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(54) **GALVANIZING OF REACTIVE STEELS**

FEUERVERZINKEN VON REAKTIONSFÄHIGEM STAHL

GALVANISATION DES ACIERS REACTIFS

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- **PATENT ABSTRACTS OF JAPAN vol. 095, no. 009, 31 October 1995 -& JP 07 153449 A (FUJI ELELCTROCHEM CO LTD), 16 June 1995**

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Description

BACKGROUND OF THE INVENTION

(i) **Field of the Invention**

[0001] This invention relates to a galvanizing alloy and process and, more particularly, relates to a galvanizing alloy and an immersion galvanization process adapted to control the undesirable effects associated with galvanizing reactive steels.

(ii) **Description of the Related Art**

[0002] The conventional process for hot dip galvanizing of low carbon steels comprises pretreatment of said steels in a 20% to 30%, by weight, zinc-ammonium-chloride ($ZnNH_4Cl$) pre-flux, followed by immersion in molten zinc or zinc allow baths. The 'normal' or 'N' coating structure produced on low reactivity steel by conventional hot dip galvanizing processes has well defined, compact alloy (intermetallic) layers. The predominant growth mode in this type of coating is by solid-state diffusion of iron and zinc, and thus well established intermetallic (delta and zeta) layers control the rate of the galvanizing reaction. The diffusion reaction rate decreases as the coating thickness increases, thus permitting predictable, consistent coverage. The normal coating has a bright metallic lustre.

[0003] Recent developments in the manufacture of low-alloy high-strength steels include continuous casting. In the continuous casting process, it is necessary to add elements that 'kill' or deoxidize the steel i.e. prevent gaseous products which produce porosity. Silicon is commonly employed for this purpose. These steels, as a result, generally contain between 0.01% to 0.3%, by weight, silicon but may include up to or more than about 0.5 wt% silicon and are known as 'reactive steels' or silicon steels.

[0004] Phosphorus in the steel also affects reactivity having an accepted measure of reactivity that is approximately 2.5 times that of silicon. Thus, the silicon content plus 2.5 times the phosphorus content is known as the effective silicon content of the steel.

[0005] Silicon steels that have high reactivity pose problems to the galvanizing process, producing thick, brittle and uneven coatings, poor adherence and/or a dull or marbled appearance. These coatings are known as 'reactive' coatings. The high reactivity of the silicon steels also causes excessive zinc consumption and excessive dross formation.

[0006] Silicon released from the steel during galvanizing is insoluble in the zeta layer. This creates an instability in the zeta layer and produces thick, porous intermetallic layers. The microstructure is characterized by a very thin and uneven delta layer overlaid by a very thick and porous zeta layer. The porous intermetallic layer allows liquid bath metal to react near the steel interface during the entire immersion period. The result is a linear growth mode with immersion time that allows the formation of excessively thick coatings. These coatings are generally very rough, undesirably thick, brittle and dull in appearance.

[0007] Steels with silicon levels between 0.05 to 0.15 (i.e. around the "Sandelin Peak" area), may also develop a 'mixed' reactivity or 'M' coating. This coating is characterized by a combination of reactive and non-reactive areas on the same steel which is believed to be due to differences in localized silicon levels on the surface of the steel.

[0008] It is known in the prior art to control reactivity by producing bath temperature and immersion time at a rate inversely proportional to the silicon content of the steel. Lower bath temperatures, in the order of 430° C, and reduced immersion times, tend to control reactivity on high silicon steels. However, using low bath temperatures and reduced times on low silicon steels produces unacceptably thin coating thicknesses. Thus, the galvanizer must know the silicon content of the steel beforehand and adjust the hot dip parameters accordingly. This approach cannot be implemented if steel reactivity is not known or if components to be galvanized comprise parts of different reactivities welded together. With low-temperature galvanizing, productivity can be poor because of the need to increase immersion times.

[0009] It is also known to control steel reactivity by adding allow elements to the zinc galvanizing bath. One such addition is nickel in a process known as the Technigalva™ (or Nickel-Zinc) process. A nickel content of 0.05 to 0.10% by weight in the zinc bath effectively controls reactive steels having up to about 0.2% by weight silicon content. For steels having silicon levels above approximately 0.2 wt%, this nickel-zinc process is not effective and thus it is only a partial solution to the reactive steel galvanizing problem. Low reactivity (normal) steels, when galvanized by the nickel-zinc process, pose the same difficulty as seen in low temperature galvanizing in that coating thickness may be unacceptably thin. With this process, it is thus preferred that the galvanizer know the reactivity of the steel beforehand and adjust galvanizing conditions accordingly, both of which are difficult to accomplish in practice. Under some conditions, this process also produces dross that tends to float in the bath and be drawn out on the workpiece, producing unacceptable coatings.

[0010] Another alloy used to control reactivity is that disclosed in French Patent No. 2,366,376, granted October 27, 1980, for galvanizing reactive steels, known as the Polygalva™ process. The alloy comprises zinc of commercial purity

containing by weight 0.1 to 1.5% lead, 0.01 to 0.05% aluminum, 0.03 to 2.0% tin, and 0.001 to 2.0% magnesium.

[0011] US Patent No. 4,439,397, granted March 27, 1984, discusses the accelerated rate at which the magnesium and aluminum are consumed or lost in this Polygalva™ process for galvanizing steel. Procedures are presented to overcome the inherent difficulty in replenishing deficient aluminum or magnesium in the zinc alloy galvanizing bath. The process has serious limitations in that the steel has to be meticulously degreased, pickled, pre-fluxed and oven-dried to obtain good quality product free of bare spots. Thus, in most cases, new high-quality installations are usually required.

[0012] US Patent No. 4,168,972, issued September 25, 1979, and US Patent No. 4,238,532, issued December 9, 1980, also disclose alloys for galvanizing reactive steels. The alloys presented include variations of the Polygalva™ alloy components of lead, aluminum, magnesium and tin in zinc.

[0013] It is known in the prior art that aluminum included in the galvanizing bath reduces the reactivity of the high silicon steels. A process known as the Supergalva™ process includes an alloy of zinc containing 5 wt% aluminum. The process requires a special flux and double dipping not generally accepted by commercial galvanizers.

[0014] Co-Pending US Patent Application No. 08/667,830 filed June 20, 1996, describes a new alloy and process for controlling reactivity in steels with silicon content up to 1 wt%. The alloy comprises zinc of commercial purity containing, by weight, one or both of vanadium in the amounts of at least 0.02% to 0.04% and titanium in the amounts of at least 0.02% to 0.05%.

[0015] It is a principal object of the present invention to provide a process and alloy to effectively control reactivity on a full range of steels including low and high silicon steels. The process should also produce coatings of acceptable and uniform thickness over the full range of steels.

[0016] Another object of the invention is to provide an alloy and process which uses standard galvanizing equipment operated under normal conditions for galvanizing steels of mixed reactivity without the need to adjust for variations in steel chemistry.

SUMMARY OF THE INVENTION

[0017] The disadvantages of the prior art thus may be substantially overcome by providing a new galvanizing alloy and process which can be readily adapted to standard hot-dip galvanizing equipment.

[0018] In its broad aspect, the process of the invention for galvanizing steel, including reactive steels, by immersion comprises immersing said steel in a molten bath of a zinc alloy comprising, by weight, aluminum in the amount of at least 0.001% to 0.007%, preferably 0.002% to 0.004%, tin in the amount of at least 0.5% to a maximum of 2%, preferably at least 0.8%, and one of an element selected from the group consisting of vanadium in the amount of at least 0.02%, preferably 0.05% to 0.12%, titanium in the amount of at least 0.03%, preferably 0.06% to 0.10%, and both vanadium and titanium together in the amount of at least 0.02% vanadium and at least 0.01% titanium for a total of at least 0.03%, preferably 0.05 wt% to 0.15%, of vanadium and titanium, the balance zinc containing up to 1.3 wt% lead. The alloy of the invention for galvanizing steel comprises, by weight, aluminum in the amount of at least 0.001% to 0.007%, preferably 0.002 to 0.004%, tin in the amount of at least 0.5% to a maximum of 2%, preferably at least 0.8%, and one of an element selected from the group consisting of vanadium in the amount of at least 0.02%, preferably 0.05% to 0.12%, titanium in the amount of at least 0.03%, preferably 0.06% to 0.10%, and both vanadium and titanium together in the amount of at least 0.02% vanadium and at least 0.01% titanium for a total of at least 0.03%, preferably 0.05% to 0.15%, of vanadium and titanium, the balance zinc containing up to 1.3 wt% lead. In an embodiment of the invention for use in zinc-nickel alloy baths, the alloy may comprise, by weight, aluminum in the amount of at least 0.001%, tin in the amount of 0.5% to 2%, and vanadium with nickel in the amount of at least 0.02% vanadium and at least 0.02% nickel to a maximum of 0.15% vanadium and nickel collectively. Titanium may be added in an amount of at least 0.01 % titanium to a maximum of 0.2% vanadium, nickel and titanium. In a further embodiment, for use in a zinc alloy bath, the alloy is comprised of aluminum in the amount of at least 0.001%, tin in the amount of about 0.5% to about 2%, vanadium in the amount of 0.02 to 0.12%, bismuth in the amount of 0.05% to 0.1%, and the balance zinc.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The process of the invention and the alloy produced thereby will now be described with reference to the following drawings, in which:

Figure 1 to 3 are graphs illustrating galvanized coating thickness of a variety of galvanizing coatings on steel surfaces having a silicon content ranging from 0 to 1.0 wt% under conditions of eight-minute immersion at 450°C, Figure 1 being a graph showing average coating thickness versus silicon content in a galvanizing bath of Prime Western (PW) zinc with tin and vanadium, Figure 2 being a graph showing average coating thickness versus silicon content in a galvanizing bath of PW zinc with tin and titanium, and Figure 3 being a graph showing average coating

thickness versus silicon content in a galvanizing bath of PW zinc with tin and both vanadium and titanium together; and

Figure 4 is a graph illustrating kettle material weight losses for a variety of galvanizing alloys.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0020] With reference to Figures 1, 2 and 3 of the drawings, curve 10 typifies the variation of thickness in microns of a coating of zinc of commercial purity, such as conventional Prime Western (PW), on a steel surface as a function of the silicon content of the steel. The term "commercial purity" used herein will be understood to include Prime Western, High Grade and Special High Grade zinc. Under these conditions of bath temperature (450°C) and immersion time (8 minutes), the thickness of zinc coating peaks at a thickness of about 260 microns at a silicon content of about 0.15 wt%, decreases to a thickness of about 175 microns at a silicon content of about 0.2 wt%, and then increases to a maximum thickness of about 375 microns at a silicon content of about 0.5 wt%, decreasing in thickness slightly to a silicon content of 1.0 wt%. This curve 10 will be recognized as being very similar to the well-known Sandelin Curve. The composition of the steels used is listed in Table 1 below.

TABLE I

STEEL COMPOSITIONS: 1995 TRIALS								
Steel Alloy #	MTL Heat #	Chemical Composition (%) wt.						Si Equivalent*
		Si	P	C	S	Mn	Al	
1	95-18	0.021	<0.006	0.11	.0071	0.59	0.019	0.021
	95-20	0.019		0.11	.0051	0.76	0.035	0.019
2	95-4a	0.15	<0.006	0.10	.0037	0.71	0.015	0.15
	95-4b	0.15		0.10	.0026	0.70	0.016	0.15
3	95-4c	0.21	<0.006	0.10	.0029	0.73	0.007	0.21
	95-4d	0.21		0.11	.0038	0.73	0.005	0.21
	95-5l	0.19		0.13	.0073	0.77	0.046	0.19
4	95-21a	0.29	<0.006	0.10	.0030	0.70	0.035	0.29
	95-21b	0.30		0.10	.0028	0.71	0.046	0.30
5	95-28	0.32	<0.006	0.09	.0069	0.76	n.a.	0.32
	95-42	0.36		0.12	.0067	0.83	0.032	0.36
6	95-21c	0.46	<0.006	0.10	.0030	0.73	0.037	0.46
	95-21d	0.46		0.10	.0029	0.73	0.036	0.46
7	95-22a	0.51	<0.006	0.09	.0036	0.68	0.040	0.51
	95-22b	0.51		0.10	.0032	0.68	0.042	0.51
8	95-22c	0.99	<0.006	0.09	.0031	0.71	0.022	0.99
	95-22d	0.98		0.09	.0031	0.71	0.022	0.98
9	95-23a	.019	0.02	0.09	n.a.	0.66	0.010	0.07
	95-23b	.018	0.02	0.09		0.65	0.010	0.07
10	95-39	.031	0.050	0.10	.0071	0.80	0.036	0.16
	95-40	.023	0.055	0.09	.0072	0.71	0.047	0.16

* Si quivalent = Si + 2.5P
n.a. = Not available

[0021] In accordance with ASTM Standards e.g. the ASTM A-123 Standard (610 g/m^2 or 86 microns for 3.2 to 6.4 mm thick steel plate), a uniform coating thickness of about 100 microns is desired in order to meet minimum thickness requirements while avoiding the expense and waste of thick coatings. Also, excessive thickness of zinc coatings on reactive steels and steels of mixed reactivity due to high or variable silicon contents, usually produce rough, porous, brittle and generally unsightly coatings which can have poor adherence to the underlying steel surface. It is generally accepted that the addition to the galvanizing bath of strong silicide formers may neutralize the influence of silicon in

reactive steels. It has been found that vanadium alone is an effective alloying element for reducing the reactivity of silicon steels with up to 0.25 wt% Si. Vanadium in the bath is believed to combine with the silicon to form vanadium silicides as inert particles that become dispersed in the zeta layer. The silicon-free iron can then react with zinc to form a very compact and smooth layer that prevents liquid bath metal from reaching the delta layer. In essence, the vanadium effectively suppresses reactivity by stabilizing the growth of the zeta layer in the coating, which controls the growth rate by a diffusion process.

[0022] It has been found that tin is also an effective element for reducing the reactivity of steels. Tests have shown that a galvanizing bath containing 2.5 wt% to 5 wt% tin can control reactivity in steels with up to 1% silicon content. However, tests have also shown that tin in amounts greater than 2 wt% react rapidly with the galvanizing kettle wall steel at galvanizing temperatures. When the tin level in the galvanizing bath is below 2%, the reaction with the kettle steel proceeds at a slow rate, which is comparable to that of the commercial grade zinc. However, when the level of tin in a galvanizing bath is 2%, the presences of tin controls reactivity in steels with only up to 0.3% silicon.

[0023] The presence of at least 0.02 wt% vanadium, preferably 0.05 wt% to 0.12 wt%, the solubility limit of vanadium, in combination with 0.5 wt% to 2 wt% tin, controls reactivity in steels having up to 1 wt% silicon. Tests have shown that in galvanizing baths containing 1 to 1.2 wt% tin, 0.002 wt% aluminium, and the balance zinc of commercial purity containing 0.8 wt% lead, the presence of 0.05 wt% and 0.08 wt% vanadium effectively controls reactivity to varying degrees in steels having silicon contents up to 1%, as shown by the Sn-V curves 11 and 12 in Figure 1.

[0024] Zinc of commercial purity, such as conventional Prime Western, contains up to 1.3 wt% lead, typically about 0.8% lead. However, other grades of zinc available such as High Grade and Special High Grade have lower contents of lead. There is a growing tendency to reduce and eliminate the presence of lead in galvanizing because of environmental, health and safety concerns. It has been observed that bare spots in galvanized coatings could be produced from galvanizing baths without lead or with reduced lead contents at lower levels of tin at about 1 wt% tin with 0.05 wt% vanadium and 0.002 wt% aluminium on steels having lower silicon contents.

[0025] It was found that by the addition of 0.05% to 0.5 wt% of bismuth, preferably 0.05% to 0.1 wt% bismuth, to Zn-Sn-V alloys containing 0.5 wt% to 2 wt% tin, 0.05 wt% to 0.12 wt% vanadium, 0.001 wt% to 0.007 wt% aluminium, the balance zinc, uniformly thick bright galvanized coatings having spangling and free of bare spots were produced. The presence of bismuth was particularly beneficial for tin contents in the range of 1 - 1.5 wt% tin.

[0026] In an alternative embodiment of the process of the present invention, titanium is used in place of vanadium. The presence of at least 0.03 wt% titanium, preferably 0.06 wt% to 0.1 wt%, in combination with 0.5 wt% to 2.0 wt% tin, controls reactivity in steels having up to about 0.5 wt% silicon. Tests have shown in a galvanizing bath containing 1.8 wt% tin, 0.002 wt% aluminum and the balance zinc of commercial purity, the presence of 0.06 wt% and 0.10 wt% titanium effectively controls reactivity to varying degrees in steels having silicon contents up to about 0.5 wt %, as shown by Sn-Ti curve 13 in Figure 2. Increasing the titanium content in the galvanizing bath to 0.1 wt% did not increase the maximum silicon level controlled as seen by Sn-Ti curve 14 in Figure 2.

[0027] However, the titanium addition to the bath forms a ternary Zn-Fe-Ti intermetallic which increases the amount of dross and ash during galvanizing and contributes to high rates of titanium consumption or depletion in the bath. It also adversely affects the appearance of the galvanized coating by eliminating the distinctive large spangle formed with the tin-vanadium alloy which most galvanizing customers favour.

[0028] Small amounts of titanium added to the tin-vanadium alloy as a substitute for a portion of the vanadium can be used to lower the level of vanadium in the alloy, without the adverse effects of the high titanium-tin alloy. The presence of at least 0.02 wt% vanadium and at least 0.01 wt% titanium, preferably 0.05 wt% to 0.1 wt% vanadium and titanium collectively, controls reactivity in steels having up to 1 wt% silicon. In a galvanizing bath containing 1 wt% tin, 0.002 wt% aluminum, and the balance zinc of commercial purity, the presence of 0.06 wt% vanadium and 0.02 wt% titanium effectively controls reactivity in steels having silicon contents up to 1 wt%, as shown by Sn-V-Ti curve 16 in Figure 3. Reducing the vanadium content in the alloy may be desirable in some cases to offset the high cost of vanadium as compared to titanium.

[0029] An other embodiment of the alloy composition of the invention has utility in zinc-nickel alloy baths containing a typical nickel content of 0.05 wt% to 0.08 wt% nickel, and up to 0.1 wt% nickel, and comprises aluminum in the amount of at least 0.001 wt%, tin in the amount of about 0.5 wt% to about 2 wt%, and vanadium with nickel in the amount of at least 0.02 wt% vanadium and at least 0.02 wt% nickel to a maximum of 0.15 wt% vanadium and nickel collectively. The alloy compositions and the process of the invention will now be described with reference to the following non-limitative examples.

EXAMPLE 1

Long term immersion experiments of kettle steel in zinc alloy baths to determine rate of attack on the steel and maximum allowable limit for tin in the galvanizing alloys.

[0030] Four alloys were prepared and samples from kettle steel were immersed in each alloy for a period of about 11 days at a temperature of 480°C. This immersion temperature was about 30°C higher than the normal galvanizing bath temperature to accelerate the reaction of the alloys with the kettle steel samples. All the baths were saturated with iron at the start of the experiments and an addition of 0.004 wt% aluminium was made. The baths were analyzed during the 11-day trial period and additions were made as needed to maintain the nominal bath compositions. The four alloy compositions are listed in Table II below.

TABLE II

Alloy		Alloy Composition % wt			
No.	**Designation**	**Sn**	**V**	**Ti**	**Ni**
1	PW	—	-	-	-
2	Sn-Ni	2.5	-	-	0.05
3	V-Ti	-	0.04	0.05	-
4	Sn-V	1.0	0.05	-	-

[0031] The composition of alloy No. 2 (Sn-Ni) is a high tin alloy. The composition of alloy No. 3 (V-Ti) is included in US Patent Application No. 08/667,830. The composition of alloy No. 4 (Sn-V) is an embodiment of alloy of the subject Patent Application.

[0032] Fifty kg melts were prepared in a SiC crucible that was heated in a radiant tube furnace. Four steel samples measuring 32 x 51 x 25 mm were immersed in each alloy bath. Analysis of the kettle steel showed its composition to contain, by weight, 0.09 wt% carbon, 0.02 wt% silicon, 0.006 wt% phosphorus and 0.27 wt% manganese. The samples were machined (to remove surface scale), degreased with acetone, pickled in hydrochloric acid, weighed, measured, and pre-fluxed in $ZnNH_4Cl$, prior to immersion in the alloy baths.

[0033] The samples were removed after approximately 2, 4, 7 and 11 days immersion. The coatings on the samples were removed by immersion in hot sodium hydroxide solution, followed by cold hydrochloric solution, and re-weighed.

[0034] The differences in weight loss were divided by the initial surface areas of the samples to determine weight loss in gms per unit area in mm^2. The results are shown in the graph of Figure 4, as weight loss in g/mm^2 versus the immersion period in hours.

[0035] The curves in Figure 4 show that the weight losses for alloy baths No. 3 (V-Ti curve) and No. 4 (Sn-V curve) are comparable to No. 1 (PW curve). The weight loss from alloy bath No. 2 (Sn-Ni curve) after 150 hours is about six times as great as the others (Nos. 1, 3 and 4). More importantly, the slope of the No. 2 alloy curve is very steep, indicating that the reaction with the steel follows a rapid linear growth with immersion time that results in the formation of excessively thick coatings.

[0036] An additional PW melt was prepared and additions of tin were made at 0.2 wt% increments, from 0.5 wt% to 2.5 wt% tin. Kettle steel samples were immersed at 480°C and inspected after 24 hours and 48 hours. If no evidence of excessive coating growth was observed after 48 hours, the tin content in the bath was increased by 0.2 wt%. When evidence of excessive growth was first observed, the tin content in the bath was reduced by 0.2 wt% and steel samples were immersed for a period of about two weeks to ensure that the coating growth rate was normal. From these experiments, it was determined that when the tin content in the bath exceeded 2 wt%, the abnormal or excessive growth rate began to occur.

EXAMPLE 2

Galvanizing Trials

[0037] Ten alloys were prepared for laboratory-scale galvanizing trials. The alloying additions were made to PW grade zinc. The typical composition of PW is shown in Table III below.

TABLE III

COMPOSITIONS OF PW ZINC			
Element	**PW (%)**	**Element**	**PW (%)**
Pb	0.80	Cd	0.0019
Fe	0.009	Ca	0.00005
Al	0.004	Zr	-
Si	0.0004	Cu	0.0032
Mn	0.007	Mg	0.00002
Ni	0.0005	As	-
Cr	0.0001	B	-
Ti	0.0002	Ga	0.00005
V	-	Ge	0.0003
Sn	0.0001	In	-
Sb	0.0004	Ti	0.0002
Bi	0.002	Zn	bal.
Ag	0.0004	-	-

[0038] The various experimental baths are listed in Table IV. All experimental baths were saturated with iron and appropriate amounts of a 5 wt% aluminum master alloy were added to maintain a 0.002 wt% (brightener) aluminum level in the bath. The tin additions were made with high purity tin ingot. The vanadium additions were made with a Zn-2.3 wt% V master alloy, and the titanium additions were made with a Zn-4 wt% Ti master alloy.

TABLE IV

BATH ALLOY COMPOSITIONS				
Trial No.	**Bath Designation**	**% Element**		
		Sn	**V**	**Ti**
1	PW	-	-	-
2	PW+Sn	1.8	-	-
3	PW+Sn+V	1.8	0.04	-
4	PW+Sn+V	0.4	0.12	-
5	PW+Sn+V	1.0	0.05	-
6	PW+Sn+V	1.2	0.08	-
7	PW+Sn+Ti	1.8	-	0.06
8	PW+Sn+Ti	1.8	-	0.10
9	PW+Sn+V+Ti	1.0	0.06	0.02
10	PW+Sn+V+Ti	1.0	0.03	0.02
Note: All baths saturated in iron and contain 0.002 wt% aluminum brightener.				

[0039] A bench scale line was set up to process the test samples consistently. The following steps were taken:

1.	Degreasing	0.25 g/cc NaOH solution at 70°C with agitation for ten minutes
2.	Rinse	Tepid flowing water
3.	Pickling	15 wt% Hcl at room temperature, inhibited with Rodine™ 85 (1:4000), for 20 minutes
4.	Pre-flux	20 wt% Zaclon™ K ($ZnNH_4Cl$) at 60°C, for two minute immersion.

(continued)

5.	Drying	Oven-dried for five minutes at 110°C.

[0040] Twenty-five kg melts were prepared in a SiC crucible that provided a galvanizing surface of 150 mm in diameter. The crucible was heated in a radiant tube furnace.

[0041] The galvanizing temperature was 450 ± 2°C. The melt surface was skimmed prior to immersion and just before the test coupons were withdrawn. The test coupons were dipped for eight-minute immersions. The immersion rate was 40 mm/sec while the withdrawal rate was 60 mm/sec. The samples were air-cooled at room temperature (no quenching).

[0042] Hot-rolled low-carbon silicon-killed steel coupons, measuring 77 mm x 39 mm x 3 mm, were used. The ten steel compositions, with silicon levels ranging from about 0.02 wt% to 1 wt%, are listed in Table 1. This table includes the respective Si-equivalent or Si + 2.5P level for the steels, which takes into account the weighted effect of phosphorus as it relates to the reactivity behaviour of the steel.

The galvanized coatings produced in the experiments were evaluated by the following methods:

Coating Appearance

[0043] The test coupons were photographed and classified under one of the three following categories: Normal, Reactive or Mixed. A description for each category of coating appearance is as follows:

Normal	The typical coating of a low-reactivity steel, usually bright and relatively smooth with visible spangle.
Reactive	The typical coating of a reactive steel, usually matte-grey with no visible spangle.
Mixed	The typical coating of a steel that has both reactive and non-reactive areas. The coating is usually very rough and varies from thin in low-reactivity areas to thick in the reactive areas.

Coating Thickness

[0044] Coating thickness measurements were made using an electromagnetic thickness gauge. The coating thickness results are presented in graph form in Figures 1 to 3 and constitute the steel reactivity curves.

Metallography

[0045] Twenty-five mm long pieces were cut from representative areas of the test coupons and prepared by conventional metallographic techniques for microscopic examination. All test samples were examined by optical microscopy. Selected samples were examined with a scanning electron microscope (SEM) and energy dispersive x-ray microanalysis (EDS) was performed on selected samples as required.

[0046] From these galvanizing trials, the maximum effective steel silicon levels controlled by the various bath alloys were determined and they are presented in Table V. As a reference, results of single element additions of tin, vanadium, titanium and nickel, obtained from past trials, are included in Table V.

TABLE V

MAXIMUM EFFECTIVE SILICON (ESI) LEVEL IN STEEL CONTROLLED BY ALLOY ADDITION					
PW Alloy	**Bath Alloy Addition (%)**				**Maximum Esi %**
	Sn	**V**	**Ti**	**Ni**	
Single	1.8*	-	-	0.09	0.20
Element	-	0.12	-	-	0.25
Addition	-	-	0.10	-	0.30
Sn+V	1.8[1]	0.04	-	-	0.50
Combination	0.4[2]	0.12	-	-	0.50
	1.0[3]	0.05	-	-	0.50
	1.2[4]	0.08	-	-	1.0
Sn+Ti	1.8	-	0.06	-	0.5M

TABLE V (continued)

MAXIMUM EFFECTIVE SILICON (ESI) LEVEL IN STEEL CONTROLLED BY ALLOY ADDITION					
PW Alloy	Bath Alloy Addition (%)				Maximum Esi %
	Sn	V	Ti	Ni	
	1.8	-	0.10	-	0.5M
Sn+V+Ti	1.0	0.06	0.02	-	1.0
	1.0	0.03	0.02	-	0.5
Notes: 1. High Sn - Low V 2. Low Sn - High V 3. Preferred composition for 0.5% Esi 4. Preferred composition for 1.0% Esi M Marginal control with various amounts of mixed reactivity and heavier coatings than when fully controlled.					

[0047] The results show that, as a single element addition, the maximum effective silicon level controlled is about 0.3 wt%. When tin and vanadium are combined, 0.5 wt% effective silicon can be controlled with a minimum level of 0.04 wt% vanadium and a tin level of 1.8 wt% (which is near the maximum allowable level), and with a minimum level of 0.4 wt% tin and a 0.12 wt% vanadium level. A preferred composition for controlling the 0.5 wt% Si level is 1.0 wt% tin with 0.05 wt% vanadium. The 1.0 wt% effective silicon can be controlled with a preferred composition of 1.2 wt% tin and 0.08 wt% vanadium.

[0048] When tin is combined with titanium, the maximum effective silicon level that was controlled was 0.5 wt%, even when the maximum allowable amount of 1.8 wt% tin and an amount of 0.1 wt% titanium were added to the galvanizing bath.

[0049] When vanadium and titanium are added together, it is possible to control the 0.5 wt% effective silicon with additions of 1.0 wt% tin, 0.03 wt% vanadium, and 0.02 wt% titanium and the 1 wt% effective silicon level with additions of 1.0 wt% tin, 0.06 wt% vanadium, and 0.02 wt% titanium. The addition of titanium to the tin and vanadium alloy allows for a reduction in the amount of vanadium needed to control at the 0.5 wt% and 1.0 wt% effective silicon levels.

EXAMPLE 3

Addition of Bismuth

[0050] Trials were conducted on 77 mm x 39 mm x 3 mm low silicon steel coupons which were pretreated by an acetone rinse and scrubbing, pickling in 15% HCL solution for 10 - 15 minutes, preflux of ZACLON K™ (20° Be) for 2 minutes at 70°C and oven-dried at 100 °C for 5 minutes.

[0051] The coupons were galvanized by immersion for 4 minutes in zinc alloy baths of Special High Grade 25 kg melt saturated with iron and containing 0.004 wt% aluminum, 1 wt% tin, 0.05 wt% vanadium and varying amounts of bismuth at a temperature of 450° C.

[0052] The test results are shown in Table VI.

TABLE VI

BATH ALLOY COMPOSITIONS -SHG + Sn + V + Bi				
Trial No.	% Element			Observations
	Sn	V	Bi	
1	1.0	0.05		Severe bare spots and small spangling
2	1.0	0.05	0.05	Substantially complete elimination of bare spots, and larger spangling
3	1.0	0.05	0.1	Free of bare spots and larger spangles
4	1.0	0.05	0.2	Free of bare spots and very large spangles
5	1.0	0.05	0.5	Free of bare spots and very large spangles
Note: all baths contain 0.004 wt% aluminum brightener.				

[0053] The presence at least 0.05 wt% bismuth was found to be effective in obviating bare spots and in enhancing spangling of the galvanized coating. An upper limit of bismuth of 0.1 wt% bismuth was found economically viable, amounts in excess of 0.1% up to 0.5% did not improve the quality of coating.

[0054] The invention provides a number of important advantages. Galvanized coatings produced in accordance with the invention are complete and uniform and of desired thickness on low and high silicon steels including steel having silicon content from 0.01 wt% to at least 0.5 wt%. The coatings produced also have a bright metallic lustre. The process can be easily adapted to conventional galvanizing production equipment using normal galvanizing temperatures and immersion times.

Claims

1. An alloy for galvanizing steel comprising by weight, aluminum in the amount of 0.001 % to 0.007%, tin in the amount of 0.5% to 2%, and one of an element selected from the group consisting of vanadium in the amount of 0.02% to 0.12%, titanium in the amount of 0.03% to 0.10%, and both vanadium and titanium together in the amount of at least 0.02% vanadium and at least 0.01% titanium for a total of 0.03% to 0.15% vanadium and titanium collectively, and optionally bismuth in the amount of 0.05% to 0.5%, the balance zinc containing up to 1.3% lead.

2. An alloy as claimed in Claim 1 for galvanizing steel comprising, by weight, vanadium in the amount of 0.05% to 0.12%.

3. An alloy for galvanizing steel comprising, by weight, aluminium in the amount of 0.001% to 0.007%, tin in the amount of 0.5% to 2%, vanadium in the amount of 0.02% to 0.12%, and optionally bismuth in the amount of 0.05% to 0.5%, the balance zinc containing up to 1.3 wt% lead.

4. An alloy as claimed in Claim 3 for galvanizing steel additionally comprising, by weight, bismuth in the amount of 0.05% to 0.1%.

5. An alloy as claimed in Claim 1 for galvanizing steel comprising, by weight, titanium in the amount of 0.06% to 0.10%.

6. An alloy as claimed in Claim 1, in which the zinc alloy contains, by weight, at least 0.03% vanadium and titanium when vanadium and titanium are present together, said vanadium being present in the amount of at least 0.02% and said titanium being present in the amount of at least 0.01%, to a maximum of 0.15% vanadium and titanium collectively.

7. An alloy as claimed in Claim 6 in which the vanadium and titanium are present together, by weight, in the amount of at least 0.05%.

8. An alloy for galvanizing steel comprising, by weight, aluminum in the amount of 0.001% to 0.007%, tin in the amount of 0.5% to 2.0%, and vanadium and nickel in the amount of at least 0.02% vanadium and at least 0.02% nickel to a maximum of 0.15% vanadium and nickel collectively, the balance zinc containing up to 1.3 wt% lead.

9. An alloy for galvanizing steel comprising, by weight, aluminum in the amount of 0.001% to 0.007%, tin in the amount of 0.5% to 2.0%, vanadium in the amount of 0.02% to 0.12%, and bismuth in the amount of 0.05% to 0.5%, the balance zinc.

10. A process for galvanizing steel by immersion in a zinc alloy galvanizing bath comprising the steps of:

    immersing the steel in a molten bath of a zinc alloy comprising, by weight, 0.001% to 0.007% aluminum, 0.5% to 2% tin, and an amount effective for reducing reactivity of the steel of at least one element selected from the group consisting of 0.02% to 0.12% vanadium, 0.03% to 0.10% titanium, and at least 0.02% vanadium and at lest 0.01% titanium for a total of 0.03% to 0.15% vanadium and titanium collectively, and optionally 0.05% to 0.5 wt% bismuth, the balance zinc containing up to 1.3 wt% lead.

11. A process as claimed in Claim 10, in which the zinc alloy contains at least 0.05%, by weight, vanadium.

12. A process as claimed in Claim 10, in which the zinc alloy contains 0.05% to 0.12%, by weight, vanadium.

13. A process as claimed in Claim 10, in which the zinc alloy contains at least 0.06%, by weight, titanium.

14. A process as claimed in Claim 10, in which the zinc alloy contains 0.06% to 0.10%, by weight, titanium.

15. A process for galvanizing steel by immersion in a zinc-nickel alloy bath comprising the steps of:

immersing the steel in a molten bath of a zinc-nickel alloy comprising, by weight, 0.001% to 0.007% aluminum, 0.5% to 2% tin, and vanadium and nickel in the amount of at least 0.02% vanadium and at least 0.02% nickel, to a maximum of 0.15% vanadium and nickel collectively, and optionally 0.05% to 0.5% bismuth, the balance zinc containing up to 1.3 wt% lead.

16. A process as claimed in claim 15 in which the alloy additionally contains at least 0.01 % titanium, to a maximum of 0.2% vanadium, nickel and titanium collectively.

17. A process of galvanizing steel by immersion in a zinc alloy galvanizing bath comprising the steps of:

immersing the steel in a molten bath of zinc alloy containing, by weight, 0.001% to 0.007% aluminum, 0.5% to 2.0% tin, 0.02% to 0.12% vanadium, and 0.05% to 0.5% bismuth, the balance zinc.

18. A process as claimed in claim 17, in which the molten zinc bath contains 0.05% to 0.1% bismuth.

Patentansprüche

1. Legierung zum Verzinken von Stahl, enthaltend, bezogen auf das Gewicht, Aluminium in einer Menge von 0,001 bis 0,007 %, Zinn in einer Menge von 0,5 bis 2 % und ein Element aus der Gruppe Vanadium in einer Menge von 0,02 bis 0,12 %, Titan in einer Menge von 0,03 bis 0,10 % und Vanadium und Titan zusammen in einer Menge von mindestens 0,02 % Vanadium und mindestens 0,01 % Titan bei einem Gesamtgehalt an Vanadium und Titan von 0,03 bis 0,15 %, sowie gegebenenfalls Wismut in einer Menge von 0,05 bis 0,5 %, wobei der Rest aus Zink mit einem Gehalt an bis zu 1,3 % Blei besteht.

2. Legierung nach Anspruch 1 zum Verzinken von Stahl, enthaltend, bezogen auf das Gewicht, Vanadium in einer Menge von 0,05 bis 0,12 %.

3. Legierung zum Verzinken von Stahl, enthaltend, bezogen auf das Gewicht, Aluminium in einer Menge von 0,001 bis 0,007 %, Zinn in einer Menge von 0,5 bis 2 %, Vanadium in einer Menge von 0,02 bis 0,12 % und gegebenenfalls Wismut in einer Menge von 0,05 bis 0,5 %, wobei der Rest aus Zink mit einem Gehalt an bis zu 1,3 Gew.-% Blei besteht.

4. Legierung nach Anspruch 3 zum Verzinken von Stahl, zusätzlich enthaltend, bezogen auf das Gewicht, Wismut in einer Menge von 0,05 bis 0,1 %.

5. Legierung nach Anspruch 1 zum Verzinken von Stahl, enthaltend, bezogen auf das Gewicht, Titan in einer Menge von 0,06 bis 0,10 %.

6. Legierung nach Anspruch 1, wobei die Zinklegierung, bezogen auf das Gewicht, mindestens 0,03 % Vanadium und Titan enthält, wenn Vanadium und Titan zusammen vorliegen, wobei das Vanadium in einer Menge von mindestens 0,02 % und das Titan in einer Menge von mindestens 0,01 % vorliegen und wobei Vanadium und Titan zusammen maximal 0,15 % ausmachen.

7. Legierung nach Anspruch 6, wobei Vanadium und Titan gemeinsam in einer Menge von mindestens 0,05 Gew.-% vorliegen.

8. Legierung zum Verzinken von Stahl, enthaltend, bezogen auf das Gewicht, Aluminium in einer Menge von 0,001 bis 0,007 %, Zinn in einer Menge von 0,5 bis 2,0 % und Vanadium und Nickel in einer Menge von mindestens 0,02 % Vanadium und mindestens 0,02 % Nickel bis maximal 0,15 % Vanadium und Nickel zusammen, wobei der Rest aus Zink mit einem Gehalt an bis zu 1,3 Gew.-% Blei besteht.

9. Legierung zum Verzinken von Stahl, enthaltend, bezogen auf das Gewicht, Aluminium in einer Menge von 0,001 bis 0,007 %, Zinn in einer Menge von 0,5 bis 2,0 %, Vanadium in einer Menge von 0,02 bis 0,12 % und Wismut in einer Menge von 0,05 bis 0,5 %, wobei der Rest aus Zink besteht.

10. Verfahren zum Verzinken von Stahl durch Eintauchen in ein Zinklegierungs-Verzinkungsbad, umfassend die folgende Stufe:

Eintauchen des Stahls in ein geschmolzenes Bad einer Zinklegierung, die, bezogen auf das Gewicht, 0,001 bis 0,007 % Aluminium, 0,5 bis 2 % Zinn und eine zur Verringerung der Reaktivität des Stahls wirksame Menge mindestens eines Elements aus der Gruppe 0,02 bis 0,12 % Vanadium, 0,03 bis 0,10 % Titan und mindestens 0,02 % Vanadium und mindestens 0,01 % Titan, bei einem Gesamtgehalt an Vanadium und Titan von 0,03 bis 0,15 %, und gegebenenfalls 0,05 bis 0,5 Gew.-% Wismut, wobei der Rest aus Zink mit einem Gehalt an bis zu 1,3 Gew.-% Blei besteht.

11. Verfahren nach Anspruch 10, wobei die Zinklegierung mindestens 0,05 Gew.-% Vanadium enthält.

12. Verfahren nach Anspruch 10, wobei die Zinklegierung 0,05 bis 0,12 Gew.-% Vanadium enthält.

13. Verfahren nach Anspruch 10, wobei die Zinklegierung mindestens 0,06 Gew.-% Titan enthält.

14. Verfahren nach Anspruch 10, wobei die Zinklegierung 0,06 bis 0,10 Gew.-% Titan enthält.

15. Verfahren zum Verzinken von Stahl durch Eintauchen in ein Bad aus einer Zink-Nickel-Legierung, umfassend die folgende Stufe:

Eintauchen des Stahls in ein geschmolzenes Bad aus einer Zink-Nickel-Legierung, die, bezogen auf das Gewicht, 0,001 bis 0,007 % Aluminium, 0,5 bis 2 % Zinn und Vanadium und Nickel in einer Menge von mindestens 0,02 % Vanadium und mindestens 0,02 % Nickel bis zu einem maximalen Gesamtgehalt an Vanadium und Nickel von 0,15 % und gegebenenfalls 0,05 bis 0,5 % Wismut enthält, wobei der Rest aus Zink mit einem Gehalt an bis zu 1,3 Gew.-% Blei besteht.

16. Verfahren nach Anspruch 15, wobei die Legierung zusätzlich mindestens 0,01 % Titan enthält, wobei der maximale Gesamtgehalt an Vanadium, Nickel und Titan 0,2 % beträgt.

17. Verfahren zum Verzinken von Stahl durch Eintauchen in ein Zinklegierungs-Verzinkungsbad, umfassend die folgende Stufe:

Eintauchen des Stahls in ein geschmolzenes Bad einer Zinklegierung, die, bezogen auf das Gewicht, 0,001 bis 0,007 % Aluminium, 0,5 bis 2,0 % Zinn, 0,02 bis 0,12 % Vanadium und 0,05 bis 0,5 % Wismut enthält, wobei der Rest aus Zink besteht.

18. Verfahren nach Anspruch 17, wobei das geschmolzene Zinkbad 0,05 bis 0,1 % Wismut enthält.

Revendications

1. Un alliage destiné à la galvanisation de l'acier comprenant, en poids, de l'aluminium à raison de 0,001 % à 0,007 %, de l'étain à raison de 0,5 % à 2 % et un élément choisi dans le groupe constitué par le vanadium à raison de 0,02 % à 0,12 %, le titane à raison de 0,03 % à 0,10 %, le vanadium et le titane considérés ensembles représentant une quantité d'au moins 0,02 % de vanadium et d'au moins 0,01 % de titane, et un total d'au moins 0,03 % à 0,15 % de vanadium et de titane pris collectivement, et, facultativement du bismuth à raison de 0,05 % à 0,5 %, le zinc constituant le reste contenant jusqu'à 1,3 % de plomb.

2. Un alliage selon la revendication 1, destiné à la galvanisation de l'acier, enfermant en poids, du vanadium à raison de 0,05 % à 0,12 %.

3. Un alliage destiné à la galvanisation de l'acier, comprenant, en poids, de l'aluminium à raison de 0,001 % à 0,007 %, de l'étain à raison de 0,5 % à 2 %, du vanadium à raison de 0,05 % à 0,5 %, le zinc constituant le reste contenant

jusqu'à 1,3 % en poids de plomb.

4. Un alliage selon la revendication 3, destiné à la galvanisation de l'acier, comprenant additionnellement, en poids, du bismuth à raison de 0,05 % à 0,1 %.

5. Un alliage selon la revendication 1, destiné à la galvanisation de l'acier, comprenant, en poids, du titane à raison de 0,06 % à 0,1 %.

6. Un alliage selon la revendication 1, dans lequel l'alliage de zinc contient, en poids, au moins 0,03 %, du vanadium et du titane quand le vanadium et le titane sont présents, ensembles, ledit vanadium étant présent à raison d'au moins 0,01 % jusqu'à un maximum de 0,15 % de vanadium et de titane pris collectivement.

7. Un alliage selon la revendication 1, dans lequel le vanadium et le titane sont présents ensembles à raison d'au moins 0,05 %.

8. Un alliage destiné à la galvanisation de l'acier, comportant, en poids, de l'aluminium à raison de 0,001 % à 0,007 %, de l'étain à raison de 0,5 % à 2 %, du vanadium et du nickel à raison d'au moins 0,02 % de vanadium et d'au moins 0,02 % de nickel pris collectivement, le zinc constituant le reste contenant jusqu'à 1,3 % en poids de plomb.

9. Un alliage destiné à la galvanisation de l'acier, comprenant, en poids, de l'aluminium à raison de 0,001 % à 0,007 %, de l'étain à raison de 0,5 % à 2 %, du vanadium à raison de 0,02 % à 0,12 % et du bismuth à raison de 0,05 % à 0,5 %, le reste étant du zinc.

10. Un procédé pour la galvanisation de l'acier par immersion dans un alliage de zinc comprenant les étapes consistant à :

    immerger l'acier dans un bain fondu d'un alliage de zinc comprenant en poids 0,001 % à 0,007 % d'aluminium, 0,05 % à 2 % d'étain, et une quantité, réduisant de manière effective la réactivité de l'acier, d'au moins un élément choisi dans le groupe constitué par 0,02 % à 0,12 % de vanadium, 0,03 % à 0,1 % de titane et au moins 0,02 % de vanadium et au moins 0,01 % de titane, pour un total de 0,03 % à 0,15 % de vanadium et de titane pris collectivement, et facultativement 0,05 % à 0,5 % en poids de bismuth, le zinc constituant le reste contenant jusqu'à 1,3 % en poids de plomb.

11. Un procédé selon la revendication 10, dans lequel un alliage en zinc contient au moins 0,05 % en poids de vanadium.

12. Un procédé selon la revendication 10, dans lequel l'alliage de zinc contient 0,05 % à 0,12 % en poids de vanadium.

13. Un procédé selon la revendication 10, dans lequel l'alliage de zinc contient au moins 0,06 % en poids de titane.

14. Un procédé selon la revendication 10, dans lequel l'alliage de zinc contient 0,06 % à 0,1 % en poids de titane.

15. Un procédé pour la galvanisation de l'acier par immersion dans un bain d'alliage zinc - nickel comprenant les étapes consistant à :

    Immerger l'acier dans un bain fondu d'un alliage zinc-nickel comprenant, en poids, 0,001 % à 0,007 % d'aluminium, 0,5 % à 2 % d'étain et du vanadium et du nickel à raison d'au moins 0,02 % de vanadium et d'au moins 0,02 % de nickel, jusqu'à un maximum de 0,15 % de vanadium et de nickel pris collectivement, et, facultativement 0,05 % à 0,5 % de bismuth, le zinc constituant le reste contenant jusqu'à 1,3 % en poids de plomb.

16. Un procédé selon la revendication 15, dans lequel l'alliage contient additionnellement au moins 0,01 % de titane, jusqu'à un maximum de 0,2 % de vanadium, de nickel et de titane pris collectivement.

17. Un procédé pour la galvanisation de l'acier par immersion dans un bain d'un alliage galvanisant à base de zinc, comprenant les étapes consistant à immerger l'acier dans un bain fondu d'un alliage de zinc contenant, en poids, 0,001 % à 0,007 % d'aluminium, 0,5 % à 2 % d'étain, 0,02 % à 0,12 % de vanadium et 0,05 % à 0,5 % de bismuth, le reste étant constitué par du zinc.

18. Un procédé selon la revendication 17, dans lequel le bain de zinc fondu contient 0,05 % à 0,1 % de bismuth.

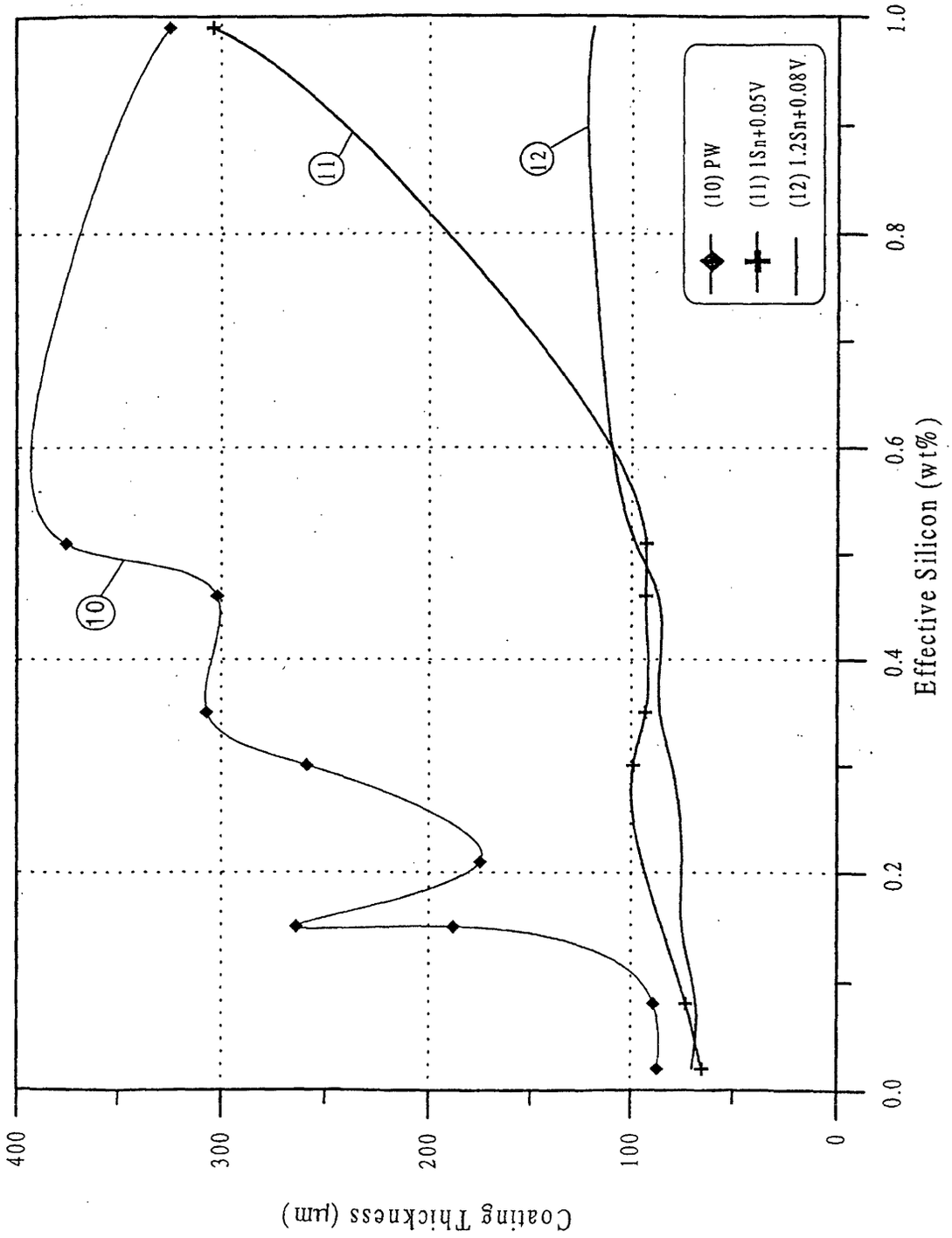

Coating Thickness (μm)
0
100
200
300
400
0.0
0.2
0.4
0.6
0.8
1.0
Effective Silicon (wt%)
(10) PW
(11) 1Sn+0.05V
(12) 1.2Sn+0.08V
10
11
12

Figure 1

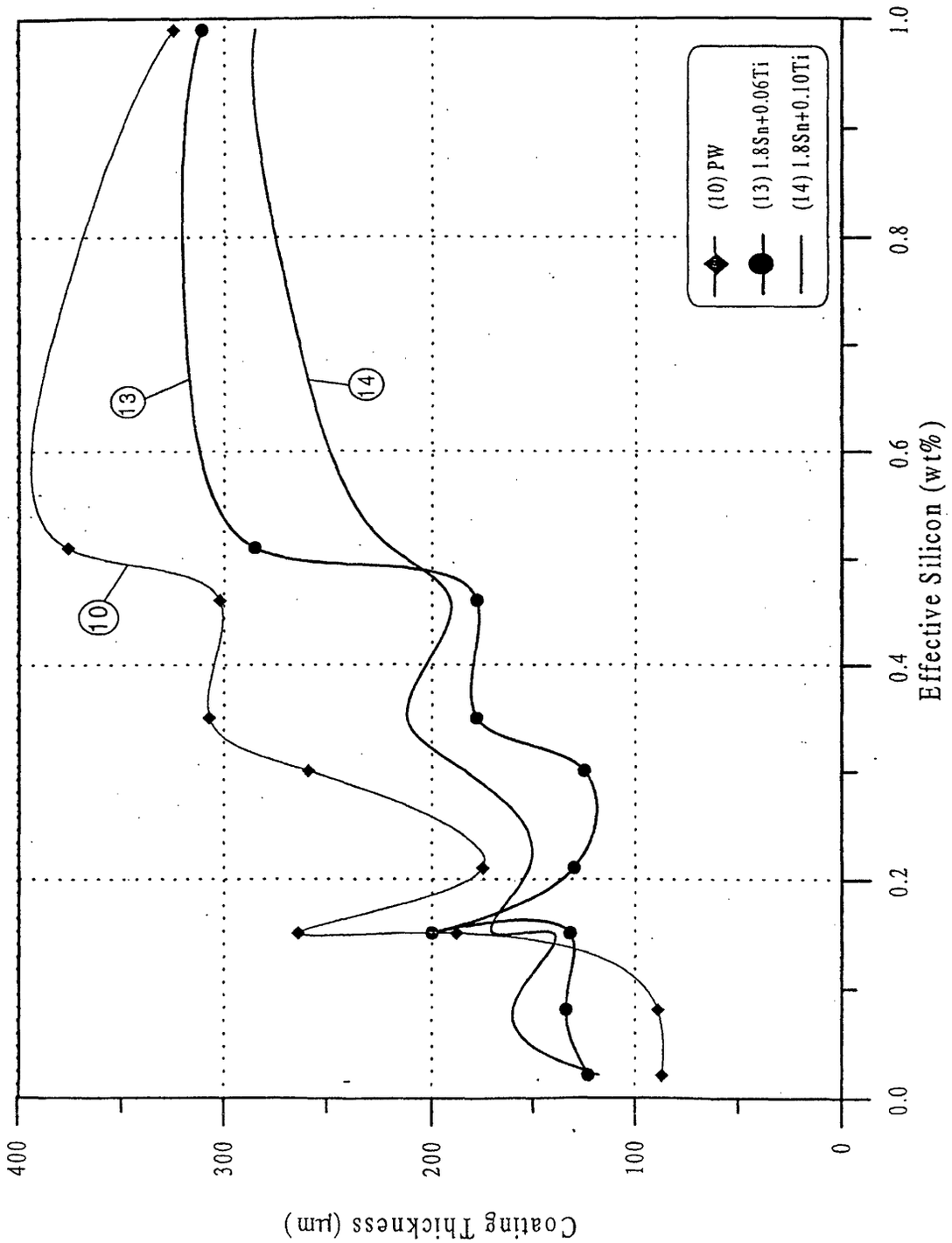

Coating Thickness (μm)
0
100
200
300
400
0.0
0.2
0.4
0.6
0.8
1.0
Effective Silicon (wt%)
(10) PW
(13) 1.8Sn+0.06Ti
(14) 1.8Sn+0.10Ti
10
13
14

Figure 2

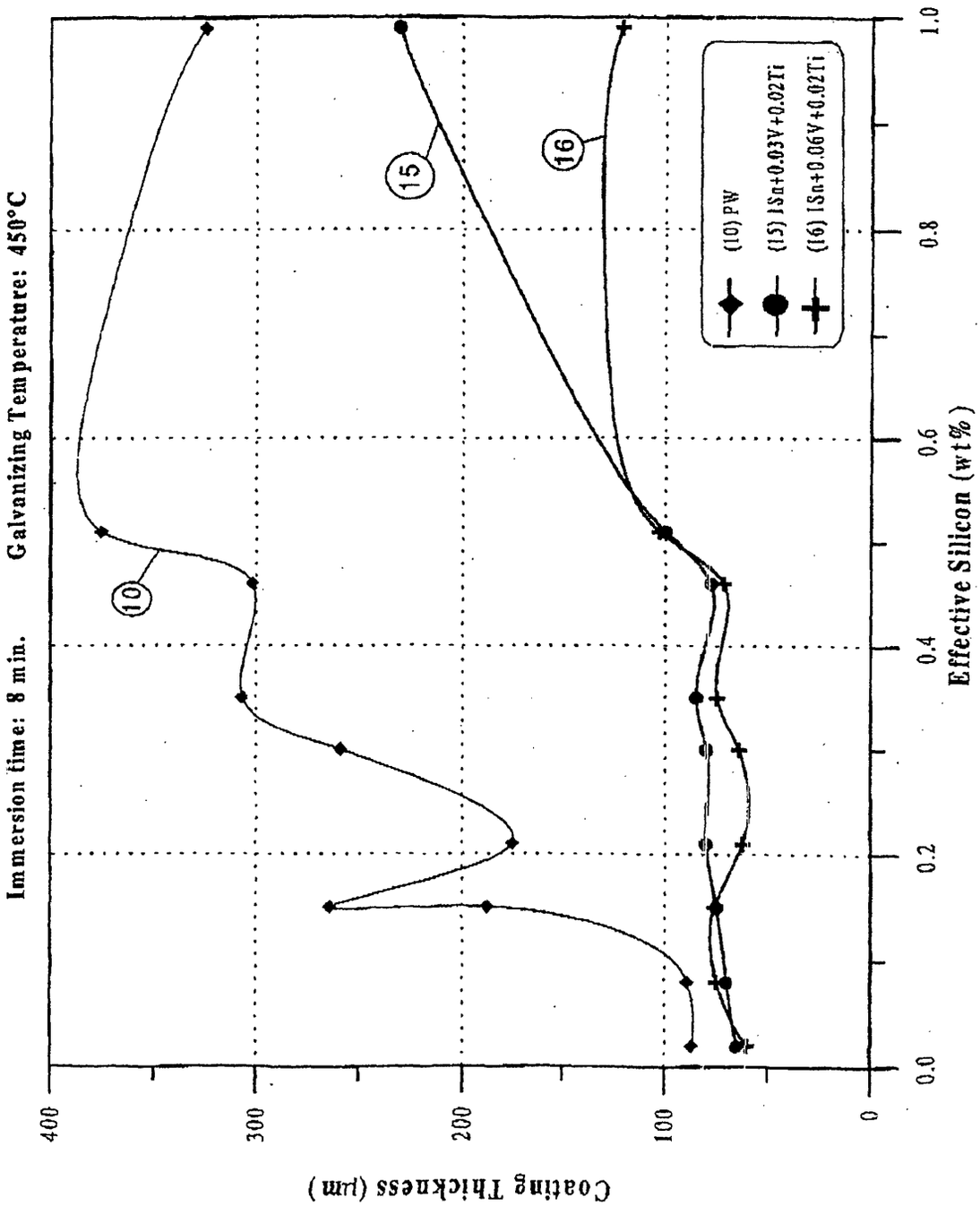

Immersion time: 8 min.
Galvanizing Temperature: 450°C
Coating Thickness (μm)
Effective Silicon (wt%)
0
100
200
300
400
0.0
0.2
0.4
0.6
0.8
1.0
(10) PW
(15) ISn+0.03V+0.02Ti
(16) ISn+0.06V+0.02Ti
10
15
16

Figure 3

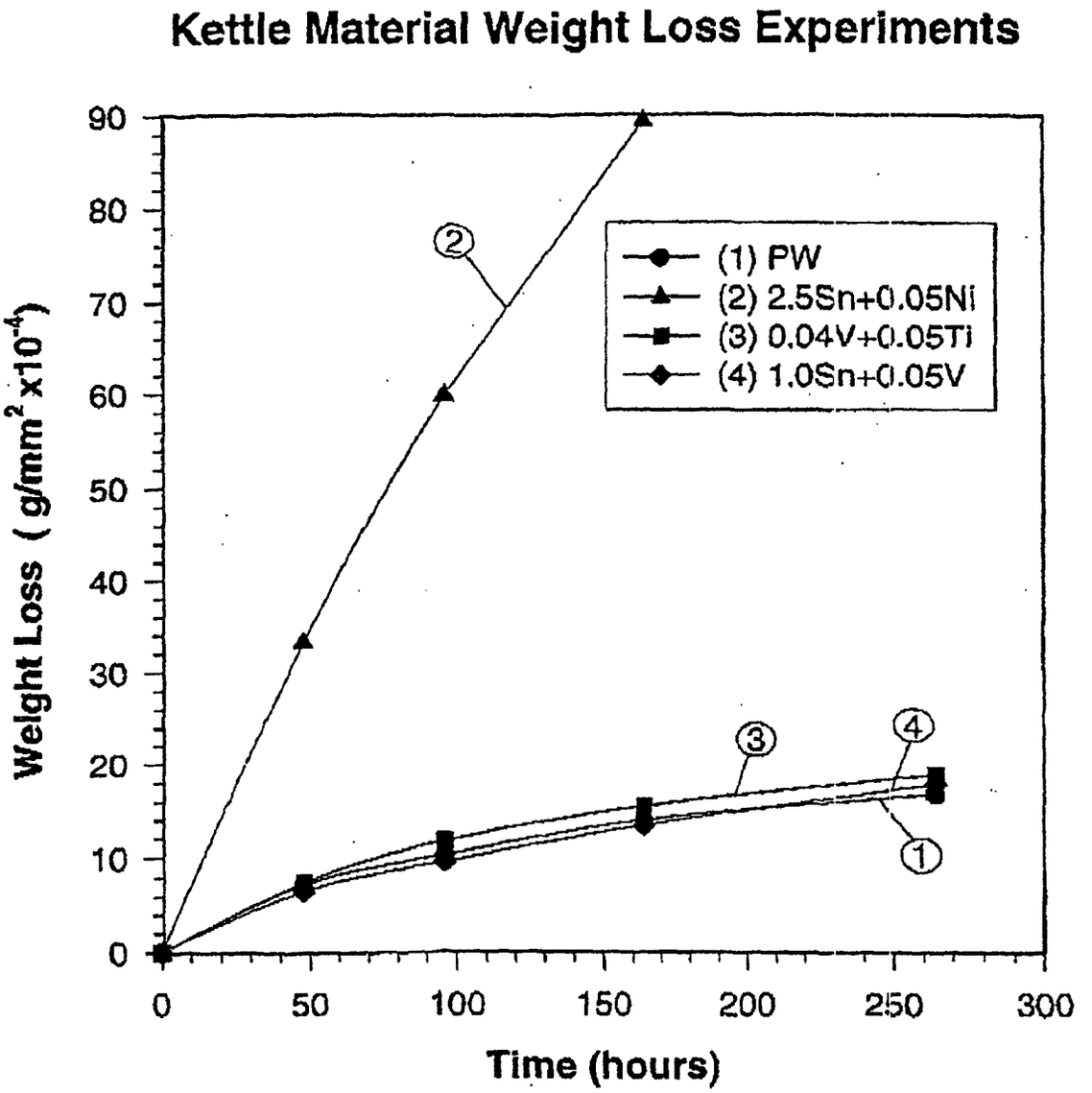

Kettle Material Weight Loss Experiments
Weight Loss (g/mm^2 x10^{-4})
Time (hours)
(1) PW
(2) 2.5Sn+0.05Ni
(3) 0.04V+0.05Ti
(4) 1.0Sn+0.05V
0
10
20
30
40
50
60
70
80
90
0
50
100
150
200
250
300
①
②
③
④

Figure 4