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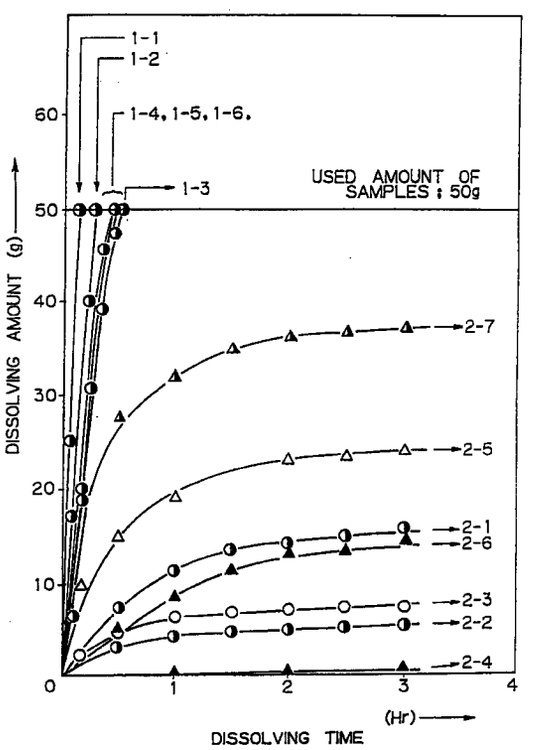
(54) Use of a Zn-Ni alloy for preparation of Zn-Ni alloy hot-dip galvanizing bath

(57) A Zn-Ni alloy having a high Ni content is used for supplying Ni and Zn into a hot dip galvanizing bath. This alloy is characterized by being produced by using a flux consisting of a fused-salt former, which forms a salt having a melting temperature of 700°C or less, and $Na_2B_4O_7$ and occasionally additionally Na_2CO_3. By using such an alloy, the bath can be quickly prepared, and Zn and Ni can be supplied to the bath without leaving the undissolved residue.

Fig. 1



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Description

BACKGROUND OF INVENTION

The present invention is related to the use of a ZN-Ni alloy for simultaneously dissolving Zn and Ni into a Zn-Ni hot-dip galvanizing bath. Furthermore, the present invention is related to a method for producing a Zn-Ni alloy.

Description of Related Arts

Japanese Unexamined Patent Publication No. 60-248855 discloses a Zn-Ni alloy with 3% or less of Ni used for preparation of a hot-dip galvanizing bath. It is described that a Zn-Ni alloy with a higher Ni content causes vigorous vaporization of Zn as the Zn-Ni alloy is dissolved, and more Ni is transferred into dross than when Zn-Ni alloy with less than 3% of Ni is dissolved. Incidentally, the zinc metal is melted and then Ni is added to the molten Zn so as to provide an alloy having a predetermined composition.

Following methods are known heretofore for producing a Zn-Ni alloy.

(1) Metallic Zn and metallic Ni are melted to produce a Zn-Ni alloy.
(2) Ni salt, for example, nickel chloride, is added to the metallic Zn.

Zn-Ni alloy with 2 wt% or less of Ni has a melting point of approximately 600°C. Such Zn-Ni alloy can therefore be melted without relying on a flux. However, since the melting point is greatly raised when the Ni content is higher than 2 wt% according to a phase diagram, the melting temperature of ZN-Ni alloy exceeds the temperature where vigorous vaporization of Zn occurs. It is therefore extremely difficult to produce a Zn-Ni alloy by melting. More specifically, when the surface temperature of Zn-Ni bath exceeds 750°C, the Zn vigorously vaporizes and is oxidized. As a result, an igniting and combusting phenomenon occurs. In addition, bumping phenomenon of the Zn-Ni bath may occur. For the reasons described above, it is recognized that production of Zn-high Ni alloy is difficult by Method (1).

In Method (2) also, a high temperature is necessary for producing a Zn-Ni alloy. In addition, since nickel chloride, which is expensive, is used in Method (2), this Method is not advisable.

Object of the present invention is to provide the use of Ni-Zn alloy for preparation of hot dip galvanizing plating bath, so that: for a short period of time, a bath having desired Ni content can be made up or replenished with Ni due to a high Ni content of the alloy; and virtually all of the Zn-Ni alloy can be melted in the hot-dip galvanizing bath.

In accordance therewith, there is provided the use of a Zn-Ni alloy for supplying Ni and Zn into a hot-dip galvanizing bath, said alloy having a composition containing from 4 to 50% by weight of Ni, the balance being essentially Zn, and being produced by using a flux consisting of a fused-salt former for forming a salt having a melting temperature of 700°C or less and $Na_2B_4O_7$, and occasionally further containing Na_2CO_3.

The Zn-Ni alloy to be used for the preparation of the hot-dip galvanizing bath advantageously contains from 10 to 30% of Ni.

There is also described herein a method for producing a Zn-Ni alloy having a high Ni content, which method can solve the operational problems of Zn vaporization and oxidation reaction, and which can avoid the bumping of the Zn-Ni alloy bath, and exhibit improved dissolving characteristics in the hot-dip galvanizing bath while generating only a small amount of dross when melting in the hot-dip galvanizing bath.

In accordance with this method, said alloy has a composition containing from 2 to 50% by weight of Ni, the balance being essentially Zn, and is melted by using a flux consisting of a fused salt-former for forming a salt having a melting temperature of 700°C or less and $Na_2B_4O_7$, and optionally further containing Na_2CO_3.

DESCRIPTION OF PREFERRED EMBODIMENTS

Purest zinc, electric zinc (99.99% Zn) or distilled zinc (98.5% Zn) can be used as the zinc metal. Ni metal having 99.5% or more of Ni-purity can be used.

The ZN-Ni alloy to be used in the present invention must have a maximum Ni content of 50% by weight, because a high-grade material having a Ni content greater than 50% is difficult to produce by melting due to its high melting point. In addition, when the Ni content is high, the surface area of Ni, which is left after the preferential solution of Zn, is so decreased that the dissolving speed of Ni is lowered. The Zn-Ni alloy to be used in the present invention must contain at least 2% of Ni, because a Zn-Ni alloy having a lower grade of Ni is not practical for the dissolving preparation of an electroplating bath, which usually has an Ni concentration of from 25 to 100g/l.

A preferred composition of Zn-Ni alloy used for the preparation of a bath for Zn-Ni electroplating is from 10 to 30% of Ni, the balance being Zn.

In order to prepare the hot-dip galvanizing bath according to the present invention, a Zn-Ni alloy having a composition containing from 4 to 50% by weight of Ni, the balance being essentially Zn, is preliminarily melted by using a flux

consisting of a fused-salt former for forming a salt having a melting temperature of 700°C or less and $Na_2B_4O_7$ and occasionally further containing Na_2CO_3, and, the so-produced alloy is then dissolved in the molten bath. The so-produced Zn-Ni alloy has a high Ni content, contains Ni uniformly distributed therein, and has a melting point which is virtually the same that is given in a phrase diagram. This alloy can therefore be melted at such temperature while not incurring the disadvantages of the Zn-Ni alloy produced by the conventional method. Even if the Zn-Ni alloy having the inventive composition could be produced by the conventional method, at the sacrifice of yield, Ni, which has a high melting point, greatly segregates, so that much of Ni is left as undissolved residue when such alloy is dissolved. Since the present invention does not involve such disadvantages, addition of Ni to the molten bath is very easy.

Particle size of the alloy to be used in the present invention is not at all limited but is practically 20mm or less. When the particle size is too small, the alloy floats on the surface of plating bath. The particle size is preferably 1mm or more.

Subsequently, the method for producing the Zn-Ni alloy according to the present invention is described in detail and more specifically so as to facilitate the understanding of the method.

The method involves a discovery that a certain composition of flux can prevent, during melting production of a Zn-Ni alloy having 2wt% or more at high temperature, oxidation of the Zn-Ni alloy on its surface and zinc vaporization, as well as ignition and combustion of the zinc-nickel bath. The flux consists, as described above, of a fused-salt former having a melting point of 700°C or less, and $Na_2B_4O_7$. Na_2CO_3 can occasionally be added. For example, NaCl and KCl can be used as the fused-salt former having a melting point of 700°C or less. The NaCl content is preferably from 30 to 70% by weight, because the melting point of the NaCl-KCl is 700°C or less, ignition of the vaporizing Zn can be prevented, and advantageous fluxing effects are attained for melting the Zn-Ni alloy. Proportion of $Na_2B_4O_7$ and Na_2CO_3 is preferably from 10-100 wt% and 90-0 wt%, because the binary $Na_2B_4O_7$-Na_2CO_3 melts at a temperature of 800°C or more and easily absorbs such oxides as ZnO and NiO. When the proportion of $Na_2B_4O_7$ and Na_2CO_3 is as described above, the NaCl-KCl composition is preferably contained in the flux at a content of from 3 to 20 wt%, because the ignition of vaporizing Zn can thoroughly be prevented during the temperature elevation of the zinc metal.

In the melting, zinc is first melted down, and then nickel is added to the molten zinc. The flux described above is dispersed on the molten zinc. The fused-salt former having a melting point of 700°C or less, e.g., NaCl and KCl, first melts at approximately 650°C, and covers the surface of the molten bath to shield it from contact with air. Neither vaporization of Zn resulting in Zn loss nor ignition and combustion of the Zn vapor therefore occur.

The fused-salt former having a melting point of 700°C or less, e.g., NaCl and KCl, does not absorb therein such oxides as ZnO and NiO slightly formed on the surface of Zn-Ni bath. These oxides therefore are present as solids in the interface between the fused salt and the molten alloy.

If the flux consists only of NaCl and KCl, and when the alloy melt is heated to a temperature higher than 800°C, amount of the oxides is so increased that it becomes difficult for the flux in molten state to cover the surface of Zn-Ni bath. Such flux exhibits no longer has effect of shielding the molten alloy from contact with air. Zn then actively vaporizes, leading to ignition and burning of Zn. Contrary to this, in the present invention, when the temperature of the metal bath, which is covered with NaCl-KCl, one of the components of the flux according to the present invention, is further heated to approximately 800°C, then the $Na_2B_4O_7$ or $Na_2B_4O_7$ and Na_2CO_3 is caused to melt. Such oxides as ZnO and NiO are absorbed in or dissolve in the resultant $Na_2B_4O_7$ or $Na_2B_4O_7$ and Na_2CO_3 fused salt. As a result, the surface of the Zn-Ni alloy melt is covered by the fused salt of NaCl-KCl and the fused salt of $Na_2B_4O_7$-Na_2CO_3. These fused salts stably cover the surface of the Zn-Ni alloy melt up to a temperature of approximately 1300°C. Their vapor pressure is so low as not to incur loss of the fused salts.

According to the method with the use of flux as described above, the oxides of Zn and Ni formed due to high-temperature oxidation are absorbed by the flux, while the vaporization of metallic Zn is suppressed. The alloy melt is protected from contact with air, so that neither ignition nor combustion of the alloy melt occurs. Since the above merits are attained, it is possible to stably produce Zn alloy having a high Ni content under high temperature. The Ni content is preferably from 2 to 50 wt%, because at a Ni content less than 2% the alloy has such low melting point that it can be produced by any method other than the present invention, and at a Ni content more than 50%, the melting point is so high as to make production by the present method impossible.

Several features of the method for producing the Zn-Ni alloy are further described.

Nickel is added to the Zn bath until the predetermined Ni grade is attained. Preferably, Ni grade of the Zn bath is gradually increased, and the temperature of the alloy melt is elevated with the increase in the Ni content. Contrary to this, if the entire amount of Ni is added at once to the Zn bath, followed by abrupt temperature-elevation, the alloy bath suddenly becomes higher than the boiling point of Zn, i.e., 906°C, when the Ni metal reacts with zinc metal and hence imparts heat to the melt due to exothermic reaction of alloying. As a result, bumping arises. This then leads to ignition and combustion of Zn. When the nickel is gradually added to the Zn bath, the temperature of the bath is raised in accordance with the increase in Ni content. The melting temperature can be raised up to 1100°C, which exceeds the boiling point of Zn.

The present invention is further described by way of examples.

BRIEF DESCRIPTION OF DRAWING

Figure 1 illustrates the melting speed in the various dissolving methods.

EXAMPLES

Example 1

In this example, 6kf of Zn-50%Ni alloy was melted.

First 3kg of Zn (99.99wt% Zn) was weighed, charged in a crucible, heated and melted.

NaCl (50g), KCl (50g), $Na_2B_4O_6$ (250g) and Na_2CO_3 (650g) were mixed in a mortar to provide a flux. The flux weighing in approximately 100g was dispersed on the surface of molten Zn bath, when temperature of this bath was elevated to approximately 450°C. The temperature of the molten bath was further enhanced. When the temperature is enhanced up to 650°C, the mixed salts of NaCl and KCl were first melted and covered the surface of molten Zn bath. At this stage the mixed salts of $Na_2B_4O_7$ and Na_2CO_3 were in half molten state.

When the temperature of the molten Zn bath was further enhanced up to 700°C, 62.5g of shot Ni (99.5wt%) was added to the molten Zn bath and was totally dissolved. The nominal Ni content became therefore 2 wt%. The temperature of molten Zn-Ni alloy bath was further raised up to 850°C. 62.5g of shot Ni was further added to the alloy melt and was totally dissolved. The nominal Ni content became therefore 4 wt%. Likewise, the temperature of the molten Zn-Ni alloy was raised higher than the melting point of such alloy by 50-100°C, and then 62.5g of shot Ni was added. Finally, temperature of the molten Zn-Ni alloy was enhanced to 1000°C which exceeded the boiling point of Zn, and 3kg of Ni was totally dissolved. The nominal composition became Zn-50% NI. The mixed salts of $Na_2B_4O_7$ and Na_2CO_3 were melted at approximately 800°C. At this temperature, the mixed, fused salts of NaCl, KCl, $Na_2B_4O_7$ and Na_2CO_3 were formed and covered the surface of the molten Zn-Ni alloy. Same amounts of ZnO and NiO, which were formed somewhat, were absorbed by the flux. Neither loss of Zn nor combustion of Zn vapor was detected.

The so-produced Zn-50% Ni alloy melt was cast into a mold, and the cast alloy was produced. A product, whose size is the same as the mold, was produced.

In addition, molten Zn-50 wt% Ni alloy was dropped into water. As a result, a spheroidal alloy shot having various shapes could be produced.

The cast product was crushed by a vibrating mill. As a result, crushed product having particle diameter of under 325 mesh (43μm) was obtained. The Ni content of the cast product was 49.9%. The balance was Zn.

Example 2.

A Zn-13 wt% Ni alloy was produced by melting 3kg of Zn and 448g of Ni. In the present example, the melting temperature was elevated, while adding Ni into the Zn melt, as in Example 1 until the melt temperature of 950°C, which exceeded the boiling point of Zn, was finally obtained.

The Zn-13 wt% Ni alloy could be cast into the same shape as a mold. In addition, alloy shot having an optional size could be produced by dropping the melt of this alloy into water. The particle size of under 325 mesh (43μm) could be obtained by crushing. The Ni content of the cast product was 12.85 wt%, the balance being Zn.

Example 3

A Zn-4 wt% Ni alloy was produced by melting 3kg of Zn and 125g of Ni. In the present example, the melting temperature was elevated as in Example 1, while adding Ni into the Zn melt, until the melt temperature of 850°C, which was directly below the boiling point of Zn, was obtained.

The Zn-4 wt% Ni alloy could be cast into a mold. In addition, alloy shot having an optional size could be produced by dropping the melt of this alloy into water. The Ni content of the cast product was 4 wt%, the balance being Zn.

Example 4

The Zn-Ni alloys melted in Examples 1-3 were atomized by the same atomizing method of Zn. The particle size became 1mm or less.

Example 5

A Zn-13 wt% Ni alloy was produced by the same method as in Example 1 except for the flux, whose composition was 13.3 wt% NaCl, 16.7 wt% of KCl, and 70 wt% of $Na_2B_4O_7$ (melting point approximately 700°C). Ni could be uniformly alloyed.

Comparative Example 1

Melting of Zn-4 wt% Ni alloy was intended in this example. It was tried in this example to raise the temperature of melt to a level 100°C higher than the melting point of Zn-4wt% Ni alloy (approximately 700°C). Oxidation of Zn on the melt surface started at approximately 600°C. Zn actively vaporized at a temperature higher than 750°C and was ignited. The combustion of Zn was so vigorous that melting of Zn-4 wt% Ni alloy was impossible.

Comparative Example 2

KCl and NaCl were weighed at 50g, respectively, and were mixed in a mortar. It was intended in this example to melt a Zn-4 wt% Ni alloy. When the melt temperature of this alloy was elevated to 450°C, 100g of this flux was dispersed on the surface of melt. When melt temperature was elevated to approximately 650°C, then the flux covered the surface of melt. Melt temperature was further elevated to approximately 800°C. The flux could not absorb Zn oxide and Ni oxide, which were formed by partial oxidation of Zn and Ni during the temperature rise. The solid ZnO and NiO were therefore mixed in the flux melt. Since the alloy melt could not be thoroughly covered by the flux melt, Zn was actively vaporized and then ignited. Vigorous combustion of Zn thus occurred. Melting of a Zn-4 wt% Ni alloy was therefore not successful because of the phenomena as described above.

Comparative Example 3

250g of $Na_2B_4O_7$ and 650g of Na_2CO_3 were weighed and were mixed in a mortar. It was intended in this example to melt a Zn-4 wt% Ni alloy. When the melt temperature of this alloy was elevated to 600°C, 100g of this flux was dispersed on the surface of melt. When melt temperature was elevated to approximately 600°C, the flux was in a half molten state. Since the melting point of this flux was approximately 800°C, Zn vaporized vigorously during a temperature elevation up to 750°C. An ignition phenomenon thus occurred. Melting of a Zn-4 wt% Ni alloy by using the flux consisting of $Na_2B_4O_7$ and Na_2CO_3 was therefore unsuccessful because of the combustion phenomenon as described above.

Example 6

Zn-15 wt% Ni alloy was melted by the method of Example 1 and was then crushed and sieved to provide the grain size as given in Table 1. A sample 13.3g in weight was taken from this alloy and was dissolved together with the zinc metal (purest zinc - 99.99wt% of Zn) in an amount of 986.7g by the mixing or stirring method given in Table 1. The melting temperature was 460°C±10°C. The flux used was NH_4Cl. This NH_4CL flux and Zn-15%wt Ni alloy was mixed in a proportion of 1:0.5, except for Nos. 6 and 7 in Table 1 in which the proportion was 1:0.2.

Table 1

Dissolving Result of Zn-0.2%Ni				
Nos.	Dissolving Time (mins)	Size of Zn-Ni Alloy	Stirring	Undissolved Amount (g)
1*	10	10-20 mm	50 rpm	5.50
2*	10	10 mm	manual stirring	6.84
3*	10	5 mm	manual stirring	3.84
4	10	44 microns	manual stirring	none
5*	10	10-20 mm	manual stirring	8.88
6	25	10-20 mm	100 rpm	none
7	35	10-20 mm	manual stirring	none
8	44	10-20 mm	manual stirring	none

The asterisked* Nos. are comparative runs, in which the dissolving time is short. It is clear that the charged materials in the size range of from 10 to 20mm could be completely dissolved by means of stirring. Charged materials with the particle size of 44 microns or less could be completely dissolved even in dissolving time of 10 minutes.

Chemical analysis of the obtained ingots of Zn-0.2 wt% Ni alloy to determine Ni content was carried out by sampling several portions in longitudinal and lateral directions. Difference between the greatest and smallest Ni contents

was 0.03 wt% at the highest. It was therefore recognized that Ni was dissolved uniformly. Also, no segregation of Ni was confirmed by an optical microscope observation.

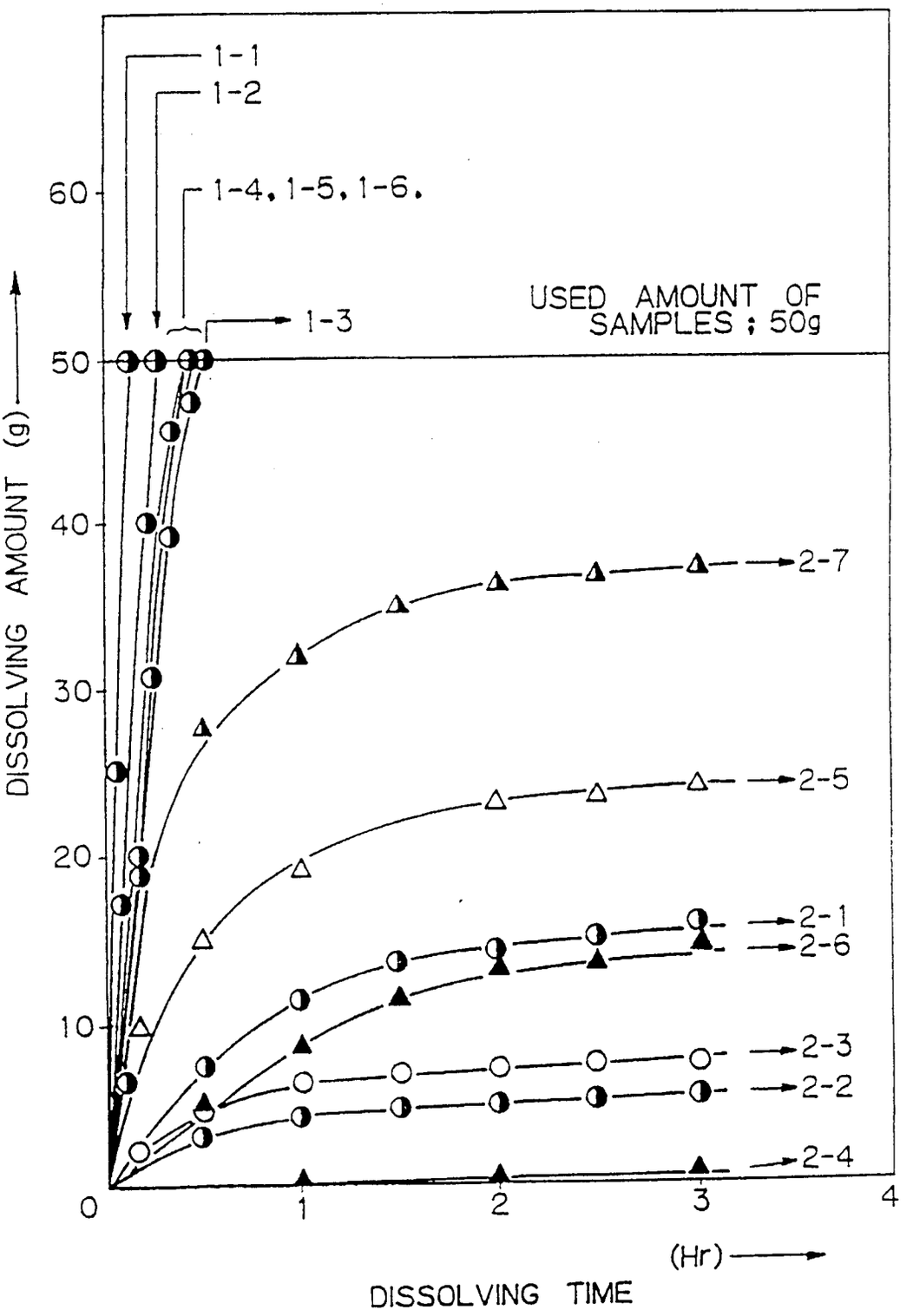
Claims

1. Use of a Zn-Ni alloy for supplying Ni and Zn into a hot-dip galvanizing bath, characterized in that said alloy has a composition containing from 4 to 50% by weight of Ni, the balance being essentially Zn and is produced by using a flux consisting of a fused-salt former, which forms a salt having a melting temperature of 700°C or less and $Na_2B_4O_7$.

2. Use of a Zn-Ni alloy according to claim 1 wherein the flux further contains Na_2CO_3.

3. Use of a Zn-Ni alloy according to claim 1 or 2, wherein the Ni content is from 10 to 30% by weight.

Fig. 1


1-1
1-2
1-4, 1-5, 1-6,
1-3
USED AMOUNT OF SAMPLES ; 50g
2-7
2-5
2-1
2-6
2-3
2-2
2-4
DISSOLVING AMOUNT (g)
60
50
40
30
20
10
0
1
2
3
4
(Hr)
DISSOLVING TIME

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 1036

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)
A	PATENT ABSTRACTS OF JAPAN vol. 15, no. 52 (C-0803), 7 February 1991 & JP-A-02 282435 (SUMITOMO METAL MINING CO LTD), 20 November 1990, * abstract * ---		C23C2/06
A	PATENT ABSTRACTS OF JAPAN vol. 15, no. 248 (C-0843), 25 June 1991 & JP-A-03 079732 (SUMITOMO METAL MINING CO LTD), 4 April 1991, * abstract * -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6) C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 August 1996	Nguyen The Nghiep, N

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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