



The present invention relates to a coated sheet metal and to a process for the manufacture of this sheet metal.

It applies in particular to the manufacture of
5 roofs of buildings.

Stainless steel sheets coated with a lead-rich alloy are already known in the state of the art. The coating of a stainless steel sheet with lead is generally carried out on lines for continuous treatment of reels by
10 immersion in a bath of molten lead-based alloy. The lead-based alloy generally contains tin to facilitate the wetting and adherence of the coating.

These coated sheets are applied for the roofing of buildings because they incorporate many advantages. In
15 particular, they have good resistance to inclement weather and good suitability for soft soldering. Also needing to be mentioned is their light weight (approximately 3 kg/m^2 at a sheet metal thickness of 0.4 mm), good mechanical strength and, in the case of sheets made
20 of ferritic stainless steel, a low coefficient of linear expansion which makes it possible to obtain an elongation of 1.06 mm/m with a change of 100°C , whereas in the case of zinc sheets an elongation of 2.20 mm/m is obtained with a change of 100°C .

25 A roof constructed in ferritic stainless steel sheets containing 17 mass% of chromium and coated with a layer of lead-based alloy has an excellent resistance to atmospheric corrosion agents such as acidic rain and the precipitation of fuel oil fumes.

30 In some particularly corrosive atmospheres, for example at the seaside and/or near industries with corrosive discharges, use is preferably made of sheet metal coated with alloyed stainless steel containing molybdenum in a mass concentration of 1 to 3 %.

35 In contact with the atmosphere lead-coated sheets gradually become covered with a protective film whose matt grey appearance resembles that of "old tin". However, this patina - valued by architects - develops slowly. Its formation, which can take a number of months,



is preceded by a transitional stage during which exposure to inclement weather results in the appearance of unsightly lead corrosion products. During this transitional stage rain water causes a partial solubilization of the lead, which has the effect of spreading harmful lead-based compounds into the environment.

The aim of the present invention is to provide sheet metal which can be employed as roofing material which does not have the harmful effects and the unsightly aspects inherent in coatings containing lead, these sheets having an aesthetic matt appearance and good solderability and being protected against atmospheric corrosion.

To this end, the subject of the invention is a process for the manufacture of coated sheet metal employed especially for the manufacture of roofs of buildings, characterized in that a layer of metallic coating of pure tin or of a tin alloy in which the alloying element is chosen especially from zinc and nickel is deposited electrolytically on at least one of the faces of a stainless steel sheet containing more than 16 % of chromium in its weight composition.

In accordance with the characteristics of different embodiments of the invention:

- the coated sheet metal is heated to a temperature higher than or equal to the melting temperature of the tin-based coating layer in order, on the one hand, to form a layer of intermetallic compound between the sheet metal and the metallic coating comprising at least tin and an element forming part of the composition of the stainless steel sheet and, on the other hand, to impart a matt appearance to the surface of the coating;

- the heating temperature is lower than 500°C;
- the sheet metal is degreased before the deposition of the coating layer;

- the sheet metal is degreased by a chemical route by employing a bath containing organic solvents or else by employing a bath containing alkaline mixtures;

- the bath contains an organic solvent chosen



from methylene chloride, 1,1,1-trichloroethane, perchloroethylene and trichloroethylene;

- the bath contains an alkaline mixture comprising at least one compound chosen from sodium hydroxide, sodium carbonate, sodium metasilicate, phosphates and complexing agents;

- the sheet metal is degreased electrolytically by employing an alkaline electrolyte and by alternating or not alternating the polarities;

10 - the electrolyte comprises an alkaline compound in a proportion of 0.5 to 20 mass%, the electrolyte being at a temperature of between 20 and 95°C, the sheet metal being subjected to a current density of between 0.1 and 20 A/dm² for a period longer than 0.1 s;

15 - the electrolyte comprises an alkaline compound chosen from sodium hydroxide and potassium hydroxide;

- the electrolyte additionally comprises a compound chosen from calcium carbonate, sodium metasilicate, phosphates, complexing agents and surface-active agents;

20 - the sheet metal is subjected to a neutral aqueous rinsing after it has been degreased;

- after the degreasing or the rinsing following this degreasing the sheet metal is pickled;

25 - the sheet metal is pickled chemically by being immersed in a bath containing an inorganic acid, the mass proportion of the acid being in a range from 0.2 to 50 %;

- the inorganic acid is chosen from sulfuric acid and hydrochloric acid;

30 - the bath contains 0.2 to 40 mass% of hydrochloric acid and is at a temperature of between 20 and 95°C, the immersion period of the sheet metal in the bath being longer than 0.1 s;

35 - the sheet metal is pickled electrolytically in an electrolyte bath containing an inorganic acid, the mass proportion of the acid being in a range from 0.2 to 50 %;

- the acid of the electrolyte bath is chosen from sulfuric acid and hydrochloric acid;



5 - the electrolyte bath contains 1 to 50 mass% of sulfuric acid and is at a temperature of between 20 and 95°C, the sheet metal being subjected to a current density of between 0.1 and 50 A/dm², the period of immersion of the sheet metal in the bath being longer than 0.1 s;

10 - while being pickled the sheet metal is subjected either to an alternately cathodic and anodic polarization, the treatment being completed with cathodic polarization, or to a continuous cathodic polarization;

1 - the sheet metal is subjected to a rinsing after being pickled;

15 - the sheet metal is activated before the deposition of the layer of metallic coating;

15 - the sheet metal is activated by a chemical route;

20 - the sheet metal is activated by being immersed in a bath containing an acid chosen from sulfuric, hydrochloric, hydrofluoric, boric, fluoroboric, phenol-sulfonic and cresolsulfonic acids, the bath having a pH lower than the pH for depassivation of the sheet metal;

25 - the bath is at a temperature of more than 15°C and the immersion period of the sheet metal in the bath is longer than 0.1 s;

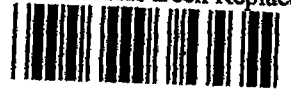
25 - the sheet metal is activated electrolytically;

30 - the sheet metal is activated by employing an acidic electrolyte bath containing an acid chosen from hydrochloric, phosphoric, sulfuric, hydrofluoric, boric, fluoroboric, phenolsulfonic and cresolsulfonic acids, the bath having a pH lower than 1;

35 - the electrolyte bath is at a temperature of more than 15°C and the sheet metal is subjected to a cathodic polarization with a current density of between 0.1 to 50 A/dm², the immersion period of the sheet metal in the bath being longer than 0.1 s;

 - the electrolyte bath additionally comprises stannous ions in a concentration of between 0.1 and 3 mass%;

 - a layer of coating comprising pure tin is



deposited on the sheet metal;

- the electrolytic deposition bath contains stannous tin and phenolsulfonic acid;

5 - the electrolytic deposition bath contains stannous tin in a proportion within the range [20-40] g/l and phenolsulfonic acid in a proportion within the range [20-40] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C;

10 - the electrolytic deposition bath contains stannous chlorides and alkali metal chlorides and fluorides;

15 - the electrolytic deposition bath contains stannous chloride SnCl₂·2H₂O in a proportion within the range [30-90] g/l, sodium fluoride NaF in a proportion within the range [40-60] g/l and sodium chloride NaCl in a proportion within the range [40-60] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C;

20 - the electrolytic deposition bath contains stannous tin and boric and fluoroboric acids;

25 - the electrolytic deposition bath contains stannous tin in a proportion within the range [40-80] g/l, fluoroboric acid in a proportion within the range [40-200] g/l, and boric acid in a proportion within the range [10-30] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C;

30 - a layer of coating comprising an alloy of tin and zinc the weight composition of which is the following:

Sn > 60 %

Zn < 40 %

35 or an alloy of tin and nickel the weight composition of which is the following:

Sn > 80 %

Ni < 20 %

is deposited on the sheet metal.

Another subject of the invention is a coated



sheet metal characterized in that it comprises a substrate made of stainless steel containing more than 16 % of chromium in its weight composition, covered on at least one of its faces with a layer of metallic coating of pure tin or of a tin alloy in which the alloying element is chosen especially from zinc and nickel.

In accordance with the characteristics of various embodiments of this sheet metal:

- the layer of metallic coating has a thickness smaller than or equal to 30 μm , preferably equal to 3 μm ;

- between the substrate and the tin-based coating layer the sheet metal comprises a layer of intermetallic compound containing at least iron, chromium and tin;

- the substrate is made of ferritic steel containing, on a mass basis, approximately 17 % of chromium, less than 0.06 % of carbon and less than 0.015 % of sulfur and being capable of containing approximately 1.2 % of molybdenum;

- the substrate is made of austenitic steel containing, on a mass basis, approximately 18 % of chromium, more than 6 % of nickel, less than 0.07 % of carbon and less than 0.015 % of sulfur and being capable of containing approximately 2.2 % of molybdenum;

- the substrate is made of ferritic steel, containing, on a mass basis, from 17 to 25 % of chromium and from 0.2 to 2 % of nickel.

The description which follows and the attached figures - the whole being given by way of nonlimiting examples - will make the invention properly understood:

- Figure 1 is a diagrammatic sectional view of a sheet metal according to the invention;

- Figure 2 is a diagrammatic sectional view of the sheet metal of Figure 1, the metallic coating layer containing chiefly tin having been dissolved in contact with air and inclement weather;

- Figure 3 is a diagram showing the change, as a function of time, in the dissolution potential of the coating of a sheet metal manufactured according to the invention;

- Figure 4 is a diagram showing, on the one hand, the polarization curve of a sheet metal coated with a layer of tin and, on the other hand, the polarization curve of a sheet metal coated with the intermetallic compound containing iron, tin and chromium.

A coated sheet metal according to the invention, indicated by the general reference 10 can be seen in Figure 1. This sheet metal 10 comprises a substrate consisting of a sheet 12 made of stainless steel containing more than 16 % of chromium in its weight composition. On one of its faces this sheet 12 comprises a layer 14 of intermetallic compound containing at least iron, tin and chromium (Fe-Sn-Cr) and a layer 16 of metallic coating, containing chiefly tin, covering the layer 14 of intermetallic compound.

The steels employed for the manufacture of the sheet 12 are of two types. A first type corresponds to ferritic grades which contain 17 % of chromium (Cr) with or without molybdenum (Mo) referred to according to the US Standard as AISI 430, AISI 434, AISI 439 and AISI 444, and the French Standard as Z3CTNb18. A second type corresponds to austenitic grades which contain 18 % of chromium and at least 6 % of nickel (Ni) with or without molybdenum, referred to according to the US Standard as AISI 304 and AISI 316.

The corrosion resistance of stainless steels is proportionately higher the higher the contents of alloy elements Cr, Ni and Mo.

The steel grades employed in the examples described are detailed in the table below.

This Sheet Has Been Replaced



	Grade	Cr %	Ni %	Mo %	Ti max %	Nb max %	C max %	S max %
5	AISI 430	17					0.06	0.015
	AISI 434	17		1.2			0.06	0.01
	AISI 439	17			0.5		0.02	0.005
	AISI 444	18.5		2.1	0.6	0.5	0.025	0.015
	Z3CTNb18	17.8			0.5	0.9	0.03	0.005
10	AISI 304	18	6.2				0.07	0.015
	AISI 316	18	11	2.2			0.07	0.015

Other stainless steels can be employed, provided that they contain at least 16 mass% of chromium. It is possible, for example, to employ a ferritic steel sheet 12 containing, on a mass basis, from 17 to 25 % of chromium and from 0.2 to 2 % of nickel.

When the sheet metal 10 is placed in the open air and is subjected to inclement weather, the layer 16 can be dissolved after a prolonged period of use over a number of years. In this case a sheet metal 10 as shown in Figure 2 is obtained, the coated face of which now comprises only the layer 14 of intermetallic compound.

The coated sheet metal 10 is manufactured by a process which will be described below.

The stages of surface treatment of a stainless sheet metal 12 manufactured with a steel from the grades defined in the table above will be described first of all, and then the deposition of a layer of pure tin on this stainless sheet metal.

In a first step the surface of the stainless steel sheet is degreased.

The degreasing operation is recommended to guarantee a good adherence of the tin coating. In fact, if the surface of the stainless steel is not degreased, the fatty substances and other surface contaminants which are not removed are liable to reduce the adherence of the tin deposit and to give rise to a nonhomogeneous deposit comprising areas without coating.





The sheet metal can be pickled chemically by being immersed in a bath containing an inorganic acid chosen from sulfuric and hydrochloric acids or other inorganic acids, the proportion of the acid on a mass basis being within a range from 0.2 to 50 %. The stainless sheet metal is kept for at least 0.1 s in the bath, which is at a temperature of more than or equal to 20°C. The bath preferably contains 0.2 to 40 mass% of hydrochloric acid and is at temperature of between 20 and 50°C.

The concentration of the acid in the pickling bath is defined so as to impose a bath pH which is lower than the pH for depassivation of the stainless steel to be treated at the temperature of the bath.

The pickling operation is preferably performed electrolytically in an electrolysis bath or electrolyte consisting of an aqueous solution containing an inorganic acid chosen from sulfuric and hydrochloric acids or other inorganic acids, in a proportion of 0.2 to 50 mass%. The acid is at a concentration such that the pH of the solution is lower than 1 at the temperature of the bath.

The sheet metal is preferably immersed in an electrolyte containing from 1 to 50 mass% of sulfuric acid which is at a temperature of between 20 and 95°C, the sheet metal being subjected to a current density of between 0.1 and 50 A/dm², the period of immersion of the sheet metal in the electrolyte being longer than 0.1 s.

The polarities may be alternately cathodic and anodic, the treatment being completed with cathodic polarization, or solely cathodic.

In the examples described the electrolyte contains 3 mass% of sulfuric acid and is at a temperature of 40°C with a current density of 10 A/dm², with polarities which are successively cathodic, anodic and cathodic.

The pickling of the stainless steel sheet 12 is followed by a rinsing with water (neutral medium) in order not to contaminate the treatment baths which will be employed subsequently.

Sheets made of stainless steel containing more



than 16 % of chromium are of industrial surface quality - arising from their process of manufacture including pickling, cold rolling and annealing stages - which does not require any finishing such as, for example, mechanical or chemical polishing.

Before the deposition of the layer of tin or tin alloy on the stainless steel sheet 12 the sheet is activated.

In fact, stainless steels have a protective layer rich in chromium oxides and hydroxides, called a passive layer, on their surface. The aim of the activation is to remove this passive layer in order to obtain good adherence of the coating, for example of tin, without requiring any premetalizing of the surface of the sheet metal, such as nickel plating.

The activation is performed under conditions which are adapted to the grade of the stainless steel to be treated, it being known that the formation of the passive layer in air is proportionally faster the more resistant the stainless steel is to corrosion. This is especially the case with steels containing more than 16 % of chromium in their weight composition, which require the use of nonpassivating acids to be activated. Consequently, an acid of nitric type cannot be suitable.

The activation of the stainless sheet metal is carried out chemically or electrolytically.

The sheet metal can be activated chemically by immersion in a bath containing one or a number of reducing acids such as hydrochloric acid, phosphoric acid, sulfuric acid, hydrofluoric, boric or fluoro-boric acid, as well as phenolsulfonic and cresolsulfonic acids or other organic acids.

The stainless sheet metal is kept for at least 0.1 s in the bath, which is at a temperature of more than or equal to 15°C.

The concentration of the acid in the activating bath is defined so as to impose a bath pH which is lower than the pH for depassivation of the stainless steel to be treated at the temperature of the bath. The pH for



depassivation is defined as being the limiting pH of the bath, below which the passive layer covering the stainless steel is no longer stable, this steel becoming vulnerable to corrosion.

5 In a first example an activation by a chemical route is carried out on a stainless steel sheet of AISI 430 type, before the deposition of a layer of tin, by immersing the sheet in a bath containing especially 9 mass% of hydrochloric acid. This bath is taken to a
10 temperature of 20°C and the sheet is kept in the bath for approximately 10 s.

 The activation of the sheet metal by a chemical route can be performed under other conditions. The sheet metal may be immersed in a bath containing 0.2 to
15 40 mass% of hydrochloric acid. The temperature of the bath may be between 15 and 95°C.

 An activation may also be performed by an electrolytic route by employing an electrolysis bath or electrolyte similar to the bath employed for the activation by a chemical route, that is to say containing an
20 acid chosen from hydrochloric, phosphoric, sulfuric, hydrofluoric, boric and fluoroboric acids and phenolsulfonic, cresolsulfonic or other organic acids, but with an acid concentration such that the pH of the bath is lower
25 than 1.

 Using an electrolytic route, the polarization of the bath is cathodic or else is alternately anodic and cathodic, the polarization being always cathodic at the end of activation. The current density employed is higher
30 than 0.1 A/dm², preferably between 0.1 and 50 A/dm². The stainless sheet metal is kept for a period longer than 0.1 s in the bath, this bath being at a temperature of more than or equal to 15°C.

 With alternating anodic/cathodic polarization it
35 is preferable to employ a bath containing an acid whose anion is electrochemically inactive. Thus, sulfuric acid is employed in preference to hydrochloric acid to avoid any release of chlorine in an anodic phase. The treatment is completed with cathodic polarization to prevent any



repassivation of the sheet metal capable of being initiated by an anodic polarization.

An activation can also be performed electrolytically by employing an acidic electrolyte chosen from the acids referred to above, in a concentration such that the pH of the bath is lower than 1, to which a quantity of stannous ions may be added in a concentration of between 0.1 and 3 mass%. The temperature of the electrolyte is higher than or equal to 15°C. The sheet metal is subjected to a cathodic polarization with a current density of between 0.1 and 50 A/dm². The period of immersion of the sheet metal in the electrolyte is longer than 0.1 s.

In a second example, the activation of a reel of stainless steel of AISI 430 type is carried out continuously by cathodic polarization at 10 A/dm², for 0.8 s, in an electrolyte containing 17 mass% of phenol-sulfonic acid at a temperature of 20°C. In this example the anodes placed facing the strip are made of ferrosilicon alloy.

The activation of the reel of stainless steel of AISI 430 type can also be carried out under the same operating conditions as above, but with stainless steel anodes, for example of AISI 316 type.

Under the operating conditions described in this first example the reel of stainless steel may be of AISI 439, AISI 434, AISI 304, AISI 444 or AISI 316 type or of Z3CTNb18 type.

In a third example an activation of stainless steel sheets of the AISI 434, AISI 304, AISI 316 and AISI 444 type is carried out electrolytically. In this example the activation of the stainless steel sheet is performed electrolytically by employing a bath containing 20 mass% of sulfuric acid. The sheet metal is kept for 20 s in the bath, the latter being at a temperature of 20°C. The current density is controlled at 10 A/dm². The polarities have been reversed during the electrolytic activation in accordance with the cathodic polarity/anodic polarity/cathodic polarity cycle.



In a fourth example the activation of a reel of AISI 316 type is carried out continuously by an electrolytic route.

5 The electrolyte contains 17 mass% of phenolsulfonic acid and 0.5 mass% of stannous ions, at a temperature of 20°C. The cathode current density is controlled at 10 A/dm². The anodes are made of alloy of ferrosilicon type and the immersion period is 0.8 s.

10 The operating conditions described in this example are also applicable to the stainless grades mentioned above.

When the stages of activation of the surface of the stainless steel sheet are completed, a layer of pure tin or of tin alloy is deposited electrolytically,
15 without intermediate rinsing, to avoid any repassivation of the sheet metal.

Consequently care will be taken that the electrolyte employed for activating the sheet metal should be compatible with the electrolyte employed for depositing
20 the layer of tin or tin alloy on the sheet metal.

A number of embodiments of a deposition of pure tin will be described below.

According to one embodiment of the deposition of pure tin, the electrolyte contains stannous (Sn²⁺) tin in
25 the presence of phenolsulfonic acid or of boric and fluoroboric acid, or stannous chloride in the presence of alkali metal chlorides or fluorides. The current density applied to the sheet metal is higher than 1 A/dm² and the temperature of the electrolyte is more than 15°C.

30 In the case of the examples described the electrolyte contains a solution of stannous (Sn²⁺) tin in phenolsulfonic acid. The stannous tin content is from approximately 20 to 40 g/l and the phenolsulfonic acid content is between 20 and 40 g/l.

35 Additives are also added, such as β-naphthol (1 g/l) and gelatin (2 g/l). They make it possible to provide the coating with fineness, compactness and uniformity. The current density is between 10 and 35 A/dm², and the temperature of the bath between 25 and



40°C.

According to another embodiment of the deposition of pure tin, the deposition bath contains stannous chlorides and alkali metal chlorides and fluorides.

5 For example, the bath contains stannous chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in a proportion within the range [30-90] g/l, sodium fluoride NaF in a proportion within the range [40-60] g/l and sodium chloride NaCl in a proportion within the range [40-60] g/l. The bath is employed with
10 a current density higher than 1 A/dm² and a temperature of more than 15°C.

According to yet another embodiment of the deposition of pure tin, the deposition bath contains stannous tin and boric and fluoroboric acids.

15 For example, the bath contains stannous tin in a proportion within the range [40-80] g/l, fluoroboric acid in a proportion within the range [40-200] g/l and boric acid in a proportion within the range [10-30] g/l. The bath is employed with a current density higher than
20 1 A/dm² and a temperature of more than 15°C.

The tin coating is of relatively low thickness. In the examples described the tin coating deposited has a thickness of 3 μm.

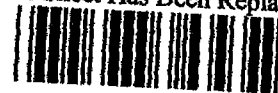
In other embodiments of the invention the
25 thickness of the tin layer may reach 30 μm.

In this state the sheet metal has a matt surface appearance and forms a product which can be employed for the manufacture of roofs of buildings.

30 The tin-coated stainless sheet metal is next heated by known means, for example an induction oven, to a temperature which is higher than or equal to the melting temperature of tin (232°C).

In the examples described the temperature for heating the tin-coated sheet metal is 250°C.

35 The purpose of the heat treatment is to form an intermetallic compound containing at least iron, tin and chromium, at the interface of the stainless steel sheet and of the tin layer, while preserving the matt surface appearance of the tin layer.



When the tin coating changes into the molten state, its roughness is minimal. If the heat treatment is stopped just after the melting of the tin with the aid of rapid cooling, the surface appearance obtained is very shiny. To avoid this shine and to obtain a coating of matt appearance, the heat treatment is prolonged for a sufficient time which depends especially on the thickness of the tin layer. The intermetallic compound grows during the heating period, developing mechanical stresses in the tin layer which perturb the free surface of this layer and result in the return of a matt appearance. The heat treatment period must therefore be sufficiently long to allow the coating not to have a shiny appearance after cooling.

The heat treatment also contributes to reinforcing the adherence of the tin layer to the stainless sheet metal through the intermediacy of the intermetallic compound.

The presence of the intermetallic compound is demonstrated, for example by dissolving the tin layer at constant intensity in a solution of hydrochloric acid at a concentration of 1 mol/l.

Figure 3 shows the curve of change in the dissolution potential of the tin layer as a function of time. The time t_1 corresponds to the baring of the layer of intermetallic Fe-Sn-Cr compound and to the end of the dissolving of the layer of pure tin. The time t_2 corresponds to the end of the dissolving of the layer of intermetallic Fe-Sn-Cr compound and to the baring of the stainless steel. The time $t_2 - t_1$ is proportional to the thickness of the layer of intermetallic compound.

In the examples described the layer of intermetallic compound has a thickness of approximately 0.7 micrometer.

The elements constituting the intermetallic compound are identified, for example, by means of an electronic microprobe. The intermetallic compound may contain other elements in addition to iron, tin and chromium.



The layer of intermetallic compound is bared after several years in use when the sheet metal is exposed to the open air and subjected to inclement weather. The intermetallic compound which remains at the surface of the stainless steel sheet is of a dark grey color, resembling that of "old tin".

The layer of intermetallic compound has a corrosion resistance which is greatly superior to that of tin.

This high corrosion resistance of the intermetallic compound is illustrated in Figure 4, which shows the plot of the curves of polarization of the intermetallic compound layer and of the tin layer which are placed in an aerated solution of sodium sulfate at a concentration of 0.01 mole/l, at ambient temperature. It is found that the current for dissolution of the intermetallic compound changes little as a function of the potential, this being characteristic of a high corrosion resistance. In contrast, tin, for which the dissolution current increases as a function of the applied potential appears to be less resistant to corrosion than the intermetallic compound.

The sheets comprising a layer of intermetallic compound exhibit good solderability.

A soldering test on a coated sheet metal of the type just described was carried out under the following conditions:

After pickling with phosphoric acid of the areas to be soldered, followed by overlapping over approximately 1 cm, the soldering was carried out using the iron and a Pb/Sn (33 % Sn) rod. The soldering was tested by a bending test at 180°C around a mandrel with a radius of curvature of 10 mm. No tearing away of the solder was found.

To form the layer of intermetallic compound the layer of pure tin may be replaced with a layer of alloy containing chiefly tin.

It is possible to employ an alloy of tin (Sn) and of zinc (Zn) the weight composition of which is the following:



Sn > 60 %

Zn < 40 %.

It is also possible to employ an alloy of tin (Sn) and nickel (Ni) the weight composition of which is
5 the following:

Sn > 80 %

Ni < 20 %.

As in the case of pure tin, the alloy is deposited electrolytically on the stainless steel sheet. The
10 alloy-coated sheet metal is then heated to a temperature higher than or equal to the melting temperature of the alloy, for a sufficient period for the alloy to retain its matt appearance.

The temperature of treatment of the coated sheet
15 metal, after deposition of a layer of pure tin or of alloyed tin, is preferably lower than 500°C in order to avoid the formation of a tin oxide of yellowish color, which is undesirable, at the surface of the coating.

The intermetallic compound which forms at the
20 interface of the stainless steel sheet and of the layer of pure tin or of alloyed tin may contain compounds other than iron, tin and chromium, depending on the type of steel employed and of the type of alloy employed.

The coating of the sheet metal may be arranged at
25 will on only one face of the sheet metal or on both faces of the sheet metal.

The invention incorporates numerous advantages.

The layer containing chiefly tin and deposited electrolytically on a stainless steel sheet exhibits an
30 aesthetic matt appearance which is appreciable when the sheet metal is installed on the roof of a building.

The intermetallic compound containing iron, tin and chromium which appears at the surface of the sheet metal when the tin-based layer has disappeared has a matt
35 appearance resembling that of "old tin" which is appreciated in the roofing of buildings.

The layer of intermetallic compound adheres strongly to the sheet metal and exhibits very good corrosion resistance.

The layer of intermetallic compound is stable under the influence of an acidic atmosphere or of a maritime climate.

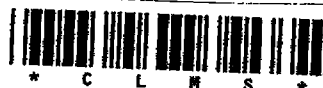
Further, the sheet metal comprising a layer of
5 intermetallic compound containing Fe, Sn and Cr exhibits very good solderability.

This Sheet Has Been Replaced



CLAIMS

1. Process for the manufacture of a coated sheet metal employed especially for the manufacture of roofs of buildings, characterized in that a layer (16) of metallic coating of pure tin or of a tin alloy in which the alloying element is chosen especially from zinc and nickel is deposited electrolytically on at least one of the faces of a stainless steel sheet (12) containing more than 16 % of chromium in its weight composition.
2. Process according to claim 1, characterized in that the coated sheet metal is heated to a temperature higher than or equal to the melting temperature of the tin-based coating layer in order, on the one hand, to form a layer (14) of intermetallic compound between the sheet metal (12) and the metallic coating (16) comprising at least tin and an element forming part of the composition of the stainless steel sheet and, on the other hand, to impart a matt appearance to the surface of the coating (16).
3. Process according to claim 2, characterized in that the heating temperature is lower than 500°C.
4. Process according to claim 1, characterized in that the sheet metal is degreased before the deposition of the coating layer.
5. Process according to claim 4, characterized in that the sheet metal is degreased by a chemical route by employing a bath containing organic solvents or else by employing a bath containing alkaline mixtures.
6. Process according to claim 5, characterized in that the bath contains an organic solvent chosen from methylene chloride, 1,1,1-trichloroethane, perchloroethylene and trichloroethylene.
7. Process according to claim 5, characterized in that the bath contains an alkaline mixture comprising at least one compound chosen from sodium hydroxide, sodium carbonate, sodium metasilicate, phosphates and complexing agents.
8. Process according to claim 4, characterized in that the sheet metal (12) is degreased electrolytically





by employing an alkaline electrolyte and by alternating or not alternating the polarities.

9. Process according to claim 8, characterized in that the electrolyte comprises an alkaline compound in a proportion of 0.5 to 20 mass%, the electrolyte being at a temperature of between 20 and 95°C, the sheet metal (12) being subjected to a current density of between 0.1 and 20 A/dm² for a period longer than 0.1 s.

10. Process according to claim 8, characterized in that the electrolyte comprises an alkaline compound chosen from sodium hydroxide and potassium hydroxide.

11. Process according to claim 10, characterized in that the electrolyte additionally comprises a compound chosen from calcium carbonate, sodium metasilicate, phosphates, complexing agents and surface-active agents.

12. Process according to claim 1, characterized in that the sheet metal (12) is subjected to a neutral aqueous rinsing after it has been degreased.

13. Process according to claim 4, characterized in that the sheet metal is pickled after the degreasing.

14. Process according to claim 13, characterized in that the sheet metal is pickled chemically by being immersed in a bath containing an inorganic acid, the mass proportion of the acid being in a range from 0.2 to 50 %.

15. Process according to claim 14, characterized in that the inorganic acid is chosen from sulfuric acid and hydrochloric acid.

16. Process according to claim 15, characterized in that the bath contains 0.2 to 40 mass% of hydrochloric acid and is at a temperature of between 20 and 95°C, the immersion period of the sheet metal (12) in the bath being longer than 0.1 s.

17. Process according to claim 13, characterized in that the sheet metal is pickled electrolytically in an electrolyte bath containing an inorganic acid, the mass proportion of the acid being in a range from 0.2 to 50 %.

18. Process according to claim 17, characterized in that the acid of the electrolyte bath is chosen from sulfuric acid and hydrochloric acid.





19. Process according to claim 18, characterized in that the electrolyte bath contains 1 to 50 mass% of sulfuric acid and is at a temperature of between 20 and 95°C, the sheet metal (12) being subjected to a current density of between 0.1 and 50 A/dm², the period of immersion of the sheet metal (12) in the bath being longer than 0.1 s.
20. Process according to claim 17, characterized in that, while being pickled, the sheet metal is subjected either to an alternately cathodic and anodic polarization, the treatment being completed with cathodic polarization, or to a continuous cathodic polarization.
21. Process according to claim 13, characterized in that the sheet metal is subjected to a rinsing after being pickled.
22. Process according to claim 1, characterized in that the sheet metal (12) is activated before the deposition of the layer of metallic coating.
23. Process according to claim 22, characterized in that the sheet metal is activated by a chemical route.
24. Process according to claim 23, characterized in that the sheet metal (12) is activated by being immersed in a bath containing an acid chosen from sulfuric, hydrochloric, hydrofluoric, boric, fluoroboric, phenolsulfonic and cresolsulfonic acids, the bath having a pH lower than the pH for depassivation of the sheet metal (12).
25. Process according to claim 24, characterized in that the bath is at a temperature of more than 15°C and the period of immersion of the sheet metal in the bath is longer than 0.1 s.
26. Process according to claim 22, characterized in that the sheet metal is activated electrolytically.
27. Process according to claim 26, characterized in that the sheet metal is activated by employing an acidic electrolyte bath containing an acid chosen from hydrochloric, phosphoric, sulfuric, hydrofluoric, boric, fluoroboric, phenolsulfonic and cresolsulfonic acids, the bath having a pH lower than 1.





28. Process according to claim 27, characterized in that the electrolyte bath is at a temperature of more than 15°C and the sheet metal is subjected to a cathodic polarization, with a current density of between 0.1 to 50 A/dm², the period of immersion of the sheet metal in the bath being longer than 0.1 s.
29. Process according to claim 27, characterized in that the electrolyte bath additionally comprises stannous ions in a concentration of between 0.1 and 3 mass%.
30. Process according to claim 1, characterized in that a layer of coating comprising pure tin is deposited on the sheet metal.
31. Process according to claim 30, characterized in that the electrolytic deposition bath contains stannous (Sn²⁺) tin and phenolsulfonic acid.
32. Process according to claim 31, characterized in that the electrolytic deposition bath contains stannous tin in a proportion within the range [20-40] g/l and phenolsulfonic acid in a proportion within the range [20-40] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C.
33. Process according to claim 30, characterized in that the electrolytic deposition bath contains stannous chlorides and alkali metal chlorides and fluorides.
34. Process according to claim 33, characterized in that the electrolytic deposition bath contains stannous chloride SnCl₂·2H₂O in a proportion within the range [30-90] g/l, sodium fluoride NaF in a proportion within the range [40-60] g/l and sodium chloride NaCl in a proportion within the range [40-60] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C.
35. Process according to claim 30, characterized in that the electrolytic deposition bath contains stannous tin and boric and fluoroboric acids.
36. Process according to claim 35, characterized in that the electrolytic deposition bath contains stannous tin in a proportion within the range [40-80] g/l,





fluoroboric acid in a proportion within the range [40-200] g/l, and boric acid in a proportion within the range [10-30] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C.

37. Process according to claim 1, characterized in that a layer of coating comprising an alloy of tin and zinc the weight composition of which is the following:

Sn > 60 %
Zn < 40 %

or an alloy of tin and nickel the weight composition of which is the following:

Sn > 80 %
Ni < 20 %

is deposited on the sheet metal.

38. Coated sheet metal characterized in that it comprises a substrate (12) made of stainless steel containing more than 16 % of chromium in its weight composition, covered on at least one of its faces with a layer (16) of metallic coating of pure tin or of a tin alloy in which the alloying element is chosen especially from zinc and nickel.

39. Coated sheet metal according to claim 38, characterized in that the layer (16) of metallic coating has a thickness smaller than or equal to 30 µm, preferably equal to 3 µm.

40. Coated sheet metal according to claim 38, characterized in that, between the substrate (12) and the tin-based coating layer (16), the sheet metal comprises a layer (14) of intermetallic compound containing at least iron, chromium and tin.

41. Coated sheet metal according to claim 38, characterized in that the substrate (12) is made of ferritic steel containing, on a mass basis, approximately 17 % of chromium, less than 0.06 % of carbon and less than 0.015 % of sulfur, and capable of containing approximately 1.2 % of molybdenum.

42. Coated sheet metal according to claim 38, characterized in that the substrate (12) is made of austenitic



steel containing, on a mass basis, approximately 18 % of chromium, more than 6 % of nickel, less than 0.07 % of carbon and less than 0.015 % of sulfur and capable of containing approximately 2.2 % of molybdenum.

- 5 43. Coated sheet metal according to claim 38, characterized in that the substrate (12) is made of ferritic steel, containing, on a mass basis, from 17 to 25 % of chromium and from 0.2 to 2 % of nickel.

This Sheet Has Been Replaced



* C L H S *

1 / 2

This Sheet Has Been Replaced

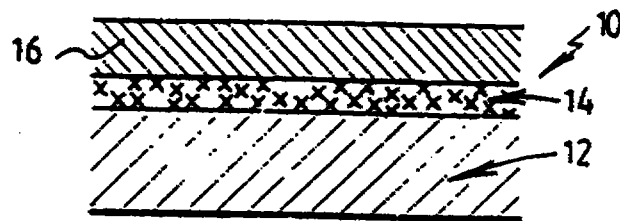


FIG. 1

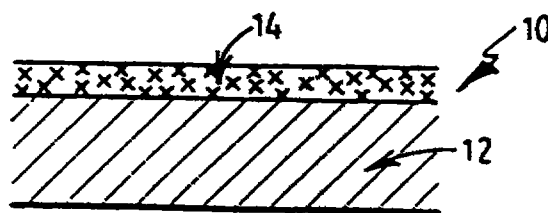
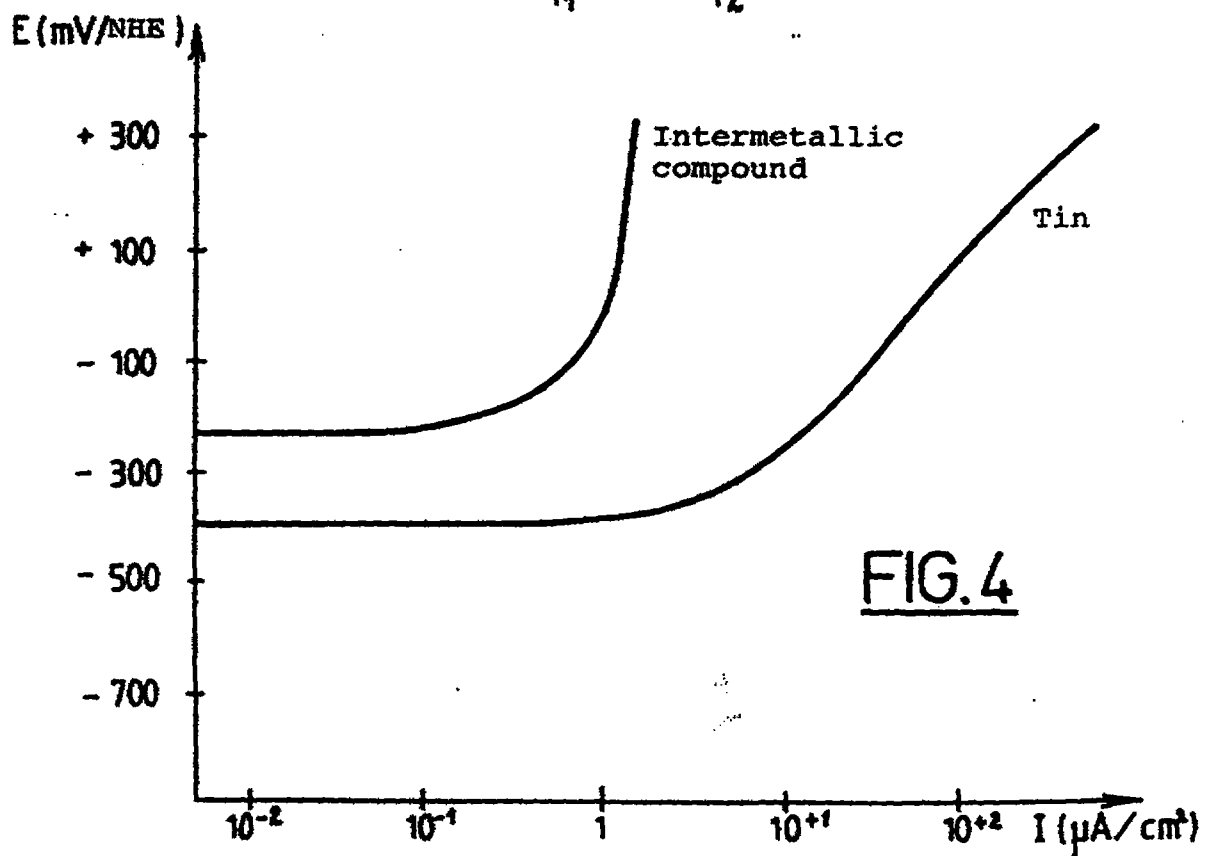
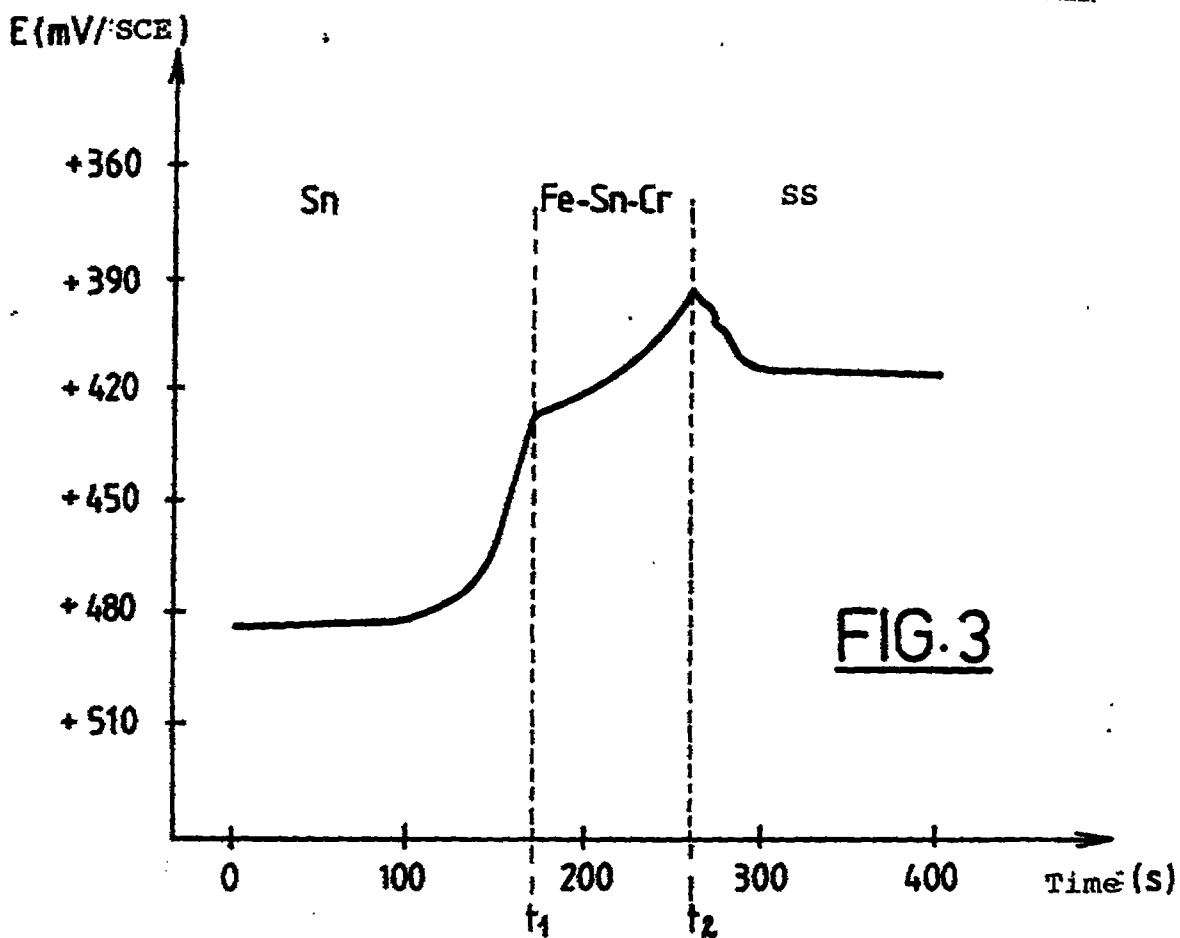
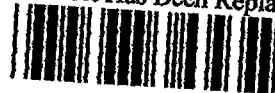


FIG. 2

2 / 2

This Sheet Has Been Replaced



REPLACED SHEETS		SG
☒	Description : paged 1 to paged 11	
☒	Claim(s) : paged 20 to paged 22	
☐	Drawing(s) : paged to paged	
☐	Abstract : paged to paged	
DATE OF RECEIPT		

9100344-8

1785

1

REPLACEMENT SHEETS		SG
☒	Description : paged 1 to paged 11	
☒	Claim(s) : paged 20 to paged 22	
☒	Drawing(s) : paged 1 to paged 11	
☒	Abstract : paged 20 to paged 22	

DATE OF RECEIPT 20/12/96

Coated Sheet Metal And Process For The Manufacture Of This Sheet Metal

The present invention relates to a coated sheet metal and to a process for the manufacture of this sheet metal.

It applies in particular to the manufacture of roofs of buildings.

Stainless steel sheets coated with a lead-rich alloy are already known in the state of the art. The coating of a stainless steel sheet with lead is generally carried out on lines for continuous treatment of reels by immersion in a bath of molten lead-based alloy. The lead-based alloy generally contains tin to facilitate the wetting and adherence of the coating.

These coated sheets are applied for the roofing of buildings because they incorporate many advantages. In particular, they have good resistance to inclement weather and good suitability for soft soldering. Also needing to be mentioned is their light weight (approximately 3 kg/m² at a sheet metal thickness of 0.4 mm), good mechanical strength and, in the case of sheets made of ferritic stainless steel, a low coefficient of linear expansion which makes it possible to obtain an elongation of 1.06 mm/m with a change of 100°C, whereas in the case of zinc sheets an elongation of 2.20 mm/m is obtained with a change of 100°C.

A roof constructed in ferritic stainless steel sheets containing 17 mass% of chromium and coated with a layer of lead-based alloy has an excellent resistance to atmospheric corrosion agents such as acidic rain and the precipitation of fuel oil fumes.

In some particularly corrosive atmospheres, for example at the seaside and/or near industries with corrosive discharges, use is preferably made of sheet metal coated with alloyed stainless steel containing molybdenum in a mass concentration of 1 to 3 %.

In contact with the atmosphere lead-coated sheets gradually become covered with a protective film whose matt grey appearance resembles that of "old tin". However, this patina - valued by architects - develops slowly. Its formation, which can take a number of months,

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996

is preceded by a transitional stage during which exposure to inclement weather results in the appearance of unsightly lead corrosion products. During this transitional stage rain water causes a partial solubilization of the lead, which has the effect of spreading harmful lead-based compounds into the environment.

The aim of the present invention is to provide sheet metal which can be employed as roofing material which does not have the harmful effects and the unsightly aspects inherent in coatings containing lead, these sheets having an aesthetic matt appearance and good solderability and being protected against atmospheric corrosion.

To this end, the subject of the invention is a process for the manufacture of coated sheet metal employed especially for the manufacture of roofs of buildings, characterized in that a layer of metallic coating of pure tin or of a tin alloy in which the alloying element is chosen especially from zinc and nickel is deposited electrolytically on at least one of the faces of a stainless steel sheet containing more than 16 % of chromium in its weight composition.

In accordance with the characteristics of different embodiments of the invention:

- the coated sheet metal is heated to a temperature higher than or equal to the melting temperature of the tin-based coating layer in order, on the one hand, to form a layer of intermetallic compound between the sheet metal and the metallic coating comprising at least tin and an element forming part of the composition of the stainless steel sheet and, on the other hand, to impart a matt appearance to the surface of the coating;

- the heating temperature is lower than 500°C;

- the sheet metal is degreased before the deposition of the coating layer;

- the sheet metal is degreased by a chemical route by employing a bath containing organic solvents or else by employing a bath containing alkaline mixtures;

- the bath contains an organic solvent chosen

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996

from methylene chloride, 1,1,1-trichloroethane, perchloroethylene and trichloroethylene;

- the bath contains an alkaline mixture comprising at least one compound chosen from sodium hydroxide, sodium carbonate, sodium metasilicate, phosphates and complexing agents;

- the sheet metal is degreased electrolytically by employing an alkaline electrolyte and by alternating or not alternating the polarities;

- the electrolyte comprises an alkaline compound in a proportion of 0.5 to 20 mass%, the electrolyte being at a temperature of between 20 and 95°C, the sheet metal being subjected to a current density of between 0.1 and 20 A/dm² for a period longer than 0.1 s;

- the electrolyte comprises an alkaline compound chosen from sodium hydroxide and potassium hydroxide;

- the electrolyte additionally comprises a compound chosen from calcium carbonate, sodium metasilicate, phosphates, complexing agents and surface-active agents;

- the sheet metal is subjected to a neutral aqueous rinsing after it has been degreased;

- after the degreasing or the rinsing following this degreasing the sheet metal is pickled;

- the sheet metal is pickled chemically by being immersed in a bath containing an inorganic acid, the mass proportion of the acid being in a range from 0.2 to 50 %;

- the inorganic acid is chosen from sulfuric acid and hydrochloric acid;

- the bath contains 0.2 to 40 mass% of hydrochloric acid and is at a temperature of between 20 and 95°C, the immersion period of the sheet metal in the bath being longer than 0.1 s;

- the sheet metal is pickled electrolytically in an electrolyte bath containing an inorganic acid, the mass proportion of the acid being in a range from 0.2 to 50 %;

- the acid of the electrolyte bath is chosen from sulfuric acid and hydrochloric acid;

This Sheet Has Been Replaced



This is the replacement sheet

Date:

20 DEC 1996

- the electrolyte bath contains 1 to 50 mass% of sulfuric acid and is at a temperature of between 20 and 95°C, the sheet metal being subjected to a current density of between 0.1 and 50 A/dm², the period of immersion of the sheet metal in the bath being longer than 0.1 s;

- while being pickled the sheet metal is subjected either to an alternately cathodic and anodic polarization, the treatment being completed with cathodic polarization, or to a continuous cathodic polarization;

- the sheet metal is subjected to a rinsing after being pickled;

- the sheet metal is activated before the deposition of the layer of metallic coating;

- the sheet metal is activated by a chemical route;

- the sheet metal is activated by being immersed in a bath containing an acid chosen from sulfuric, hydrochloric, hydrofluoric, boric, fluoroboric, phenolsulfonic and cresolsulfonic acids, the bath having a pH lower than the pH for depassivation of the sheet metal;

- the bath is at a temperature of more than 15°C and the immersion period of the sheet metal in the bath is longer than 0.1 s;

- the sheet metal is activated electrolytically;

- the sheet metal is activated by employing an acidic electrolyte bath containing an acid chosen from hydrochloric, phosphoric, sulfuric, hydrofluoric, boric, fluoroboric, phenolsulfonic and cresolsulfonic acids, the bath having a pH lower than 1;

- the electrolyte bath is at a temperature of more than 15°C and the sheet metal is subjected to a cathodic polarization with a current density of between 0.1 to 50 A/dm², the immersion period of the sheet metal in the bath being longer than 0.1 s;

- the electrolyte bath additionally comprises stannous ions in a concentration of between 0.1 and 3 mass%;

- a layer of coating comprising pure tin is

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996

deposited on the sheet metal;

- the electrolytic deposition bath contains stannous tin and phenolsulfonic acid;

- the electrolytic deposition bath contains stannous tin in a proportion within the range [20-40] g/l and phenolsulfonic acid in a proportion within the range [20-40] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C;

- the electrolytic deposition bath contains stannous chlorides and alkali metal chlorides and fluorides;

- the electrolytic deposition bath contains stannous chloride SnCl₂·2H₂O in a proportion within the range [30-90] g/l, sodium fluoride NaF in a proportion within the range [40-60] g/l and sodium chloride NaCl in a proportion within the range [40-60] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C;

- the electrolytic deposition bath contains stannous tin and boric and fluoroboric acids;

- the electrolytic deposition bath contains stannous tin in a proportion within the range [40-80] g/l, fluoroboric acid in a proportion within the range [40-200] g/l, and boric acid in a proportion within the range [10-30] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C;

- a layer of coating comprising an alloy of tin and zinc the weight composition of which is the following:

Sn > 60 %

Zn < 40 %

or an alloy of tin and nickel the weight composition of which is the following:

Sn > 80 %

Ni < 20 %

is deposited on the sheet metal.

Another subject of the invention is a coated

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996

sheet metal characterized in that it comprises a substrate made of stainless steel containing more than 16 % of chromium in its weight composition, covered on at least one of its faces with a layer of metallic coating of pure tin or of a tin alloy in which the alloying element is chosen especially from zinc and nickel.

In accordance with the characteristics of various embodiments of this sheet metal:

- the layer of metallic coating has a thickness smaller than or equal to 30 μm , preferably equal to 3 μm ;
- between the substrate and the tin-based coating layer the sheet metal comprises a layer of intermetallic compound containing at least iron, chromium and tin;
- the substrate is made of ferritic steel containing, on a mass basis, approximately 17 % of chromium, less than 0.06 % of carbon and less than 0.015 % of sulfur and being capable of containing approximately 1.2 % of molybdenum;
- the substrate is made of austenitic steel containing, on a mass basis, approximately 18 % of chromium, more than 6 % of nickel, less than 0.07 % of carbon and less than 0.015 % of sulfur and being capable of containing approximately 2.2 % of molybdenum;
- the substrate is made of ferritic steel, containing, on a mass basis, from 17 to 25 % of chromium and from 0.2 to 2 % of nickel.

The description which follows and the attached figures - the whole being given by way of nonlimiting examples - will make the invention properly understood:

- Figure 1 is a diagrammatic sectional view of a sheet metal according to the invention;
- Figure 2 is a diagrammatic sectional view of the sheet metal of Figure 1, the metallic coating layer containing chiefly tin having been dissolved in contact with air and inclement weather;
- Figure 3 is a diagram showing the change, as a function of time, in the dissolution potential of the coating of a sheet metal manufactured according to the invention;

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996

- Figure 4 is a diagram showing, on the one hand, the polarization curve of a sheet metal coated with a layer of tin and, on the other hand, the polarization curve of a sheet metal coated with the intermetallic compound containing iron, tin and chromium.

A coated sheet metal according to the invention, indicated by the general reference 10 can be seen in Figure 1. This sheet metal 10 comprises a substrate consisting of a sheet 12 made of stainless steel containing more than 16 % of chromium in its weight composition. On one of its faces this sheet 12 comprises a layer 14 of intermetallic compound containing at least iron, tin and chromium (Fe-Sn-Cr) and a layer 16 of metallic coating, containing chiefly tin, covering the layer 14 of intermetallic compound.

The steels employed for the manufacture of the sheet 12 are of two types. A first type corresponds to ferritic grades which contain 17 % of chromium (Cr) with or without molybdenum (Mo) referred to according to the US Standard as AISI 430, AISI 434, AISI 439 and AISI 444, and the French Standard as Z3CTNb18. A second type corresponds to austenitic grades which contain 18 % of chromium and at least 6 % of nickel (Ni) with or without molybdenum, referred to according to the US Standard as AISI 304 and AISI 316.

The corrosion resistance of stainless steels is proportionately higher the higher the contents of alloy elements Cr, Ni and Mo.

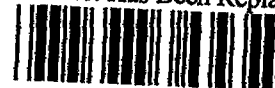
The steel grades employed in the examples described are detailed in the table below.

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996



Grade	Cr %	Ni %	Mo %	Ti max %	Nb max %	C max %	S max %
AISI 430	17					0.06	0.015
AISI 434	17		1.2			0.06	0.01
AISI 439	17			0.5		0.02	0.005
AISI 444	18.5		2.1	0.6	0.5	0.025	0.015
Z3CTNb18	17.8			0.5	0.9	0.03	0.005
AISI 304	18	6.2				0.07	0.015
AISI 316	18	11	2.2			0.07	0.015

Other stainless steels can be employed, provided that they contain at least 16 mass% of chromium. It is possible, for example, to employ a ferritic steel sheet 12 containing, on a mass basis, from 17 to 25 % of chromium and from 0.2 to 2 % of nickel.

When the sheet metal 10 is placed in the open air and is subjected to inclement weather, the layer 16 can be dissolved after a prolonged period of use over a number of years. In this case a sheet metal 10 as shown in Figure 2 is obtained, the coated face of which now comprises only the layer 14 of intermetallic compound.

The coated sheet metal 10 is manufactured by a process which will be described below.

The stages of surface treatment of a stainless sheet metal 12 manufactured with a steel from the grades defined in the table above will be described first of all, and then the deposition of a layer of pure tin on this stainless sheet metal.

In a first step the surface of the stainless steel sheet is degreased.

The degreasing operation is recommended to guarantee a good adherence of the tin coating. In fact, if the surface of the stainless steel is not degreased, the fatty substances and other surface contaminants which are not removed are liable to reduce the adherence of the tin deposit and to give rise to a nonhomogeneous deposit comprising areas without coating.

The degreasing of the sheet metal can be performed either chemically or electrolytically.

This is the replacement sheet

Date: 20 DEC 1996

The sheet metal can be degreased chemically by being placed in contact with a solution containing halogenated organic solvents such as methylene chloride, 1,1,1-trichloroethane, perchloroethylene or trichloroethylene. The sheet metal can also be degreased chemically by employing a solution based on alkaline mixtures containing especially sodium hydroxide, sodium carbonate, sodium metasilicate, phosphates, complexing agents and surface-active agents.

The degreasing operation is preferably performed electrolytically in an electrolysis bath or electrolyte consisting of an aqueous solution containing alkaline mixtures similar to those just specified or else calcium carbonate or potassium hydroxide. In the examples described the electrolyte contains 2 mass% of sodium hydroxide and is at a temperature of 90°C. The stainless sheet metal is immersed in the electrolyte for 20 seconds at an intensity of 10 A/dm². According to a known process the polarities are reversed during electrolytic degreasing, following the cycle cathodic polarity/anodic polarity/cathodic polarity.

The operation of degreasing by an electrolytic route can be performed under other conditions. The electrolyte may contain an alkaline compound in a proportion of 0.5 to 20 mass%. The temperature of the electrolyte may be between 20 and 95°C. The sheet metal may be subjected to a current density of between 0.1 and 20 A/dm² for a period longer than 0.1 s.

The degreasing of the stainless steel sheet 12 is followed by a rinsing with water (neutral medium) in order not to contaminate the treatment baths which will be employed subsequently.

The stage of degreasing of the sheet metal 12 is preferably followed by a stage of pickling of the surface of the sheet metal.

The pickling of the stainless sheet metal is carried out chemically or electrolytically.

The sheet metal can be pickled chemically by being immersed in a bath containing an inorganic acid

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996



- 10 -

chosen from sulfuric and hydrochloric acids or other inorganic acids, the proportion of the acid on a mass basis being within a range from 0.2 to 50 %. The stainless sheet metal is kept for at least 0.1 s in the bath, which is at a temperature of more than or equal to 20°C. The bath preferably contains 0.2 to 40 mass% of hydrochloric acid and is at temperature of between 20 and 50°C.

The concentration of the acid in the pickling bath is defined so as to impose a bath pH which is lower than the pH for depassivation of the stainless steel to be treated at the temperature of the bath.

The pickling operation is preferably performed electrolytically in an electrolysis bath or electrolyte consisting of an aqueous solution containing an inorganic acid chosen from sulfuric and hydrochloric acids or other inorganic acids, in a proportion of 0.2 to 50 mass%. The acid is at a concentration such that the pH of the solution is lower than 1 at the temperature of the bath.

The sheet metal is preferably immersed in an electrolyte containing from 1 to 50 mass% of sulfuric acid which is at a temperature of between 20 and 95°C, the sheet metal being subjected to a current density of between 0.1 and 50 A/dm², the period of immersion of the sheet metal in the electrolyte being longer than 0.1 s.

The polarities may be alternately cathodic and anodic, the treatment being completed with cathodic polarization, or solely cathodic.

In the examples described the electrolyte contains 3 mass% of sulfuric acid and is at a temperature of 40°C with a current density of 10 A/dm², with polarities which are successively cathodic, anodic and cathodic.

The pickling of the stainless steel sheet 12 is followed by a rinsing with water (neutral medium) in order not to contaminate the treatment baths which will be employed subsequently.

Sheets made of stainless steel containing more than 16 % of chromium are of industrial surface quality - arising from their process of manufacture including

This is the replacement sheet

Date: 20 DEC 1996

pickling, cold rolling and annealing stages - which does not require any finishing such as, for example, mechanical or chemical polishing.

Before the deposition of the layer of tin or tin alloy on the stainless steel sheet 12 the sheet is activated.

In fact, stainless steels have a protective layer rich in chromium oxides and hydroxides, called a passive layer, on their surface. The aim of the activation is to remove this passive layer in order to obtain good adherence of the coating, for example of tin, without requiring any premetalizing of the surface of the sheet metal, such as nickel plating.

The activation is performed under conditions which are adapted to the grade of the stainless steel to be treated, it being known that the formation of the passive layer in air is proportionally faster the more resistant the stainless steel is to corrosion. This is especially the case with steels containing more than 16 % of chromium in their weight composition, which require the use of nonpassivating acids to be activated. Consequently, an acid of nitric type cannot be suitable.

The activation of the stainless sheet metal is carried out chemically or electrolytically.

The sheet metal can be activated chemically by immersion in a bath containing one or a number of reducing acids such as hydrochloric acid, phosphoric acid, sulfuric acid, hydrofluoric, boric or fluoroboric acid, as well as phenolsulfonic and cresolsulfonic acids or other organic acids.

The stainless sheet metal is kept for at least 0.1 s in the bath, which is at a temperature of more than or equal to 15°C.

The concentration of the acid in the activating bath is defined so as to impose a bath pH which is lower than the pH for depassivation of the stainless steel to be treated at the temperature of the bath. The pH for depassivation is defined as being the limiting pH of the bath, below which the passive layer covering the stain-

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996

less steel is no longer stable, this steel becoming vulnerable to corrosion.

In a first example an activation by a chemical route is carried out on a stainless steel sheet of AISI 430 type, before the deposition of a layer of tin, by immersing the sheet in a bath containing especially 9 mass% of hydrochloric acid. This bath is taken to a temperature of 20°C and the sheet is kept in the bath for approximately 10 s.

The activation of the sheet metal by a chemical route can be performed under other conditions. The sheet metal may be immersed in a bath containing 0.2 to 40 mass% of hydrochloric acid. The temperature of the bath may be between 15 and 95°C.

An activation may also be performed by an electrolytic route by employing an electrolysis bath or electrolyte similar to the bath employed for the activation by a chemical route, that is to say containing an acid chosen from hydrochloric, phosphoric, sulfuric, hydrofluoric, boric and fluoroboric acids and phenolsulfonic, cresolsulfonic or other organic acids, but with an acid concentration such that the pH of the bath is lower than 1.

Using an electrolytic route, the polarization of the bath is cathodic or else is alternately anodic and cathodic, the polarization being always cathodic at the end of activation. The current density employed is higher than 0.1 A/dm², preferably between 0.1 and 50 A/dm². The stainless sheet metal is kept for a period longer than 0.1 s in the bath, this bath being at a temperature of more than or equal to 15°C.

With alternating anodic/cathodic polarization it is preferable to employ a bath containing an acid whose anion is electrochemically inactive. Thus, sulfuric acid is employed in preference to hydrochloric acid to avoid any release of chlorine in an anodic phase. The treatment is completed with cathodic polarization to prevent any repassivation of the sheet metal capable of being initiated by an anodic polarization.

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996



- 13 -

An activation can also be performed electrolytically by employing an acidic electrolyte chosen from the acids referred to above, in a concentration such that the pH of the bath is lower than 1, to which a quantity of stannous ions may be added in a concentration of between 0.1 and 3 mass%. The temperature of the electrolyte is higher than or equal to 15°C. The sheet metal is subjected to a cathodic polarization with a current density of between 0.1 and 50 A/dm². The period of immersion of the sheet metal in the electrolyte is longer than 0.1 s.

In a second example, the activation of a reel of stainless steel of AISI 430 type is carried out continuously by cathodic polarization at 10 A/dm², for 0.8 s, in an electrolyte containing 17 mass% of phenol-sulfonic acid at a temperature of 20°C. In this example the anodes placed facing the strip are made of ferrosilicon alloy.

The activation of the reel of stainless steel of AISI 430 type can also be carried out under the same operating conditions as above, but with stainless steel anodes, for example of AISI 316 type.

Under the operating conditions described in this first example the reel of stainless steel may be of AISI 439, AISI 434, AISI 304, AISI 444 or AISI 316 type or of Z3CTNb18 type.

In a third example an activation of stainless steel sheets of the AISI 434, AISI 304, AISI 316 and AISI 444 type is carried out electrolytically. In this example the activation of the stainless steel sheet is performed electrolytically by employing a bath containing 20 mass% of sulfuric acid. The sheet metal is kept for 20 s in the bath, the latter being at a temperature of 20°C. The current density is controlled at 10 A/dm². The polarities have been reversed during the electrolytic activation in accordance with the cathodic polarity/anodic polarity/cathodic polarity cycle.

In a fourth example the activation of a reel of AISI 316 type is carried out continuously by an electro-

This is the replacement sheet

Date: 20 DEC 1996

lytic route.

The electrolyte contains 17 mass% of phenolsulfonic acid and 0.5 mass% of stannous ions, at a temperature of 20°C. The cathode current density is controlled at 10 A/dm². The anodes are made of alloy of ferrosilicon type and the immersion period is 0.8 s.

The operating conditions described in this example are also applicable to the stainless grades mentioned above.

When the stages of activation of the surface of the stainless steel sheet are completed, a layer of pure tin or of tin alloy is deposited electrolytically, without intermediate rinsing, to avoid any repassivation of the sheet metal.

Consequently care will be taken that the electrolyte employed for activating the sheet metal should be compatible with the electrolyte employed for depositing the layer of tin or tin alloy on the sheet metal.

A number of embodiments of a deposition of pure tin will be described below.

According to one embodiment of the deposition of pure tin, the electrolyte contains stannous (Sn²⁺) tin in the presence of phenolsulfonic acid or of boric and fluoroboric acid, or stannous chloride in the presence of alkali metal chlorides or fluorides. The current density applied to the sheet metal is higher than 1 A/dm² and the temperature of the electrolyte is more than 15°C.

In the case of the examples described the electrolyte contains a solution of stannous (Sn²⁺) tin in phenolsulfonic acid. The stannous tin content is from approximately 20 to 40 g/l and the phenolsulfonic acid content is between 20 and 40 g/l.

Additives are also added, such as β -naphthol (1 g/l) and gelatin (2 g/l). They make it possible to provide the coating with fineness, compactness and uniformity. The current density is between 10 and 35 A/dm², and the temperature of the bath between 25 and 40°C.

According to another embodiment of the deposition



of pure tin, the deposition bath contains stannous chlorides and alkali metal chlorides and fluorides.

For example, the bath contains stannous chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in a proportion within the range [30-90] g/l, sodium fluoride NaF in a proportion within the range [40-60] g/l and sodium chloride NaCl in a proportion within the range [40-60] g/l. The bath is employed with a current density higher than 1 A/dm² and a temperature of more than 15°C.

According to yet another embodiment of the deposition of pure tin, the deposition bath contains stannous tin and boric and fluoroboric acids.

For example, the bath contains stannous tin in a proportion within the range [40-80] g/l, fluoroboric acid in a proportion within the range [40-200] g/l and boric acid in a proportion within the range [10-30] g/l. The bath is employed with a current density higher than 1 A/dm² and a temperature of more than 15°C.

The tin coating is of relatively low thickness. In the examples described the tin coating deposited has a thickness of 3 µm.

In other embodiments of the invention the thickness of the tin layer may reach 30 µm.

In this state the sheet metal has a matt surface appearance and forms a product which can be employed for the manufacture of roofs of buildings.

The tin-coated stainless sheet metal is next heated by known means, for example an induction oven, to a temperature which is higher than or equal to the melting temperature of tin (232°C).

In the examples described the temperature for heating the tin-coated sheet metal is 250°C.

The purpose of the heat treatment is to form an intermetallic compound containing at least iron, tin and chromium, at the interface of the stainless steel sheet and of the tin layer, while preserving the matt surface appearance of the tin layer.

When the tin coating changes into the molten state, its roughness is minimal. If the heat treatment is



stopped just after the melting of the tin with the aid of rapid cooling, the surface appearance obtained is very shiny. To avoid this shine and to obtain a coating of matt appearance, the heat treatment is prolonged for a sufficient time which depends especially on the thickness of the tin layer. The intermetallic compound grows during the heating period, developing mechanical stresses in the tin layer which perturb the free surface of this layer and result in the return of a matt appearance. The heat treatment period must therefore be sufficiently long to allow the coating not to have a shiny appearance after cooling.

The heat treatment also contributes to reinforcing the adherence of the tin layer to the stainless sheet metal through the intermediacy of the intermetallic compound.

The presence of the intermetallic compound is demonstrated, for example by dissolving the tin layer at constant intensity in a solution of hydrochloric acid at a concentration of 1 mol/l.

Figure 3 shows the curve of change in the dissolution potential of the tin layer as a function of time. The time t_1 corresponds to the baring of the layer of intermetallic Fe-Sn-Cr compound and to the end of the dissolving of the layer of pure tin. The time t_2 corresponds to the end of the dissolving of the layer of intermetallic Fe-Sn-Cr compound and to the baring of the stainless steel. The time $t_2 - t_1$ is proportional to the thickness of the layer of intermetallic compound.

In the examples described the layer of intermetallic compound has a thickness of approximately 0.7 micrometer.

The elements constituting the intermetallic compound are identified, for example, by means of an electronic microprobe. The intermetallic compound may contain other elements in addition to iron, tin and chromium.

The layer of intermetallic compound is bared after several years in use when the sheet metal is



exposed to the open air and subjected to inclement weather. The intermetallic compound which remains at the surface of the stainless steel sheet is of a dark grey color, resembling that of "old tin".

The layer of intermetallic compound has a corrosion resistance which is greatly superior to that of tin.

This high corrosion resistance of the intermetallic compound is illustrated in Figure 4, which shows the plot of the curves of polarization of the intermetallic compound layer and of the tin layer which are placed in an aerated solution of sodium sulfate at a concentration of 0.01 mole/l, at ambient temperature. It is found that the current for dissolution of the intermetallic compound changes little as a function of the potential, this being characteristic of a high corrosion resistance. In contrast, tin, for which the dissolution current increases as a function of the applied potential appears to be less resistant to corrosion than the intermetallic compound.

The sheets comprising a layer of intermetallic compound exhibit good solderability.

A soldering test on a coated sheet metal of the type just described was carried out under the following conditions:

After pickling with phosphoric acid of the areas to be soldered, followed by overlapping over approximately 1 cm, the soldering was carried out using the iron and a Pb/Sn (33 % Sn) rod. The soldering was tested by a bending test at 180°C around a mandrel with a radius of curvature of 10 mm. No tearing away of the solder was found.

To form the layer of intermetallic compound the layer of pure tin may be replaced with a layer of alloy containing chiefly tin.

It is possible to employ an alloy of tin (Sn) and of zinc (Zn) the weight composition of which is the following:

Sn > 60 %

Zn < 40 %.

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996

It is also possible to employ an alloy of tin (Sn) and nickel (Ni) the weight composition of which is the following:

Sn > 80 %

Ni < 20 %.

As in the case of pure tin, the alloy is deposited electrolytically on the stainless steel sheet. The alloy-coated sheet metal is then heated to a temperature higher than or equal to the melting temperature of the alloy, for a sufficient period for the alloy to retain its matt appearance.

The temperature of treatment of the coated sheet metal, after deposition of a layer of pure tin or of alloyed tin, is preferably lower than 500°C in order to avoid the formation of a tin oxide of yellowish color, which is undesirable, at the surface of the coating.

The intermetallic compound which forms at the interface of the stainless steel sheet and of the layer of pure tin or of alloyed tin may contain compounds other than iron, tin and chromium, depending on the type of steel employed and of the type of alloy employed.

The coating of the sheet metal may be arranged at will on only one face of the sheet metal or on both faces of the sheet metal.

The invention incorporates numerous advantages.

The layer containing chiefly tin and deposited electrolytically on a stainless steel sheet exhibits an aesthetic matt appearance which is appreciable when the sheet metal is installed on the roof of a building.

The intermetallic compound containing iron, tin and chromium which appears at the surface of the sheet metal when the tin-based layer has disappeared has a matt appearance resembling that of "old tin" which is appreciated in the roofing of buildings.

The layer of intermetallic compound adheres strongly to the sheet metal and exhibits very good corrosion resistance.

The layer of intermetallic compound is stable under the influence of an acidic atmosphere or of a

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996

maritime climate.

Further, the sheet metal comprising a layer of intermetallic compound containing Fe, Sn and Cr exhibits very good solderability.

This Sheet Has Been Replaced



This is the replacement sheet

Date: 20 DEC 1996



CLAIMS

1. Process for the manufacture of a coated sheet metal employed especially for the manufacture of roofs of buildings, characterized in that a layer (16) of metallic coating of pure tin or of a tin alloy in which the alloying element is chosen especially from zinc and nickel is deposited electrolytically on at least one of the faces of a stainless steel sheet (12) containing more than 16 % of chromium in its weight composition.
2. Process according to claim 1, characterized in that the coated sheet metal is heated to a temperature higher than or equal to the melting temperature of the tin-based coating layer in order, on the one hand, to form a layer (14) of intermetallic compound between the sheet metal (12) and the metallic coating (16) comprising at least tin and an element forming part of the composition of the stainless steel sheet and, on the other hand, to impart a matt appearance to the surface of the coating (16).
3. Process according to claim 2, characterized in that the heating temperature is lower than 500°C.
4. Process according to any one of claims 1 to 3, characterized in that the sheet metal is degreased before the deposition of the coating layer.
5. Process according to claim 4, characterized in that the sheet metal is degreased by a chemical route by employing a bath containing organic solvents or else by employing a bath containing alkaline mixtures.
6. Process according to claim 5, characterized in that the bath contains an organic solvent chosen from methylene chloride, 1,1,1-trichloroethane, perchloroethylene and trichloroethylene.
7. Process according to claim 5, characterized in that the bath contains an alkaline mixture comprising at least one compound chosen from sodium hydroxide, sodium carbonate, sodium metasilicate, phosphates and complexing agents.
8. Process according to claim 4, characterized in that the sheet metal (12) is degreased electrolytically



This is the replacement sheet

Date: 20 DEC 1996



by employing an alkaline electrolyte and by alternating or not alternating the polarities.

9. Process according to claim 8, characterized in that the electrolyte comprises an alkaline compound in a proportion of 0.5 to 20 mass%, the electrolyte being at a temperature of between 20 and 95°C, the sheet metal (12) being subjected to a current density of between 0.1 and 20 A/dm² for a period longer than 0.1 s.

10. Process according to claim 8 or 9, characterized in that the electrolyte comprises an alkaline compound chosen from sodium hydroxide and potassium hydroxide.

11. Process according to claim 10, characterized in that the electrolyte additionally comprises a compound chosen from calcium carbonate, sodium metasilicate, phosphates, complexing agents and surface-active agents.

12. Process according to any one of claims 1 to 11, characterized in that the sheet metal (12) is subjected to a neutral aqueous rinsing after it has been degreased.

13. Process according to any one of claims 4 to 12, characterized in that the sheet metal is pickled after the degreasing or the rinsing following this degreasing.

14. Process according to claim 13, characterized in that the sheet metal is pickled chemically by being immersed in a bath containing an inorganic acid, the mass proportion of the acid being in a range from 0.2 to 50 %.

15. Process according to claim 14, characterized in that the inorganic acid is chosen from sulfuric acid and hydrochloric acid.

16. Process according to claim 15, characterized in that the bath contains 0.2 to 40 mass% of hydrochloric acid and is at a temperature of between 20 and 95°C, the immersion period of the sheet metal (12) in the bath being longer than 0.1 s.

17. Process according to claim 13, characterized in that the sheet metal is pickled electrolytically in an electrolyte bath containing an inorganic acid, the mass proportion of the acid being in a range from 0.2 to 50 %.

18. Process according to claim 17, characterized in that the acid of the electrolyte bath is chosen from





sulfuric acid and hydrochloric acid.

19. Process according to claim 18, characterized in that the electrolyte bath contains 1 to 50 mass% of sulfuric acid and is at a temperature of between 20 and 95°C, the sheet metal (12) being subjected to a current density of between 0.1 and 50 A/dm², the period of immersion of the sheet metal (12) in the bath being longer than 0.1 s.

20. Process according to any one of claims 17 to 19, characterized in that, while being pickled, the sheet metal is subjected either to an alternately cathodic and anodic polarization, the treatment being completed with cathodic polarization, or to a continuous cathodic polarization.

21. Process according to any one of claims 13 to 20, characterized in that the sheet metal is subjected to a rinsing after being pickled.

22. Process according to any one of claims 1 to 21, characterized in that the sheet metal (12) is activated before the deposition of the layer of metallic coating.

23. Process according to claim 22, characterized in that the sheet metal is activated by a chemical route.

24. Process according to claim 23, characterized in that the sheet metal (12) is activated by being immersed in a bath containing an acid chosen from sulfuric, hydrochloric, hydrofluoric, boric, fluoroboric, phenol-sulfonic and cresolsulfonic acids, the bath having a pH lower than the pH for depassivation of the sheet metal (12).

25. Process according to claim 24, characterized in that the bath is at a temperature of more than 15°C and the period of immersion of the sheet metal in the bath is longer than 0.1 s.

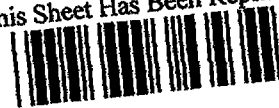
26. Process according to claim 22, characterized in that the sheet metal is activated electrolytically.

27. Process according to claim 26, characterized in that the sheet metal is activated by employing an acidic electrolyte bath containing an acid chosen from hydrochloric, phosphoric, sulfuric, hydrofluoric, boric,



This is the replacement sheet

Date: 20 DEC 1996



fluoroboric, phenolsulfonic and cresolsulfonic acids, the bath having a pH lower than 1.

28. Process according to claim 27, characterized in that the electrolyte bath is at a temperature of more than 15°C and the sheet metal is subjected to a cathodic polarization, with a current density of between 0.1 to 50 A/dm², the period of immersion of the sheet metal in the bath being longer than 0.1 s.

29. Process according to claim 27 or 28, characterized in that the electrolyte bath additionally comprises stannous ions in a concentration of between 0.1 and 3 mass%.

30. Process according to any one of claims 1 to 29, characterized in that a layer of coating comprising pure tin is deposited on the sheet metal.

31. Process according to claim 30, characterized in that the electrolytic deposition bath contains stannous (Sn²⁺) tin and phenolsulfonic acid.

32. Process according to claim 31, characterized in that the electrolytic deposition bath contains stannous tin in a proportion within the range [20-40] g/l and phenolsulfonic acid in a proportion within the range [20-40] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C.

33. Process according to claim 30, characterized in that the electrolytic deposition bath contains stannous chlorides and alkali metal chlorides and fluorides.

34. Process according to claim 33, characterized in that the electrolytic deposition bath contains stannous chloride SnCl₂·2H₂O in a proportion within the range [30-90] g/l, sodium fluoride NaF in a proportion within the range [40-60] g/l and sodium chloride NaCl in a proportion within the range [40-60] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C.

35. Process according to claim 30, characterized in that the electrolytic deposition bath contains stannous tin and boric and fluoroboric acids.

This is the replacement sheet



* C L M S *

Date: 20 DEC 1996



36. Process according to claim 35, characterized in that the electrolytic deposition bath contains stannous tin in a proportion within the range [40-80] g/l, fluoroboric acid in a proportion within the range [40-200] g/l, and boric acid in a proportion within the range [10-30] g/l, the current density being higher than 1 A/dm² and the temperature of the bath being higher than 15°C.

37. Process according to any one of claims 1 to 29, characterized in that a layer of coating comprising an alloy of tin and zinc the weight composition of which is the following:

Sn > 60 %

Zn < 40 %

or an alloy of tin and nickel the weight composition of which is the following:

Sn > 80 %

Ni < 20 %

is deposited on the sheet metal.

38. Coated sheet metal characterized in that it comprises a substrate (12) made of stainless steel containing more than 16 % of chromium in its weight composition, covered on at least one of its faces with a layer (16) of metallic coating of pure tin or of a tin alloy in which the alloying element is chosen especially from zinc and nickel.

39. Coated sheet metal according to claim 38, characterized in that the layer (16) of metallic coating has a thickness smaller than or equal to 30 µm, preferably equal to 3 µm.

40. Coated sheet metal according to claim 38 or 39, characterized in that, between the substrate (12) and the tin-based coating layer (16), the sheet metal comprises a layer (14) of intermetallic compound containing at least iron, chromium and tin.

41. Coated sheet metal according to any one of claims 38 to 40, characterized in that the substrate (12) is made of ferritic steel containing, on a mass basis, approximately 17 % of chromium, less than 0.06 % of



This is the replacement sheet

Date: 20 DEC 1996

carbon and less than 0.015 % of sulfur, and capable of containing approximately 1.2 % of molybdenum.

42. Coated sheet metal according to any one of claims 38 to 40, characterized in that the substrate (12) is made of austenitic steel containing, on a mass basis, approximately 18 % of chromium, more than 6 % of nickel, less than 0.07 % of carbon and less than 0.015 % of sulfur and capable of containing approximately 2.2 % of molybdenum.

43. Coated sheet metal according to any one of claims 38 to 40, characterized in that the substrate (12) is made of ferritic steel, containing, on a mass basis, from 17 to 25 % of chromium and from 0.2 to 2 % of nickel.

This Sheet Has Been Replaced



* C L M S *

This is the replacement sheet

Date: 20 DEC 1996

Coated sheet metal and process for the manufacture
of this sheet metal.

ABSTRACT

This sheet metal comprises a substrate (12) made of stainless steel containing more than 16 % of chromium in its weight composition, coated with a metal layer (16) containing chiefly tin. Between the metal layer (16) and the substrate (12) the sheet metal comprises a layer (14) of an intermetallic compound containing at least iron, chromium and tin. To manufacture this sheet metal, a layer (16) of metallic coating containing chiefly tin is deposited by an electrolytic route on a sheet (12) made of stainless steel. The coated sheet metal is heated to a temperature above the melting temperature of the coating layer (16) to permit the formation of the intermetallic compound. The heating is maintained for a sufficient period for the surface of the coating layer (16) to have a matt appearance.

Fig. 1

This is the replacement sheet

Date: 20 DEC 1996

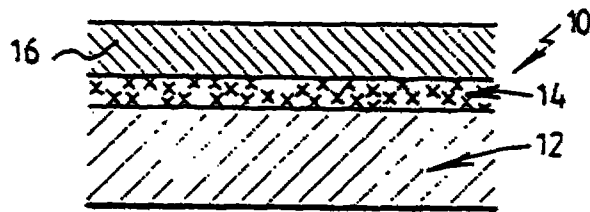


FIG. 1

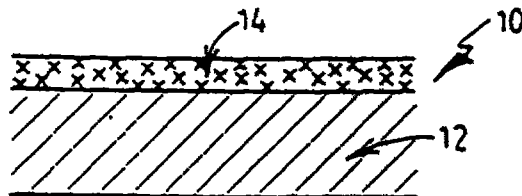
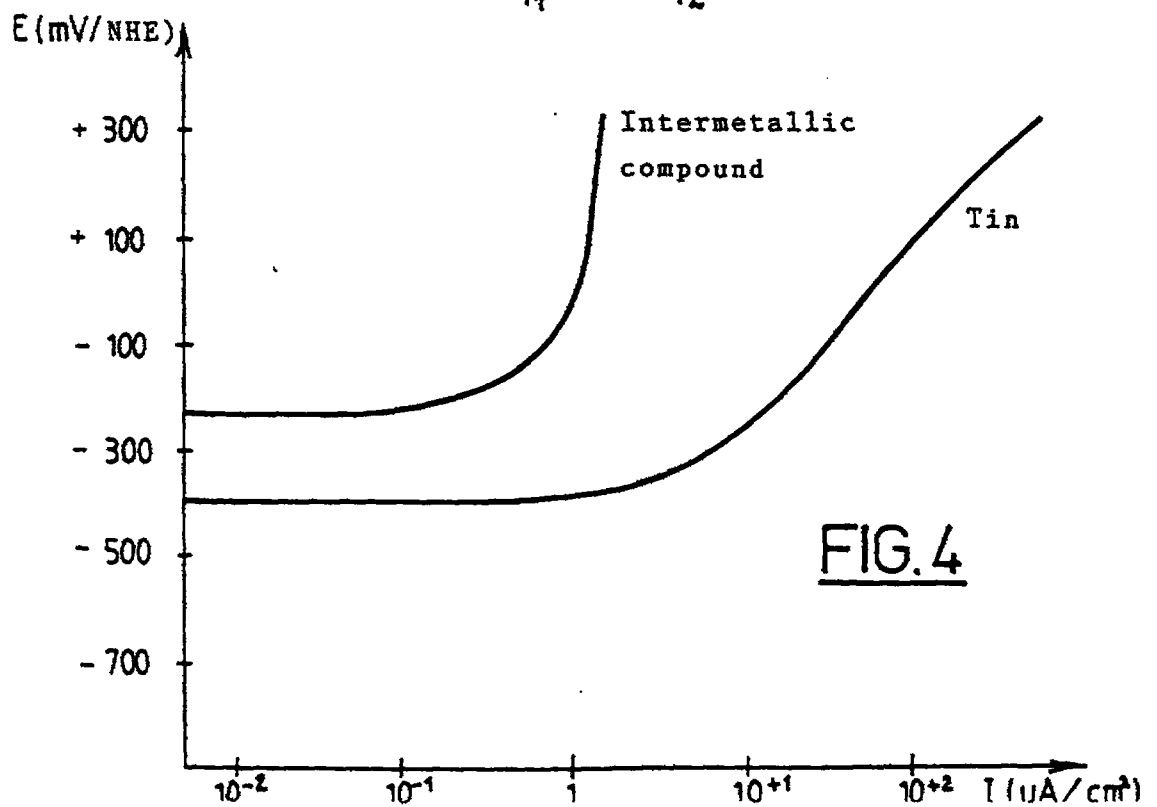
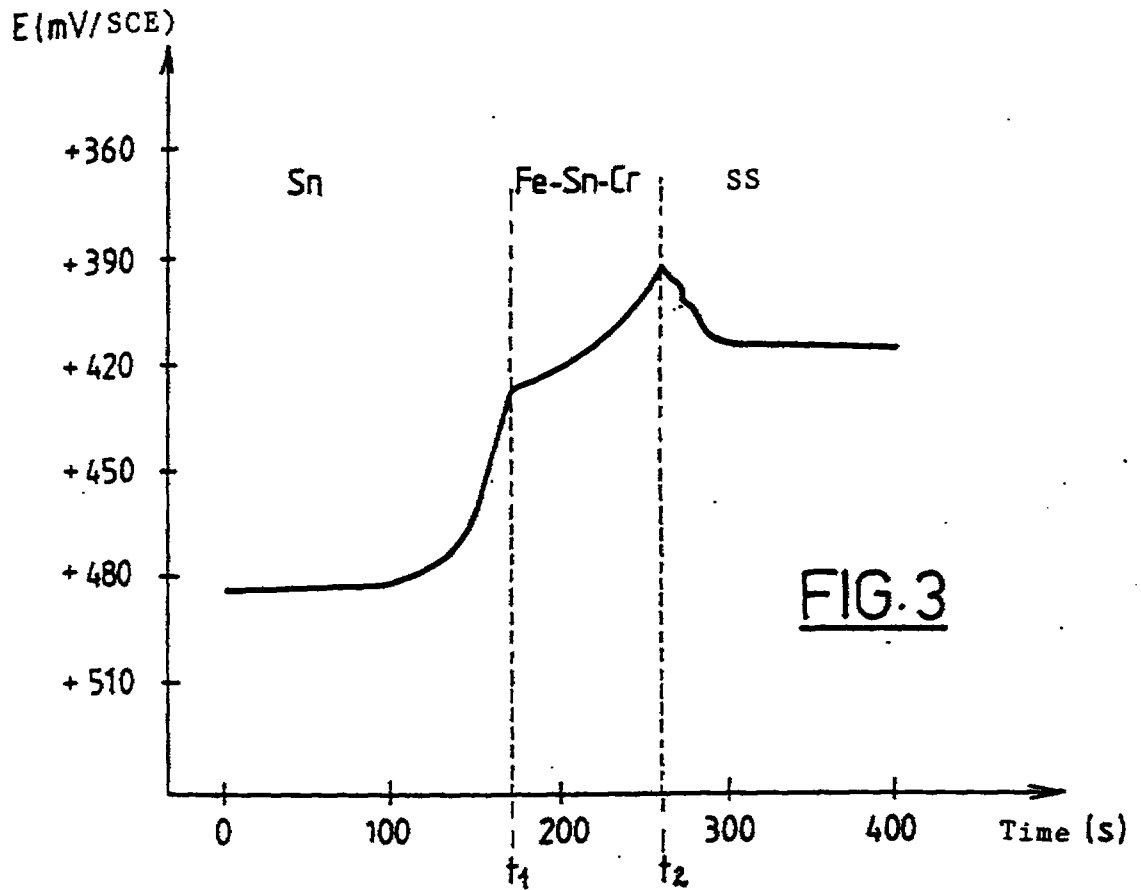


FIG. 2

8 This is the replacement sheet

Date: 2 0 DEC 1996



REPLACEMENT SHEET

1

REPLACEMENT SHEETS		SG
☒	Description : paged to paged	
☒	Claim(s) : paged to paged	
☐	Drawing(s) : paged to paged	
☐	Abstract : paged to paged	
DATE OF RECEIPT ..14/10/98.....		

COATED SHEET METAL AND PROCESS FOR THE MANUFACTURE OF THIS SHEET METAL

The present invention relates to a coated metal sheet and a process for manufacturing said sheet.

It relates, in particular, to manufacturing coverings for buildings.

Sheets of stainless steel, coated with a lead-rich alloy, are already known from the state of the art. The process of coating a stainless steel sheet with lead is usually carried out along the lines of the continuous treatment of coils by immersion in a bath of molten lead-based alloy. The lead-based alloy generally contains tin to facilitate wetting and adhesion of the coating.

These coated metal sheets are used for covering buildings because they have numerous advantages. In particular, they have good resistance to bad weather conditions and a good propensity for soft soldering. One should also mention their lightness (approximately 3 kg/m² for a sheet thickness of 0.4 mm), good mechanical strength and, in the case of ferritic stainless steel sheets, their low co-efficient of linear expansion, resulting in an elongation of 1.06 mm/m for a variation of 100°C, whereas in the case of zinc sheets, an elongation of 2.20 mm/m is obtained for a variation of 100°C.

This is the replacement sheet

Date: 16 OCT 1998

A covering manufactured from sheets of ferritic stainless steel containing 17% by mass chromium, covered with a layer of a lead-based alloy, has excellent resistance to corrosive atmospheric media such as acid rain and debris from fuel fumes.

In certain particularly aggressive atmospheres, for example at the seashore and/or in the vicinity of industries producing corrosive waste, it is preferable to use coated, alloyed stainless steel sheets containing molybdenum in a concentration of 1 to 3% by mass.

In contact with the atmosphere, lead-coated sheets gradually become covered with a protective film, the matt grey appearance of which is reminiscent of "old tin". However, this patina, valued by architects, develops slowly. Its formation, which may take several months, is preceded by a transitory phase, during which exposure to bad weather leads to the manifestation of the unattractive effects of lead corrosion. During this transitory phase, rainwater causes partial solubilisation of the lead, which has the effect of releasing harmful, lead-based compounds into the environment.

EP-A-0 080 971 describes a process for coating a stainless steel object, in particular a casing for an oil well, wherein a layer of a metal coating chiefly comprising tin is electrolytically deposited on a surface of the said object.

US-A-1 776 603, JP-A-59 145 795, JP-A-62 1 896 and JP-A-29 7 695 each describe a metal sheet comprising a stainless steel substrate covered on at least one of its surfaces with a layer of a tin-based metal coating, the coating having been electrolytically deposited.

This is the replacement sheet

Date: 16 OCT 1998

More particularly, JP-A-62 1 896 describes a process for manufacturing a coated metal sheet, of the type wherein a layer of a tin-based metal coating is electrolytically deposited on at least one of the surfaces of a sheet of stainless steel containing more than 16% by weight chromium, the deposition of the tin-based coating being preceded by chemical or electrolytic activation of the metal sheet by immersing it in an acid bath.

The object of the present invention is to provide metal sheets usable as a covering material not having the harmful effects and the unattractive appearance linked with coatings containing lead, these metal sheets having an attractive matt appearance, a good propensity for soldering and being protected against atmospheric corrosion.

To this end, the subject of the invention is a process of the type described in JP-A-62 1 896, characterised in that:

- the metal sheet is chemically or electrolytically pickled by immersing it in a mineral acid bath;
- the metal sheet is rinsed after it has been pickled;
- the metal sheet is chemically or electrolytically activated by immersing it in a bath containing at least phenolsulphonic acid, this bath having a pH lower than the depassivation pH of the metal sheet, and
- a coating layer of pure tin is deposited on the metal sheet in an electroplating bath containing stannous tin and phenolsulphonic acid.

According to features of various embodiments of the invention:

This is the replacement sheet

1 6 OCT 1998

- the coated metal sheet is heated to a temperature greater than or equal to the melting point of the tin-based coating layer, on the one hand so as to form a layer of intermetallic compound between the metal sheet and the metal coating comprising at least tin and an element from the composition of the stainless steel sheet, and on the other hand so as to impart a matt appearance to the surface of the coating;
- the heating temperature is lower than 500°C;
- the metal sheet is degreased prior to pickling;
- the metal sheet is electrolytically degreased by using an alkaline electrolyte and by alternating or not alternating the polarities;
- the electrolyte comprises an alkaline compound in a proportion of 0.5 to 20% by mass, the electrolyte having a temperature between 20 and 95°C, and the metal sheet being subjected to a current density between 0.1 and 20 A/dm² for a period greater than 0.1 s;
- the electrolyte comprises an alkaline compound selected from soda and potash;
- the electrolyte additionally comprises a compound selected from calcium carbonate, sodium metasilicate, phosphates, sequestering agents and surfactants;
- the metal sheet undergoes neutral aqueous rinsing after it has been degreased;
- the metal sheet is chemically pickled and the pickling bath contains 0.2 to 40% by mass hydrochloric acid and has a temperature between 20 and 95°C, the immersion period of the metal sheet in the bath being greater than 0.1 s;
- the metal sheet is electrolytically pickled and the pickling bath contains 1 to 50% by mass sulphuric acid and has a temperature between 20 and 95°C, the metal sheet being subjected to a

This is the replacement sheet

Date: 16 OCT 1998

- current density between 0.1 and 50 A/dm², and the immersion period of the metal sheet in the bath being greater than 0.1 s;
- during pickling, the metal sheet is subjected to alternate cathodic and anodic polarisation, the treatment ending with cathodic polarisation, or to continuous cathodic polarisation;
 - the metal sheet is chemically activated and the activation bath is at a temperature higher than 15°C and the immersion period of the metal sheet in the bath is greater than 0.1 s;
 - the metal sheet is electrolytically activated and the activation bath is at a temperature higher than 15°C and the metal sheet is subjected to cathodic polarisation with a current density between 0.1 and 50 A/dm², the immersion period of the metal sheet in the bath being greater than 0.1 s, and the anodes being made of stainless steel or ferrosilicon alloy;
 - the electroplating bath contains stannous tin in a proportion in the range [20-40] g/l and phenolsulphonic acid in a proportion in the range [20-40] g/l, the current density being greater than 1 A/dm² and the temperature of the bath being higher than 15°C;
 - the electroplating bath contains phenolsulphonic acid, stannous chlorides and alkaline chlorides and fluorides;
 - the electroplating bath contains stannous chloride SnCl₂ · 2H₂O in a proportion in the range [30-90] g/l, sodium fluoride NaF in a proportion in the range [40-60] g/l and sodium chloride NaCl in a proportion in the range [40-60] g/l, the current density being greater than 1 A/dm² and the temperature of the bath being higher than 15°C.

The invention will be understood by way of the following description and the accompanying drawings, all provided as non-limiting examples:

This is the replacement sheet

Date: 16 OCT 1998

- Figure 1 is a schematic sectional view of a metal sheet according to the invention;
- Figure 2 is a schematic sectional view of the metal sheet according to Figure 1, the metal coating layer, chiefly containing tin, having been dissolved on contact with the air and subjected to bad weather conditions;
- Figure 3 is a graph showing the evolution of the dissolution potential, as a function of time, of the coating of a metal sheet manufactured according to the invention;
- Figure 4 is a graph showing the polarisation curve of a metal sheet coated with a layer of tin, and the polarisation curve of a metal sheet coated with the intermetallic compound containing iron, tin and chromium.

Figure 1 shows a coated metal sheet according to the invention, designated by the general reference numeral 10. The metal sheet 10 comprises a substrate formed by a sheet 12 of stainless steel containing more than 16% by weight chromium. One of the surfaces of the sheet 12 is provided with a layer 14 of intermetallic compound containing at least iron, tin and chromium (Fe-Sn-Cr), and a metal coating layer 16 chiefly containing tin covers the layer 14 of intermetallic compound.

The steels used for manufacturing the metal sheet 12 are of two types. A first type corresponds to ferritic grades containing 17% chromium (Cr), with or without molybdenum (Mo), classified according to American standard AISI 430, AISI 434, AISI 439, AISI 444 and French standard Z3CTNb18. A second type corresponds to austenitic grades containing

This is the replacement sheet

Date: 16 OCT 1998

18% chromium and at least 6% nickel (Ni), with or without molybdenum, classified according to American standard AISI 304 and AISI 316.

The corrosion resistance of the stainless steels increases as the proportions of the alloying elements Cr, Ni and Mo increase.

The grades of steel used in the examples described are specified in the table below.

Grade	% Cr	% Ni	% Mo	% TiMax	% NbMax	% CMax	% SMax
AISI 430	17					0.06	0.015
AISI 434	17		1.2			0.06	0.01
AISI 439	17			0.5		0.02	0.005
AISI 444	18.5		2.1	0.6	0.5	0.025	0.015
Z3CTNb18	17.8			0.5	0.9	0.03	0.005
AISI 304	18	6.2				0.07	0.015
AISI 316	18	11	2.2			0.07	0.015

Other stainless steels may be used, provided they contain at least 16% by mass chromium. For example, one can use a ferritic steel sheet 12 comprising 17 to 25% by mass chromium and 0.2 to 2% by mass nickel.

When the metal sheet 10 is placed in the open air and subjected to bad weather conditions, the layer 16 may be dissolved after a prolonged period of use of several years. In this case, a metal sheet 10 as shown in Figure 2 is obtained, the coated surface of which now only comprises the layer 14 of intermetallic compound.

This is the replacement sheet

Date: 16 OCT 1998

The coated metal sheet 10 is manufactured by a process which will be described below.

First of all, the steps for treating the surface of a stainless steel sheet 12, manufactured using a steel selected from the grades specified in the table above, will be described, then the deposition of a layer of pure tin on the stainless steel sheet.

First, the surface of the stainless steel sheet is degreased.

The degreasing operation is advisable in order to ensure good adhesion of the tin coating. Indeed, if the surface of the stainless steel is not degreased, greasy substances and other non-removed surface pollutants are liable to reduce the adhesion of the tin deposit and produce a non-homogeneous deposit comprising uncoated areas.

The metal sheet can be degreased either chemically or electrolytically.

The metal sheet can be degreased chemically by placing it in contact with a solution containing organic halogenated solvents such as methylene chloride, 1,1,1-trichloroethane, perchloroethylene or trichloroethylene. The metal sheet can also be degreased chemically by using a solution based on alkaline mixtures containing, in particular, soda, sodium carbonate, sodium metasilicate, phosphates, sequestering agents and surfactants.

Preferably, the degreasing operation is carried out electrolytically in an electrolytic bath or electrolyte comprising an aqueous solution

This is the replacement sheet

Date: 16 OCT 1998

containing alkaline mixtures similar to those just mentioned, or calcium carbonate or potash. In the examples described, the electrolyte contains 2% by mass soda and has a temperature of 90°C. The stainless steel sheet is immersed in the electrolyte for 20 seconds and subjected to a current intensity of 10 A/dm². According to a known process, the polarities are reversed during the course of electrolytic degreasing according to the cycle: cathodic polarity / anodic polarity / cathodic polarity.

The electrolytic degreasing operation can be carried out under other conditions. The electrolyte can comprise an alkaline compound in a proportion of 0.5 to 20% by mass. The temperature of the electrolyte can be between 20 and 95°C. The metal sheet can be subjected to a current density between 0.1 and 20 A/dm² for a period greater than 0.1 s.

The degreasing of the stainless steel sheet 12 is followed by rinsing in water (neutral medium) so as not to contaminate the treatment baths to be used subsequently.

The step of degreasing the metal sheet 12 is preferably followed by a step of pickling the surface of the metal sheet.

The stainless steel sheet is pickled chemically or electrolytically.

The metal sheet can be pickled chemically by immersing it in a bath containing a mineral acid selected from sulphuric acid and hydrochloric acid or other mineral acids, the proportion of acid by mass being in a range from 0.2 to 50%. The stainless steel sheet is held for at least 0.1 s in

This is the replacement sheet

Date: 16 OCT 1998

the bath, the latter having a temperature greater than or equal to 20°C. Preferably, the bath contains 0.2 to 40% by mass hydrochloric acid and has a temperature between 20 and 50°C.

The concentration of the acid in the pickling bath is selected so that the bath has a pH lower than the depassivation pH of the stainless steel to be treated at the temperature of the bath.

Preferably, the pickling operation is carried out electrolytically in an electrolytic bath or electrolyte comprising an aqueous solution containing a mineral acid selected from sulphuric acid and hydrochloric acid or other mineral acids in a proportion of 0.2 to 50% by mass. The concentration of the acid is such that the pH of the solution is lower than 1 at the temperature of the bath.

Preferably, the metal sheet is immersed in an electrolyte containing 1 to 50% by mass sulphuric acid and having a temperature between 20 and 95°C, the metal sheet being subjected to a current density between 0.1 and 50 A/dm², and the immersion period of the metal sheet in the electrolyte being greater than 0.1 s.

The polarities can be cathodic and anodic alternately, the treatment ending with cathodic polarisation, or cathodic only.

In the examples described, the electrolyte contains 3% by mass sulphuric acid and has a temperature of 40°C and a current density of 10 A/dm², with successive cathodic, anodic and cathodic polarities.

This is the replacement sheet

Date: 16 OCT 1998

The pickling of the stainless steel sheet 12 is followed by rinsing in water (neutral medium) so as not to contaminate the treatment baths to be used subsequently.

Stainless steel sheets containing more than 16% chromium have an industrial surface quality - generated by their manufacturing process comprising pickling, cold-rolling and annealing steps - which does not require a finishing operation such as mechanical or chemical polishing.

The stainless steel sheet 12 is activated prior to the layer of tin or tin alloy being deposited on the metal sheet.

Stainless steels have on their surface a protective layer rich in oxides and chromium hydroxides, known as a passive layer. The purpose of activation is to remove this passive layer in order to achieve good adhesion of the coating, for example tin, without premetallisation of the surface of the metal sheet, for example nickel-plating, being necessary.

Activation is carried out under conditions adapted to the grade of stainless steel to be treated, bearing in mind that the more corrosion-resistant the stainless steel is, the faster the formation of the passive layer in the air. This is particularly the case with steels containing more than 16% by weight chromium, which require the use of non-passivating acids in order to be activated. Consequently, a nitric acid is not suitable.

The stainless steel sheet is activated chemically or electrolytically.

The metal sheet can be activated chemically by immersion in a bath containing one or more reducing acids, such as hydrochloric acid,

This is the replacement sheet

Date: 16 OCT 1998

phosphoric acid, sulphuric acid, hydrofluoric acid, boric acid, fluoboric acid, as well as phenolsulphonic and cresolsulphonic acids or other organic acids.

The stainless steel sheet is held for at least 0.1 s in the bath, which has a temperature greater than or equal to 15°C.

The concentration of the acid in the activation bath is selected so that the bath has a pH lower than the depassivation pH of the stainless steel to be treated at the temperature of the bath. The depassivation pH is defined as being the limit pH of the bath, below which the passive layer covering the stainless steel is no longer stable, the steel becoming vulnerable to corrosion.

In a first example, prior to the deposition of a layer of tin, a sheet of stainless steel of the AISI 430 type is chemically activated by immersing it in a bath containing, in particular, 9% by mass hydrochloric acid. The bath is brought to a temperature of 20°C and the metal sheet is held in the bath for approximately 10 s.

The chemical activation of the metal sheet can be carried out under other conditions. The metal sheet can be immersed in a bath containing 0.2 to 40% by mass hydrochloric acid. The temperature of the bath can be between 15 and 95°C.

Electrolytic activation can also be carried out by using an electrolytic bath or electrolyte similar to the bath used for chemical activation, i.e. containing an acid selected from hydrochloric, phosphoric, sulphuric, hydrofluoric, boric, fluoboric, phenolsulphonic and cresolsulphonic acid

This is the replacement sheet

Date: 15 OCT 1998

or other organic acids, but with an acid concentration such that the pH of the bath is lower than 1.

With electrolytic activation, the polarisation of the bath is cathodic, or anodic and cathodic alternately, the polarisation always being cathodic at the end of the activation process. The current density used is greater than 0.1 A/dm^2 , preferably between 0.1 and 50 A/dm^2 . The stainless steel sheet is held in the bath for a period greater than 0.1 s , the bath having a temperature greater than or equal to 15°C .

With alternate anodic / cathodic polarisation, it is preferable to use a bath containing an acid, the anion of which is electrochemically inactive. Thus sulphuric acid is used in preference to hydrochloric acid in order to avoid the liberation of chlorine in the anodic phase. The treatment ends with cathodic polarisation to prevent any repassivation of the metal sheet, which could be initiated by anodic polarisation.

Electrolytic activation can also be carried out using an acid electrolyte selected from the aforementioned acids and having a concentration such that the pH of the bath is lower than 1, to which a quantity of stannous ions can be added in a concentration between 0.1 and 3% by mass. The temperature of the electrolyte is greater than or equal to 15°C . The metal sheet is subjected to cathodic polarisation with a current density between 0.1 and 50 A/dm^2 . The period of immersion of the metal sheet in the electrolyte is greater than 0.1 s .

In a second example, the activation of a coil of stainless steel of the AISI 430 type is carried out continuously by cathodic polarisation at 10 A/dm^2 for 0.8 s in an electrolyte containing 17% by mass phenolsulphonic acid

This is the replacement sheet

Date: 16 OCT 1998

at a temperature of 20°C. In this example, the anodes arranged opposite the strip are made of ferrosilicon alloy.

The AISI 430 stainless steel coil can also be activated under the same operating conditions as above, but with stainless steel anodes, for example of the AISI 316 type.

Under the operating conditions described in this first example, the stainless steel coil can be of the following types: AISI 439, AISI 434, AISI 304, AISI 444, AISI 316 or Z3CTNb18.

In a third example, sheets of stainless steel of the AISI 434, AISI 304, AISI 316 and AISI 444 types are electrolytically activated. In this example, the activation of the stainless steel sheet is carried out electrolytically using a bath containing 20% by mass sulphuric acid. The metal sheet is held for 20 s in the bath, which has a temperature of 20°C. The current density is set at 10 A/dm². The polarities were reversed during electrolytic activation according to the cycle: cathodic polarity / anodic polarity / cathodic polarity.

In a fourth example, an AISI 316-type coil is electrolytically activated continuously.

The electrolyte contains 17% by mass phenolsulphonic acid and 0.5% by mass stannous ions at a temperature of 20°C. The cathodic current density is set to 10 A/dm². The anodes are made of a ferrosilicon alloy and the immersion time is 0.8 s.

This is the replacement sheet

Date: 16 OCT 1998

The operating conditions described in this example are also applicable to the aforementioned stainless steel grades.

When the stages of activating the surface of the stainless steel sheet are complete, a layer of pure tin or tin alloy is electrolytically deposited, without intermediate rinsing, to prevent repassivation of the metal sheet.

Consequently, it must be ensured that the electrolyte used for activating the metal sheet is compatible with the electrolyte used for the deposition of the layer of tin or tin alloy on the metal sheet.

A plurality of embodiments of the deposition of pure tin will be described below.

According to one embodiment of the deposition of pure tin, the electrolyte contains stannous tin (Sn^{2+}) in the presence of phenolsulphonic acid or boric and fluoboric acid, or stannous chloride in the presence of alkaline chlorides or fluorides. The current density applied to the metal sheet is greater than 1 A/dm^2 and the temperature of the electrolyte is higher than 15°C .

For the examples described, the electrolyte contains a solution of stannous tin (Sn^{2+}) in phenolsulphonic acid. The stannous tin content is approximately 20 to 40 g/l and the phenolsulphonic acid content is between 20 and 40 g/l.

Additives such as β -naphthol (1 g/l) and gelatin (2 g/l) are also added. They ensure that the coating has fineness, compactness and uniformity.

This is the replacement sheet

Date: 16 OCT 1998

The current density is between 10 and 35 A/dm², and the temperature of the bath is between 25 and 40°C.

According to another embodiment of the deposition of pure tin, the plating bath contains stannous chlorides and alkaline chlorides and fluorides.

For example, the bath contains stannous chloride SnCl₂ · 2H₂O in a proportion in the range [30-90] g/l, sodium fluoride NaF in a proportion in the range [40-60] g/l and sodium chloride NaCl in a proportion in the range [40-60] g/l. The bath is used with a current density greater than 1 A/dm² and a temperature higher than 15°C.

According to a further embodiment of the deposition of pure tin, the plating bath contains stannous tin and boric and fluoboric acids.

For example, the bath contains stannous tin in a proportion in the range [40-80] g/l, fluoboric acid in a proportion in the range [40-200] g/l and boric acid in a proportion in the range [10-30] g/l. The bath is used with a current density greater than 1 A/dm² and a temperature higher than 15°C.

The tin coating has a relatively low thickness. In the examples described, the deposited tin layer has a thickness of 3 μm.

In other embodiments of the invention, the thickness of the tin layer can attain 30 μm.

This is the replacement sheet

Date: 16 OCT 1998

In this state, the metal sheet has a matt surface and constitutes a product usable for manufacturing coverings for buildings.

The tin-coated stainless steel sheet is then heated by known means, for example in an induction furnace, up to a temperature greater than or equal to the melting point of the tin (232°C).

In the examples described, the heating temperature of the tin-coated metal sheet is 250°C.

The purpose of the thermal treatment is to form an intermetallic compound comprising at least iron, tin and chromium at the boundary between the stainless steel sheet and the layer of tin, while preserving the matt appearance of the surface of the layer of tin.

When the tin coating passes into the molten state, its roughness is minimal. If the thermal treatment is terminated just after the fusion of the tin by means of rapid cooling, the surface appearance obtained is very bright. To avoid this brightness and obtain a matt coating, the thermal treatment is extended for a suitable period, which depends in particular on the thickness of the layer of tin. The intermetallic compound increases throughout the heating process, generating within the layer of tin mechanical stresses which disturb the free surface of this layer and cause the recurrence of a matt appearance. Therefore, the duration of the thermal treatment must be sufficiently long to ensure that the coating does not have a bright appearance after cooling.

This is the replacement sheet

Date: 16 OCT 1998

The thermal treatment also contributes towards increasing the adhesion of the tin layer on the stainless steel sheet by means of the intermetallic compound.

The presence of the intermetallic compound is revealed by, for example, potentiostatic dissolution of the layer of tin in a solution of hydrochloric acid in a concentration of 1 mole/l.

Figure 3 shows the curve of evolution of the dissolution potential of the layer of tin as a function of time. The time t_1 corresponds to the exposure of the layer of intermetallic compound Fe-Sn-Cr and to the end of the dissolution of the layer of pure tin. The time t_2 corresponds to the end of the dissolution of the layer of intermetallic compound Fe-Sn-Cr and to the exposure of the stainless steel. The time $t_2 - t_1$ is proportional to the thickness of the layer of intermetallic compound.

In the examples described, the layer of intermetallic compound has a thickness of approximately 0.7 micrometer.

The elements forming the intermetallic compound are identified by means of an electronic microprobe, for example. The intermetallic compound can contain other elements in addition to iron, tin and chromium.

The layer of intermetallic compound is exposed after a few years of use when the metal sheet is open to the air and subjected to bad weather conditions. The intermetallic compound subsisting on the surface of the stainless steel sheet has a dark grey colour reminiscent of the colour of "old tin".

This is the replacement sheet

Date: 16 OCT 1998

The layer of intermetallic compound is substantially more corrosion-resistant than the tin.

This high corrosion resistance of the intermetallic compound is illustrated in Figure 4, which shows the path of the polarisation curves of the layer of intermetallic compound and the layer of tin placed in a solution of sodium sulphate in a concentration of 0.01 mole/l, aerated and at ambient temperature. It can be seen that the dissolution current of the intermetallic compound scarcely evolves as a function of the potential, which is characteristic of high corrosion resistance. In contrast, the tin, the dissolution current of which increases as a function of the potential applied, is shown to be less resistant to corrosion than the intermetallic compound.

The metal sheets comprising a layer of intermetallic compound have a good propensity for soldering.

A soldering test on a coated metal sheet of the type just described was carried out under the following conditions.

After pickling in phosphoric acid the areas to be soldered, then coating them over approximately 1 cm, soldering was carried out using an iron and a Pb/Sn rod (33% Sn). The soldered joint was tested in a bending test at 180°C round a pin with a 10 mm radius of curvature. No tearing of the soldered joint was detected.

To form the layer of intermetallic compound, the layer of pure tin can be replaced by a layer of alloy chiefly containing tin.

This is the replacement sheet

Date: 16 OCT 1998

An alloy of tin (Sn) and zinc (Zn) can be used, with the following composition by weight:

Sn > 60%

Zn < 40%

An alloy of tin (Sn) and nickel (Ni) can also be used, with the following composition by weight:

Sn > 80%

Ni < 20%

As in the case of pure tin, the alloy is electrolytically deposited on the stainless steel sheet. The alloy-coated metal sheet is then heated to a temperature greater than or equal to the melting point of the alloy for a duration sufficient for the alloy to preserve its matt appearance.

After the deposition of a layer of pure tin or alloyed tin, the treatment temperature of the coated metal sheet is preferably lower than 500°C in order to prevent the undesirable formation of a yellowish tin oxide on the surface of the coating.

The intermetallic compound which forms at the boundary between the stainless steel sheet and the layer of pure tin or alloyed tin can contain compounds other than iron, tin and chromium as a function of the type of steel used and the type of alloy used.

This is the replacement sheet

Date: 16 OCT 1998

The coating of the metal sheet can be provided either on a single surface of the metal sheet or on both surfaces of the metal sheet.

The invention has numerous advantages.

The layer chiefly containing tin, electrolytically deposited on a stainless steel sheet, has an aesthetic matt appearance, which is desirable when the metal sheet forms a covering for a building.

The intermetallic compound containing iron, tin and chromium, which appears on the surface of the metal sheet when the tin-based layer disappears, has a matt appearance reminiscent of that of "old tin", desirable for the covering of buildings.

The layer of intermetallic compound adheres strongly to the metal sheet and has very good resistance to corrosion.

The layer of intermetallic compound is stable under the influence of an acid atmosphere or a sea climate.

Furthermore, the metal sheet comprising a layer of intermetallic compound containing Fe, Sn and Cr has a very good propensity for soldering.

This is the replacement sheet

Date: 16 OCT 1998

Claims

1. A process for manufacturing a coated metal sheet used, in particular, for manufacturing coverings for buildings, of the type wherein a layer (16) of a tin-based metal coating is electrolytically deposited on at least one of the surfaces of a sheet (12) of stainless steel containing more than 16% by weight chromium, the deposition of the tin-based coating being preceded by chemical or electrolytic activation of the metal sheet by immersing it in an acid bath, characterised in that:
 - the metal sheet is chemically or electrolytically pickled by immersing it in a mineral acid bath;
 - the metal sheet is rinsed after it has been pickled;
 - the metal sheet (12) is chemically or electrolytically activated by immersing it in a bath containing at least phenolsulphonic acid, this bath having a pH lower than the depassivation pH of the metal sheet (12), and
 - a coating layer of pure tin is deposited on the metal sheet in an electroplating bath containing stannous tin (Sn^{2+}) and phenolsulphonic acid.
2. A process according to claim 1, characterised in that the coated metal sheet is heated to a temperature greater than or equal to the melting point of the tin-based coating layer, on the one hand so as to form a layer (14) of intermetallic compound between the metal sheet (12) and the metal coating (16) comprising at least tin and an element from the composition of the stainless steel sheet, and on the other hand so as to impart a matt appearance to the surface of the coating (16).



This is the replacement sheet

Date: 16 OCT 1998

3. A process according to claim 2, characterised in that the heating temperature is lower than 500°C.
4. A process according to any one of claims 1 to 3, characterised in that the metal sheet is degreased prior to pickling.
5. A process according to claim 4, characterised in that the metal sheet (12) is electrolytically degreased by using an alkaline electrolyte and by alternating or not alternating the polarities.
6. A process according to claim 5, characterised in that the electrolyte comprises an alkaline compound in a proportion of 0.5 to 20% by mass, the electrolyte having a temperature between 20 and 95°C, and the metal sheet (12) being subjected to a current density between 0.1 and 20 A/dm² for a period greater than 0.1 s.
7. A process according to claim 5 or 6, characterised in that the electrolyte comprises an alkaline compound selected from soda and potash.
8. A process according to claim 7, characterised in that the electrolyte additionally comprises a compound selected from calcium carbonate, sodium metasilicate, phosphates, sequestering agents and surfactants.
9. A process according to any one of claims 4 to 8, characterised in that the metal sheet (12) undergoes neutral aqueous rinsing after it has been degreased.



This is the replacement sheet

Date: 16 OCT 1998

10. A process according to any one of claims 1 to 9, characterised in that the metal sheet is chemically pickled and in that the pickling bath contains 0.2 to 40% by mass hydrochloric acid and has a temperature between 20 and 95°C, the immersion period of the metal sheet (12) in the bath being greater than 0.1 s.
11. A process according to any one of claims 1 to 9, characterised in that the metal sheet is electrolytically pickled and in that the pickling bath contains 1 to 50% by mass sulphuric acid and has a temperature between 20 and 95°C, the metal sheet (12) being subjected to a current density between 0.1 and 50 A/dm², and the immersion period of the metal sheet (12) in the bath being greater than 0.1 s.
12. A process according to claim 11, characterised in that, during pickling, the metal sheet is subjected to alternate cathodic and anodic polarisation, the treatment ending with cathodic polarisation, or to continuous cathodic polarisation.
13. A process according to any one of claims 1 to 12, characterised in that the metal sheet is chemically activated and in that the activation bath is at a temperature higher than 15°C and the immersion period of the metal sheet in the bath is greater than 0.1 s.
14. A process according to any one of claims 1 to 12, characterised in that the metal sheet is electrolytically activated and in that the activation bath is at a temperature higher than 15°C and the



This is the replacement sheet

Date: 16 OCT 1998

metal sheet is subjected to cathodic polarisation with a current density between 0.1 and 50 A/dm², the immersion period of the metal sheet in the bath being greater than 0.1 s, and the anodes being made of stainless steel or ferrosilicon alloy.

15. A process according to any one of claims 1 to 14, characterised in that the electroplating bath contains stannous tin in a proportion in the range [20-40] g/l and phenolsulphonic acid in a proportion in the range [20-40] g/l, the current density being greater than 1 A/dm² and the temperature of the bath being higher than 15°C.
16. A process according to any one of claims 1 to 15, characterised in that the electroplating bath contains phenolsulphonic acid, stannous chlorides and alkaline chlorides and fluorides.
17. A process according to claim 16, characterised in that the electroplating bath contains stannous chloride SnCl₂ · 2H₂O in a proportion in the range [30-90] g/l, sodium fluoride NaF in a proportion in the range [40-60] g/l and sodium chloride NaCl in a proportion in the range [40-60] g/l, the current density being greater than 1 A/dm² and the temperature of the bath being higher than 15°C.



This is the replacement sheet

Date: 16 OCT 1998

Coated sheet metal and process for the manufacture of this sheet metal.

ABSTRACT

This sheet metal comprises a substrate (12) made of stainless steel containing more than 16 % of chromium in its weight composition, coated with a metal layer (16) containing chiefly tin. Between the metal layer (16) and the substrate (12) the sheet metal comprises a layer (14) of an intermetallic compound containing at least iron, chromium and tin. To manufacture this sheet metal, a layer (16) of metallic coating containing chiefly tin is deposited by an electrolytic route on a sheet (12) made of stainless steel. The coated sheet metal is heated to a temperature above the melting temperature of the coating layer (16) to permit the formation of the intermetallic compound. The heating is maintained for a sufficient period for the surface of the coating layer (16) to have a matt appearance.

Fig. 1

REPLACED SHEETS	SG
☒ Description : paged to paged	
☒ Claim(s) : paged to paged	
☒ Drawing(s) : paged to paged	
☒ Abstract : paged to paged	
DATE OF RECEIPT	

This Sheet Has Been Replaced

