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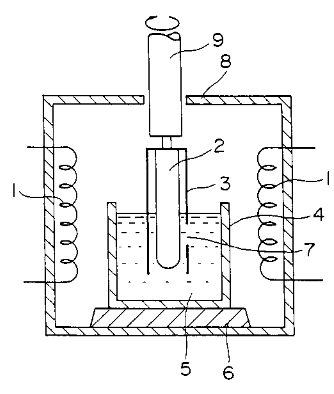
(54) Calvanizing bath members effectively protected against the deposition of alloy layers, a process for producing said members, and a method of hot-dip galvanizing that uses said members.

(57) To develop the invention, alloy layers that deposited on the surfaces of test samples were evaluated by performing a simulation with an experimental setup, in which a heater 1 held the interior of a furnace 8 at a predetermined temperature, a crucible 4 placed on a table 6 on the bottom of the furnace 8 contained a molten zinc-aluminum alloy 5, a thermal sprayed sample 2 retained by a rotating shaft 9 was mounted rotatably in a soft iron cylinder 3 having a window 7. Aluminum is added to ceramics or cermets having high resistance to the erosive action of molten zinc alloys in such an amount that the aluminum content is 0.5 - 10 wt% in the as-sprayed composition. The powder thus prepared is thermal sprayed to form coatings on those members which are to be used submerged in the bath of a continuous hot-dip galvanizing process. The members with such thermal sprayed coatings are protected very effectively against the deposition of unwanted alloy layers. Also provided are the articles having such protective coatings formed thereon, as well the process for producing them and the method of hot-dip galvanizing using those articles.

FIG. 1



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BACKGROUND OF THE INVENTION

This invention relates to the development of a means that is effective in preventing the deposition of alloy layers on the surfaces of members, such as sunk rolls and Support rolls, that are used as submerged in zinc baths or zinc-aluminum alloy baths in facilities for the production of galvanized steel plates and sheets. More specifically, the invention relates to galvanizing bath members such as those to be submerged in galvanizing baths that have many chances to contact the molten zinc and which have coatings deposited on their surfaces by thermal spraying in order to impart not only high resistance to the erosive action of the molten zinc but also effective protection against the deposition of alloy layers. The invention also relates to a process for producing said galvanizing bath members, as well as a method of hot-dip galvanizing that uses said bath members.

Galvanized steel plates and sheets have primarily been produced by continuous hot-dip galvanizing, in which a steel strip with cleaned surfaces is passed through a molten zinc alloy bath usually containing 0.1 - 0.2% aluminum, has the direction of its travel changed by a sunk (submerged) roll and passes by support rolls, wiping nozzles, etc. to be sent to a heating furnace, where alloying is effected and furnace-cooled to room temperature.

During the passage of the steel strip through the aluminum-containing molten zinc alloy bath, the iron will dissolve out of the steel strip to be transferred into the molten zinc alloy, forming an Fe- and Al-supersaturated region in the liquid phase between the surfaces of the steel strip and the sunk roll. The metallic components precipitated out of this liquid phase supersaturated with Fe and Al nucleate on the surface of the sunk roll to have alloy layers deposited in solid phase, which is a phenomenon generally referred to as "dross formation".

The solid-phase deposits of such alloy layers are hard and adhere to the sunk roll so tenaceously that they are deleterious to the surface quality of high-grade galvanized steel sheets such as those for use in automotive body parts. Therefore, preventing the alloy layers from being deposited on the surfaces of sunk rolls and support rolls is extremely important in the effort to improve the quality of galvanized steel plates or sheets.

With a view to preventing the deposition of unwanted alloy layers, it has been proposed that specified materials be thermal sprayed onto the surfaces of sunk rolls or support rolls. The thermal spraying has two functions, one is to prevent the erosion of the surfaces of steel rolls by the molten zinc alloy and the other is to prevent the formation of unwanted alloy layers that are deposited on roll surfaces. Many proposals on the first approach have already been made, as exemplified by the use of non-oxide ceramics (e.g. Cr_3C_2, WC and TiC) or cermets (e.g. TiB_2, CrB_2, ZrB_2) in Unexamined Published Japanese Patent Application (kokai) Hei 4-116147. As for the second approach, the use of a 22% Al-containing iron alloy layer on the surface of a roll has been proposed in Unexamined Published Japanese Patent Application (kokai) Hei 5-78801 whereas the use of an Al_2O_3-TiO_2 pseudo-binary metal oxide System as a thermal spraying material has been proposed in Unexamined Published Japanese Patent Application (kokai) Hei 5-106011.

The coatings formed by thermal spraying the Conventional oxide ceramics have high resistance not only to the erosive action of molten zinc but also against the deposition of unwanted alloy layers. However, the thermal expansion coefficient and mechanical strength of the coatings are so small that if they are actually applied to the surfaces of sunk rolls and other steel rolls, cracks will often develop, making them unsuitable as protective coatings.

The coatings formed by thermal spraying non-oxide ceramics are as poor in adhesion and mechanical strength as those formed by thermal spraying the oxide ceramics. To solve this problem, the addition of metallic components is essential. For example, it has been proposed in Unexamined Published Japanese Patent Application (kokai) Hei 4-358055 that at least one element selected from among Co, Ni and Cr be added to non-oxide ceramics or carbides. As it turned out, however, the coatings formed by thermal spraying the mixtures with Co, Ni or Cr were eroded by either alloying with the galvanizing metal or reacting with diffusing added elements; alternatively, the addition of Co, Ni or Cr promoted the formation of alloy layers deposits on the surface of the coatings.

The coating formed by spray fusing the 22% Al-containing iron alloy taught in Unexamined Published Japanese Patent Application (kokai) Hei 5-78801 is an intermetallic compound of the same kind as the alloy layers to be deposited on the roll surface and, hence, the use of this alloy often induced the deposition of unwanted alloy layers.

Thus, all of the conventional thermal sprayed or spray fused coatings have been unsatisfactory in terms of resistance to the deposition of unwanted alloy layers.

SUMMARY OF THE INVENTION

The present invention has been accomplished under these circumstances and has as an object providing such an article for use either submerged in molten zinc baths or in contact with the molten zinc during continuous hot-dip galvanizing that it has a thermal sprayed coating that not only has high resistance to the molten zinc alloy but is also protected effectively against the deposition of unwanted alloy layers.

Another object of the invention is to provide a process for producing said article.

Still another object of the invention is to provide a method of hot-dip galvanizing that employs said article as a sunk roll or support rolls in the production of galvanized steel plates or sheets and thereby assures maximum protection against the deposition of unwanted alloy layers on the surfaces of those rolls.

The present inventors made studies to attain these objects of the invention and formed coatings using various thermal spraying materials. And in order to investigate the deposition profile of unwanted alloy layers formed on the surfaces of the coatings during hot-dip galvanizing, the inventors conducted a simulation with an experimental setup of the type shown in Fig. 1 and to be described below in details in Example 1. Based on the results of the simulation, the inventors analyzed and evaluated the alloy layers that deposited on the surfaces of test samples. They continued their studies intensively such as by analyzing the mechanism behind the formation of the deposited alloy layers and found that the coatings formed by thermal spraying oxide ceramic or Mo-base cermet matrix that already had high resistance to the erosive action of molten zinc alloy and to which aluminum was added in such an amount as to give 0.5 - 10 wt% Al in the as-sprayed compositon could be protected very effectively against the deposition of alloy layers such as an intermetallic Zn-Fe-Al compound.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic section of the experimental setup which was used not only in Examples 1 and 2 but also in Comparative Examples 1 - 4 to simulate the process of the formation of alloy layers on test samples.

DETAILED DESCRIPTION OF THE INVENTION

The alloy layers deposited on the surfaces of sunk rolls and support rolls are mostly made of an intermetallic Zn-Fe-Al compound. As already mentioned, the deposition of the Zn-Fe-Al alloy layer starts with the dissolution of iron from the steel strip into the molten zinc alloy, goes through the formation of an Fe- and Al- supersaturated region in the liquid phase between the surfaces of the steel strip and the sunk roll, and ends with the nucleation of the supersaturated metallic components on the roll surface. Papers on nucleation have pointed out that its frequency is generally determined by the matching in Crystalline structure on the surface of the material in which nuclei are to be formed, namely, the crystal matching between the surface of hot material and the precipitate, and by the surface tension of the material.

Details of the mechanism behind the effectiveness of Al addition are not completely clear but it may well be assumed that the added aluminum affects the crystal matching at the surface of the material or its surface tension and, thereby, lowers the frequency of the formation of nuclei of the alloy which would otherwise occur and that, as a result, the chance of dross formation on the roll surfaces having the thermal sprayed coating is reduced.

The coating formed by thermal spraying an oxide Ceramic or Mo-base cermet matrix that already has high resistance to the erosive action of molten zinc alloys and to which aluminum has been added in such an amount as to give 0.5 - 10 wt% Al in the as-sprayed state has not only outstanding resistance to molten zinc alloys but it also is protected effectively against the deposition of unwanted alloy layers. If the addition of aluminum is less than 0.5 wt%, the proportion of Al that occupies the coating's surface is too small to assure satisfactory protection against the deposition of unwanted alloy layers; if the addition of aluminum exceeds 10 wt%, aluminum will dissolve out of steel plates or sheets in an excessive amount to potentially cause adverse effects on their quality.

If the oxide ceramic matrix is spinel ($MgAl_2O_4$) or zircon ($ZrSiO_4$), the coating formed by thermal spraying it in the presence of the specified amount of Al is not only protected effectively against the deposition of intermetallic compounds but also improved in adherence and mechanical strength.

Sunk rolls on the surface of which a coating has been formed by thermal spraying Mo-base cermets containing MoB, Mo_2B or Mo_2B_5 have high resistance to molten zinc but, in actual use, the intermetallic Zn-Fe-Al compound will deposit and can be a serious potential trouble. Hence, after their development as thermal spraying materials having extremely high resistance to molten zinc alloys, the Mo-base cermets containing MoB, Mo_2B or Mo_2B_5 have been limited in actual use. However, this problem is completely solved by the present invention and it has been found that the deposition of the intermetallic compound can be prevented very effectively by forming a thermal sprayed coating that has Al added to said Mo-base cermets in such an amount that 0.5 - 10 wt%, say, 2 wt% Al will eventually be incorporated in the coating.

Aluminum has a much lower melting point than ceramics and cermets and if a given amount of aluminum as mixed with a ceramic or cermet powder is thermally sprayed, a significant portion of the sprayed aluminum will be evaporated or lost upon impinging on the substrate surface. In other words, the amount of aluminum that remains in the thermal sprayed coating varies with the type of the spray method used and it is necessary to control the feed's formulation in such a way that the amount of residual aluminum will be at a preset level. This is why the range of aluminum addition to ceramics or cermets is specified by "weight percent in the as-sprayed state".

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

EXAMPLE 1

Fig. 1 is a schematic presentation of the experimental setup which was used not only in Examples 1 and 2 but also in Comparative Examples 1 - 4. The following description should be read with reference to Fig. 1.

A heater 1 holds the interior of a furnace 8 at a predetermined temperature. A crucible 4 placed on a table 6 in the bottom of the furnace 8 contains a molten zinc-aluminum alloy 5. A SUS rod (20 mm^{ϕ} x 120 mm^{L}) coupled and retained by a rotating shaft 9 is thermally sprayed with Mo-MoB + Al to prepare a thermal sprayed sample 2, which is mounted rotatably in a soft iron cylinder 3 having a window 7.

With a hydrogen-nitrogen atmosphere introduced into the furnace and held at 460 - 550 °C, the thermal sprayed sample was rotated for 6 hours and its surface was examined under a microscope (X 30) and the severity of the deposition of alloyed layers was evaluated by counting the number of Zn-Fe-Al base precipitates (number of dross deposits) as identified within the visual field, as well as measuring their size (size of dross deposits).

The results of the experiment are shown in Table 1.

EXAMPLE 2

The procedure of Example 1 was repeated except that spinel + Al was substituted as a thermal spraying material. The thermal sprayed sample 2 thus prepared was immersed in the molten Zn-Al bath 5 and the severity of the deposition of alloyed layers was evaluated as in Example 1.

The results of the experiment are also shown in Table 1.

COMPARATIVE EXAMPLES 1 - 4

Using the same experimental Setup as in Example 1, the procedure of Example 1 was repeated except that the thermal spraying material was Mo-MoB (Comparative Example 1), Fe-Al (Comparative Example 2), Al_2O_3 + TiO_2 (Comparative Example 3)and WC-Co(Comparative Example 4). After 6 hours of the experiment, the number of dross deposits was counted and their size was measured.

The results of the experiment are also shown in Table 1.

Table 1

Run	Substrate	Coating	No. of dross deposits (12mm^2)	Size of dross deposits (mm)
Comparative Example				
1	SUS403	Mo-MoB	86	0.08-0.4
2	SUS403	Fe-Al	52	0.1 -0.6
3	SUS403	$Al_2O_3 + TiO_2$	42	0.13-0.3
4	SUS403	WC-Co	over the entire surface	
Example				
1	SUS403	Mo-MoB + Al	12	0.05-0.2
2	SUS403	Spinel + Al	10	0.06-0.3

As one can see from Table 1, the comparative samples with the coatings formed by thermal spraying of Mo-MoB and Fe-Al, respectively, had Fe-Al dross deposited in fairly large quantities on their surface. The comparative sample with the coating formed by thermal spraying of WC-Co had dross deposited over the entire surface.

In contrast, the sample with the coating formed by thermal spraying of Mo-MoB plus 2 wt% Al (in the as-sprayed coating), as well as the sample with the coating formed by thermal spraying of spinel plus 2 wt% Al had much fewer dross deposits of smaller size than the comparative sample with the coating formed by thermal spraying of $Al_2O_3 + TiO_2$ ceramics.

Additional experiments were conducted by replacing spinel with zircon ($ZrO_2 \bullet SiO_2$ or $Zr \bullet SiO_4$) and the results were essentially the same.

As described on the foregoing pages, the thermal sprayed coating of the present invention comprises a ceramic or cermet matrix having high resistance to the erosive action of molten zinc alloys and which has aluminum added thereto in an amount of 0.5 - 10 wt% in the as-sprayed composition. The coating offers the advantage that if it is applied to a sunk roll and other bath members that are to be used submerged in the molten zinc bath during Continuous hot-dip galvanizing, those members are not only provided with high resistance to the erosive action of molten zinc alloys but also protected very effectively against the deposition of unwanted alloy layers which would otherwise form on the bath members during galvanizing by the prior art.

Claims

1. A galvanizing bath member effectively protected against the deposition of unwanted alloy layers, which has on its surface a coating that is formed by thermal spraying a ceramic or cermet matrix that has resistance to the erosive action of molten zinc and which contains 0.5 - 10 wt% of aluminum in the as-sprayed coating.

2. A galvanizing bath member according to claim 1 wherein said ceramic matrix is spinel or zircon.

3. A galvanizing bath member according to claim 1 wherein said cermet matrix is based on Mo and contains at least one boride base refractory selected from the group consisting of MoB, Mo_2B and Mo_2B_5.

4. A galvanizing bath member according to any one of claims 1 - 3 which is a sunk roll or support roll for use in a continuous hot-dip galvanizing bath.

5. A process for producing a galvanizing bath member comprising the steps of:

adding and dispersing aluminum in a ceramic or cermet matrix having resistance to the erosive action of molten zinc in such an amount that the aluminum content is 0.5 - 10 wt% in the as-sprayed coating, thereby preparing a thermal spraying powder material; and

thermally spraying the surface of a steel member with the powder material, thereby forming on the surface of said member a coating that is not only resistant to the erosive action of molten zinc but also protected effectively against the deposition of unwanted alloy layers.

6. A process according to claim 5 wherein said ceramic matrix is spinel or zircon.

7. A process according to claim 5 wherein said cermet matrix is based on Mo and contains at least one boride base refractory selected from the group consisting of MoB, Mo_2B and Mo_2B_5.

8. A process according to any one of claims 1 - 3 wherein said galvanizing bath member is a sunk roll or support roll for use in a continuous hot-dip galvanizing bath.

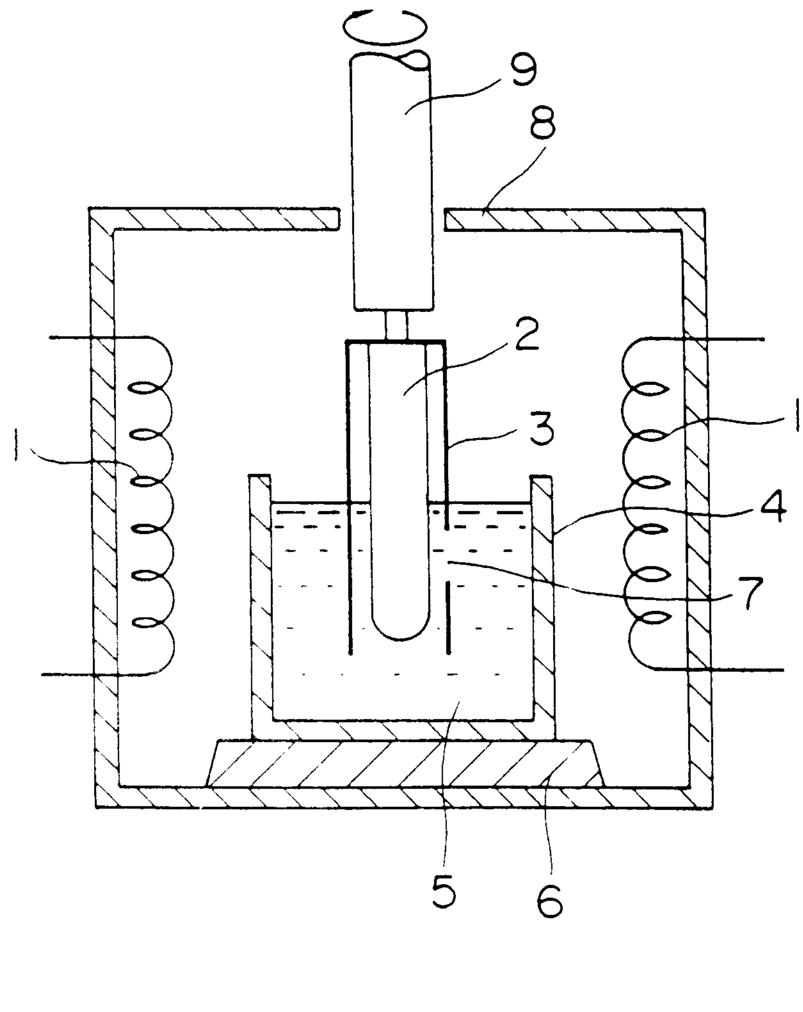
9. A method of hot-dip galvanizing comprising the steps of:

adding and dispersing aluminum in a ceramic or cermet matrix having resistance to the erosive action of molten zinc in such an amount that the aluminum content is 0.5 - 10 wt% in the as-sprayed coating, thereby preparing a thermal spraying powder material;

thermally spraying the surface of an article to be protected with said powder material, thereby forming on the surface of said article a coating that is effectively protected against the deposition of unwanted alloy layers; and

using said article as a hot-dip galvanizing bath member.

FIG. 1



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 94113648.3

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. 6)
D,A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C section, vol. 17, no. 406, July 29, 1993 THE PATENT OFFICE JAPANESE GOVERNMENT page 166 C 1090; & JP-A-05 78 801 (TOCALO CO LTD) --	1,2,9	C 23 C 2/06 C 23 C 4/10
D,A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C section, vol. 17, no. 221, May 7, 1993 THE PATENT OFFICE JAPANESE GOVERNMENT page 64 C 1054; & JP-A-04 358 055 (TOCALO CO LTD) --	1,2,9	
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C section, vol. 9, no. 153, June 27, 1985 THE PATENT OFFICE JAPANESE GOVERNMENT page 6 C 288; & JP-A-60 29 457 (SHIN NIPPON SEITETSU) ----	1,2,9	TECHNICAL FIELDS SEARCHED (Int. Cl.6) C 23 C 2/00 C 23 C 4/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	29-11-1994	HOFBAUER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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