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(54) **HEAT TRANSFER LIMITING FLUX AND ITS USE IN GALVANISING STEEL**

DIE WÄRMEÜBERTRAGUNG BEGRENZENDES FLUSSMITTEL UND DESSEN VERWENDUNG BEI DER GALVANISIERUNG VON STAHL

FLUX LIMITANT LE TRANSFERT DE CHALEUR ET SON UTILISATION DANS LA GALVANISATION DE L'ACIER

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• **PATENT ABSTRACTS OF JAPAN** vol. 010, no. 280 (C-374), 24 September 1986 (1986-09-24) & JP 61 099664 A (KOBE STEEL LTD; others: 01), 17 May 1986 (1986-05-17)

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EP 1 694 880 B1

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Description

[0001] The present invention relates to a water based flux for hot-dip batch galvanising of steel articles. It also relates to the operations of fluxing of the surface to be coated, followed by hot-dip galvanising in a molten zinc-based alloy bath, in particular when the articles are highly stressed or when using a highly wetting zinc alloy.

[0002] In a hot dip galvanising process, steel articles are dipped in a bath of molten zinc or zinc alloy. The molten zinc reacts with the steel and, through a process of diffusion, zinc-iron components are formed at the steel-zinc interface. To facilitate this reaction, the steel surface is fluxed before it is dipped in the zinc melt. This fluxing operation cleans the surface to ensure the complete coverage of the steel by a layer of zinc. The most common fluxing practice comprises a short immersion of the article in a diluted zinc chloride and ammonium chloride solution. After fluxing, the steel surface is thoroughly dried, as any water that would remain on the steel surface would evaporate explosively upon contacting the zinc melt.

[0003] In the prior art, many different flux compositions were proposed for a multitude of purposes, e.g.: fluxes with added wetting agents to obtain a more uniform flux layer on the steel, special fluxes for galvanising using zinc alloys with high aluminium concentrations, fluxes that generates less fumes, fluxes that form less ashes and fluxes that are easier to dry.

[0004] During the process of submerging an article in a molten zinc bath, the differential thermal expansion between the part already submerged and the part that is not yet submerged, creates stress in the articles being coated. This thermally induced stress, combined with any residual stress in the article, can become so high that permanent deformation and cracking occurs. This is especially true in articles with a significant residual stress, such as articles comprising sharp bends or holes, or which are made up of several welded parts. To guarantee the integrity of articles, it is in fact useful to limit the thermal stress as much as possible.

[0005] The thermal stress problem is moreover exacerbated when galvanising with recently developed highly wetting alloys. Such alloys, typically containing tin or bismuth, have been introduced to avoid so-called "black spots", i.e. small areas on the steel surface that remain uncovered after the galvanising process. These alloys are particularly useful, as they tend to stabilise the thickness of the galvanised layer for a wide range of steel types. However, their good wetting capability increases the heat transfer, which leads to accelerated warm-up of articles being dipped and to increased thermal stress as a direct consequence.

[0006] Up to now, in order to alleviate above problems, several recommendations were made to the galvanisers, including increasing the speed of immersion in the zinc melt, changing the angle of dipping, or even modifying the design of the structural elements to be coated. These techniques introduce new constraints to the process or to the articles, and tend to degrade the productivity.

[0007] It has been surprisingly been found that the thermal stress problem can be alleviated by using the invented fluxes, which provide for a significant reduction of the heat transfer between the steel and the zinc melt at the initial stage of immersing the steel articles in molten zinc.

[0008] The invention concerns a water based flux for hot-dip batch galvanising of steel articles, comprising, in total, 200 to 600 g/l of $ZnCl_2$ and NH_4Cl , with a NH_4Cl to $ZnCl_2$ molar ratio of 1.7 to 3.3, characterised in that the flux comprises 8 to 80 g/l $AlCl_3$. The preferred $AlCl_3$ concentration is 10 to 50 g/l; a still more preferred range is 10 to 25 g/l. A suitable flux can be prepared by using 250 to 600 g/l of the double-salt $ZnCl_2 \cdot 2NH_4Cl$, or by using 200 to 500 g/l of the triple-salt $ZnCl_2 \cdot 3NH_4Cl$. It is preferred to limit the Fe concentration of the flux to less than 15 g/l, and even more preferably to less than 10 g/l.

[0009] The invention also concerns a galvanisation process, comprising the steps of: fluxing a steel article utilising the above-mentioned fluxes; drying the article; and immersing the article in a molten bath of a zinc alloy comprising, by weight, 0.1 to less than 5 % of either one or both of Bi and Sn. The zinc bath advantageously comprises, by weight, 0.5 to 5% of either one or both of Sn and Bi, 0 to saturation of Pb, 0.025 to 0.200% of at least one of V, Ni, Cr or Mn, 0 to 0.05% of at least one of Al, Ca and Mg, the remainder being zinc and unavoidable impurities.

[0010] The upper limit of the $AlCl_3$ content of the flux is dictated by the increased viscosity of the flux. Too high a viscosity will indeed impair the replacement of the flux on the surface of the article by zinc alloy from the melt. The $AlCl_3$ concentration in the flux should therefore preferably be limited to 50 g/l, or even to 25 g/l.

[0011] To reach the required amounts of $ZnCl_2$ and NH_4Cl , it is particularly practical to use commercially available double-salts, being $ZnCl_2 \cdot 2NH_4Cl$, or triple-salt, being $ZnCl_2 \cdot 3NH_4Cl$. This will automatically ensure that a suitable NH_4Cl to $ZnCl_2$ molar ratio of respectively 2 and 3 is obtained. The experiments show that with mono-salts, being $ZnCl_2 \cdot NH_4Cl$, or quadruple-salts, being $ZnCl_2 \cdot 4NH_4Cl$, the heat transfer between the steel and the zinc melt becomes unsuitably high, even with proper additions of $AlCl_3$. The flux may further contain well known surfactants that are typically added to improve the wetting of the steel articles in the flux tank and to enhance drainage of excess flux solution when the steel articles are extracted from the flux tank. Typically, a surface tension of less than 40 dynes/cm is recommended. It is common practice in general galvanising to check the surface tension on a regular basis, and to add surfactants as needed.

[0012] It is also recommended to limit Fe in the flux to maximum 15 g/l. It was indeed observed that Fe increases the

heat transfer between the steel and the zinc melt, which is clearly undesired.

[0013] It should furthermore be noted that with '0 to saturation of Pb' is meant a concentration of 1.2 wt.% Pb at most. With 'zinc and unavoidable impurities' is meant zinc with a purity according to the galvanising standard EN ISO 1461.

[0014] As explained above, the use of zinc alloys containing wetting promoters such as Sn or Bi results in accelerated warm-up of the articles upon dipping. The invented flux is particularly well suited for being combined with such alloys, as it greatly alleviates the high risk of permanent damage to most articles.

[0015] The influence of flux and alloy on the thermal stress is evaluated by measuring the heating rate inside a fluxed steel article upon its immersion into a zinc alloy bath. To standardise this measurement, use is made of a probe consisting of a small hollow steel chamber with a wall thickness of 1.3 mm, equipped with a thermocouple brazed against the inner surface of a wall. Upon immersion in the molten alloy at a descent rate of 2.5 cm/s, the temperature rise is recorded and the rate of heating is calculated (°C/s). The descent rate is sufficiently high to ensure that it is not a critical nor a limiting parameter. The highest rate of heating reached during the immersion phase is reported. It is assumed that this rate is closely related to the maximal thermal stress endured during dipping and to the ensuing damages.

Example 1

[0016] Steel strips with a thickness of 13 mm are sharply bent at an angle of 160 degrees. This induces residual stress in the articles, which therefore will be more sensitive to the additional stress endured during dipping.

[0017] No significant deformation or cracking was evidenced, as long as the chosen combination of flux and alloy resulted in a maximum rate of heating, as measured with the above probe, of 200 °C/s or less. The same articles, processed in circumstances generating a heating rate, as measured with the above probe, of 260 °C/s, did show limited stress degradation such as small cracks along the bending line. Using conditions leading to a heating rate of 300 °C/s or more resulted in some catastrophic failures, such as the fracture of articles.

[0018] It should be noted that large articles could be even more sensitive to thermal stress, in particular when residual stress is also present. Small, unstressed articles would of course be less prone to develop defects. In fact, any significant reduction of the heating rate is useful to better guarantee the integrity of the coated articles. A 10% reduction is deemed significant.

Example 2

[0019] In Experiment 1, the above-described probe is fluxed in a 500 g/l aqueous solution of Florflux®, a commercial product manufactured by La Floridienne of Belgium which contains a ZnCl₂.2NH₄Cl double-salt. The probe is dried, and subsequently dipped at an immersion rate of 2.5 cm/s in a Technigalva® zinc alloy melt heated at 450 °C. This alloy consists of zinc with 1 wt% Pb, 0.05 wt% Ni and 0.004 wt% Al. It thus contains no wetting promoters such as Sn or Bi.

[0020] The process according to Experiment 1 is repeated in Experiments 2 to 9, using various amounts of AlCl₃ added to the commercial flux. The results are reported in Table 1.

Table 1: Maximum heating rate as a function of AlCl₃ in a 500 g/l double-salt flux, using a conventional zinc alloy bath

| N° | AlCl ₃ (g/l) | Heating rate (°C/s) |
|-----------------------|-------------------------|---------------------|
| 1* | 0 | 175 |
| 2* | 5 | 172 |
| 3 | 8 | 155 |
| 4 | 20 | 142 |
| 5 | 40 | 140 |
| 6 | 60 | 135 |
| 7 | 70 | 128 |
| 8 | 80 | 140 |
| 9* | 100 | 172 |
| *: counter-experiment | | |

[0021] From this table and from other measurements, it appears that a significant effect of AlCl₃ on the heating rate is achieved from about 8 g/l up to about 80 g/l AlCl₃.

Example 3

[0022] In the following series of experiments, a typical highly wetting alloy is used, namely Galveco®, which consists of Zn with 1.1 wt% Sn, 1 wt% Pb, 0.075 wt% Bi, 0.05 wt% Ni and 0.004 wt% Al.

[0023] The influence of the composition of the flux upon the maximum rate of heating is measured according to the above-described standardised method. In Experiment 10, the same commercial flux was used as in Experiment 1. In Experiments 11 to 19, various amounts of AlCl₃ are again added. The results are reported in Table 2.

Table 2: Maximum rate of heating as a function of AlCl₃ in the flux, using a zinc alloy bath with wetting promoters

| N° | AlCl ₃ (g/l) | Heating rate (°C/s) |
|-----------------------|-------------------------|---------------------|
| 10* | 0 | 345 |
| 11* | 5 | 275 |
| 12 | 8 | 220 |
| 13 | 20 | 180 |
| 14 | 40 | 148 |
| 15 | 60 | 190 |
| 16 | 70 | 153 |
| 17 | 80 | 192 |
| 18* | 100 | 265 |
| *: counter-experiment | | |

[0024] From Experiment 10, which is a counter-example, it can be seen that using a known commercial flux together with a zinc alloy with enhanced wetting, results in a very rapid heating of 345 °C/s. This may lead to severe thermal stress damage. However, for concentrations of AlCl₃ in the flux according to the invention, the rate of heating drops to 260 °C/s or less, a level that is considered as adequate to avoid permanent damage to most articles.

Example 4

[0025] In the following series of experiments, additions of AlCl₃ to mono-salts, being ZnCl₂.NH₄Cl, double-salts, being ZnCl₂.2NH₄Cl, triple-salts, being ZnCl₂.3NH₄Cl, and quadruple-salts, being ZnCl₂.4NH₄Cl, are tested. The same alloy is used as in Example 2.

The influence of the composition of the flux upon the maximum rate of heating is measured according to the above-described standardised method. The results are reported in Table 3.

Table 3: Influence of the type of ZnCl₂.xNH₄Cl salt on the maximum rate of heating, using a zinc alloy bath with wetting promoters

| N° | Salt | ZnCl ₂ + NH ₄ Cl total (g/l) | AlCl ₃ (g/l) | Heating rate (°C/s) |
|-----|--------|--|-------------------------|---------------------|
| 19* | Mono | 300 | 40 | 300 |
| 20* | Double | 300 | 0 | 333 |
| 21 | Double | 300 | 10 | 250 |
| 22 | Double | 300 | 14 | 195 |
| 23* | Double | 400 | 0 | 390 |
| 24 | Double | 400 | 10 | 200 |
| 25 | Double | 400 | 14 | 190 |
| 26* | Double | 500 | 0 | 345 |
| 27 | Double | 500 | 10 | 255 |

EP 1 694 880 B1

(continued)

| N° | Salt | ZnCl ₂ + NH ₄ Cl total (g/l) | AlCl ₃ (g/l) | Heating rate (°C/s) |
|-----------------------|-----------|--|-------------------------|---------------------|
| 28 | Double | 500 | 14 | 200 |
| 29* | Triple | 250 | 0 | 330 |
| 30 | Triple | 250 | 10 | 260 |
| 31 | Triple | 250 | 14 | 240 |
| 32 | Triple | 400 | 14 | 220 |
| 33* | Quadruple | 240 | 20 | 380 |
| 34* | Quadruple | 240 | 30 | 340 |
| *: counter-experiment | | | | |

[0026] In Experiments 20 to 28, the addition of AlCl₃ to a double-salt has a significant beneficial influence on the heating rate. The same applies for experiment 29 to 32, where triple-salt is used. However, using a mono-salt, as in Experiments 19, or a quadruple-salt, as in Experiments 33 and 34, does not lead to heating rates considered as adequate to avoid permanent damage to most articles. It is to be noted that in the industrial practice, the NH₄Cl to ZnCl₂ molar ratio may vary between 1.7 and 3.3, when using double-salts or triple-salts, because of exhaustion and/or adjustment of the various flux components.

Example 5

[0027] Fe is a common pollutant in industrial flux tanks. This example demonstrates that, in addition to the known consequences, extreme Fe concentrations are also to be avoided to limit thermal stress when dip-galvanising steel articles. The galvanising composition of Example 3 was used.

Table 4: Influence of dissolved Fe in a double-salt flux at 500 g/l

| N° | Dissolved Fe (g/l) | AlCl ₃ (g/l) | Heating rate °C/s) |
|-----------------------|--------------------|-------------------------|--------------------|
| 14 | 0 | 40 | 148 |
| 35 | 5 | 40 | 155 |
| 36 | 10 | 40 | 200 |
| 37 | 15 | 40 | 240 |
| 38* | 40 | 40 | 350 |
| *: counter-experiment | | | |

Claims

1. Water based flux for hot-dip batch galvanising of steel articles, comprising, in total, 200 to 600 g/l of ZnCl₂ and NH₄Cl, with a NH₄Cl to ZnCl₂ molar ratio of 1.7 to 3.3, **characterised in that** the flux comprises 8 to 80 g/l AlCl₃.
2. Water based flux according to claim 1, **characterised in that** the flux comprises 10 to 50 g/l AlCl₃.
3. Water based flux according to claims 1 or 2, **characterised in that** the flux comprises 250 to 600 g/l of the double-salt ZnCl₂.2NH₄Cl.
4. Water based flux according to any one of claims 1 to 3, **characterised in that** the flux comprises between 200 and 500 g/l triple-salt ZnCl₂.3NH₄Cl.
5. Water based flux according to any one of claims 1 to 4, **characterised in that** the flux comprises less than 15 g/l Fe, and preferably less than 10 g/l Fe.

6. A process for hot-dip galvanising a steel article, comprising the steps of:

- fluxing the article with a flux according to any one of claims 1 to 5;
- drying the article; and
- immersing the article in a molten bath of a zinc alloy comprising, by weight, 0.1 to less than 5 % of either one or both of Bi and Sn.

7. A process according to claim 6, **characterised in that** the zinc alloy comprises, by weight, 0.5 to 5% of either one or both of Sn and Bi, 0 to saturation of Pb, 0.025 to 0.200% of at least one of V, Ni, Cr or Mn, 0 to 0.05% of at least one of Al, Ca and Mg, the remainder being zinc and unavoidable impurities.

Patentansprüche

1. Auf Wasser basierendes Flußmittel für die diskontinuierliche Feuerverzinkung von Stahlgegenständen, enthaltend insgesamt 200 bis 600 g/l $ZnCl_2$ und NH_4Cl mit einem $NH_4Cl/ZnCl_2$ -Molverhältnis von 1,7 bis 3,3, **dadurch gekennzeichnet, daß** das Flußmittel 8 bis 80 g/l $AlCl_3$ enthält.

2. Auf Wasser basierendes Flußmittel nach Anspruch 1, **dadurch gekennzeichnet, daß** es 10 bis 50 g/l $AlCl_3$ enthält.

3. Auf Wasser basierendes Flußmittel nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß** es 250 bis 600 g/l des Doppelsalzes $ZnCl_2 \cdot 2NH_4Cl$ enthält.

4. Auf Wasser basierendes Flußmittel nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, daß** es zwischen 200 und 500 g/l Tripelsalz $ZnCl_2 \cdot 3NH_4Cl$ enthält.

5. Auf Wasser basierendes Flußmittel nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, daß** es weniger als 15 g/l Fe und vorzugsweise weniger als 10 g/l Fe enthält.

6. Verfahren zur Feuerverzinkung eines Stahlgegenstands, bei dem:

- der Gegenstand mit einem Flußmittel nach einem der Ansprüche 1 bis 5 gefluxt wird;
- der Gegenstand getrocknet wird und
- der Gegenstand in ein schmelzflüssiges Bad einer Zinklegierung, die 0,1 bis weniger als 5 Gew.-% Bi und/oder Sn enthält, eingetaucht wird.

7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet, daß** die Zinklegierung 0,5 bis 5 Gew.-% Sn und/oder Bi, 0 Gew.-% bis zur Sättigung Pb, 0,025 bis 0,200 Gew.-% V, Ni, Cr und/oder Mn und 0 bis 0,05 Gew.-% Al, Ca und/oder Mg, Rest Zink und unvermeidbare Verunreinigungen, enthält.

Revendications

1. Flux à base d'eau pour galvanisation dans un bain d'immersion à chaud d'articles en acier, comprenant, au total, 200 à 600 g/l de $ZnCl_2$ et NH_4Cl , avec un rapport molaire de NH_4Cl à $ZnCl_2$ de 1,7 à 3,3, **caractérisé en ce que** le flux comprend 8 à 80 g/l de $AlCl_3$.

2. Flux à base d'eau selon la revendication 1, **caractérisé en ce que** le flux comprend 10 à 50 g/l de $AlCl_3$.

3. Flux à base d'eau selon la revendication 1 ou 2, **caractérisé en ce que** le flux comprend 250 à 600 g/l du sel double $ZnCl_2 \cdot 2NH_4Cl$.

4. Flux à base d'eau selon l'une quelconque des revendications 1 à 3, **caractérisé en ce que** le flux comprend entre 200 à 500 g/l du sel triple $ZnCl_2 \cdot 3NH_4Cl$.

5. Flux à base d'eau selon l'une quelconque des revendications 1 à 4, **caractérisé en ce que** le flux comprend moins de 15 g/l de Fe, et de préférence moins de 10 g/l de Fe.

EP 1 694 880 B1

6. Procédé de galvanisation par immersion à chaud d'un article en acier, comprenant les étapes de :

- fluxage de l'article avec un flux selon l'une quelconque des revendications 1 à 5 ;
- séchage de l'article ; et
- immersion de l'article dans un bain fondu d'un alliage de zinc comprenant, en poids, 0,1 à moins de 5 % de l'un ou l'autre de Bi et Sn ou des deux.

7. Procédé selon la revendication 6, **caractérisé en ce que** l'alliage de zinc comprend, en poids, 0,5 à 5 % de l'un ou l'autre de Sn et Bi ou des deux, 0 à la teneur à saturation de Pb, 0,025 à 0, 200 % de l'un au moins parmi V, Ni, Cr et Mn, 0 à 0,05 % de l'un au moins parmi Al, Ca et Mg, le reste étant du zinc et des impuretés inévitables.