.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/01383

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl^6 C23C4/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl^6 C23C4/00-4/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922 - 1996
Kokai Jitsuyo Shinan Koho 1971 - 1996
Toroku Jitsuyo Shinan Koho 1994 - 1996

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 59-145776, A (Hitachi Zosen Corp.), August 21, 1984 (21. 08. 84), Claim 1 (Family: none)	1-5, 7
Y	JP, 61-235551, A (Kobe Steel, Ltd.), October 20, 1986 (20. 10. 86), Claim 1; page 2, lower left column, lines 14 to 17 (Family: none)	1 - 7
Y	Microfilm of the specification and drawings annexed to the written application of Japanese Utility Model Application No. 64411/1989 (Laid-open No. 6458/1991) (Osaka Titanium Seizo K.K.), January 22, 1991 (22. 01. 91), Claims 1, 2 (Family: none)	1 - 7
E	JP, 8-158034, A (Nittetsu Hard K.K.), June 18, 1996 (18. 06. 96), Claims 1 to 7 (Family: none)	1 - 7

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
August 12, 1996 (12. 08. 96)	August 20, 1996 (20. 08. 96)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/01383

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 7-268594, A (Sumitomo Metal Industries, Ltd.), October 17, 1995 (17. 10. 95), Claims 1, 2; column 6, line 41 to column 8, line 34 (Family: none)	4 - 7
A	JP, 56-90969, A (Nippon Tungsten Co., Ltd.), July 23, 1981 (23. 07. 81), Claim 1 (Family: none)	4 - 7
A	JP, 57-70275, A (Mitsubishi Heavy Industries, Ltd.), April 30, 1982 (30. 04. 82), Claims 1, 2 (Family: none)	4 - 7

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