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(54) Aluminum-coated steel sheets for enameling.

(57) An aluminum-coated steel sheet for enameling comprising a base steel sheet characterized in that the coated aluminum layer has a rolled-and-recrystallized structure. The aluminum-coated steel sheet enables the formation of an excellent enamel coating free from blister defect and having good adhesion to the substrate.

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Title of the Invention

Aluminum-coated steel sheets for enameling

Technical Field of the Invention

This invention relates to aluminum-coated steel sheets for enameling on which excellent enamel coatings can be obtained.

Background of the Invention

Steel sheets the surface of which is coated with aluminum, hot-dip aluminum-coated steel sheets for instance, have excellent heat resistance, corrosion resistance, etc., and are widely used for automobile exhaust gas treatment apparatuses, parts of driers and stoves which are exposed to high temperature, roofing, interior finish, etc.

Recently, production of aluminum-coated steel sheets the surface of which is enameled or porcelainized has been developed on an industrial scale. Enamel-coating is effected by applying an enamel glaze on the surface of the substrate and firing it at a suitable temperature.

When a substrate of an aluminum-coated steel sheet is, whether as is or after being formed into the shape of the finished product by bending or press work, enameled, there is a problem that a lot of minute blisters and craters occurs (referred to as "blister defect" hereinafter) on the surface of the formed enamel layer, which deteriorate corrosion resistance and appearance of the products.

We have endeavored to solve this problem and found that the blister defect is caused by microscopic pinholes, non-plated portions and minute cracks generated when the plated sheets are worked for shaping, etc., which exist in the plated aluminum layer. That is, a plated aluminum layer as plated is of the cast structure so to speak, and therefore it is inevitably accompanied by incidental minute pinholes and non-plated portions, and is poor in ductility and elongation, easily developing cracking when worked. These defects are rather slight and harmless for the heat resistance and corrosion resistance uses. However, when the sheet is enameled, these defects become initiation points of the above mentioned blister defect. Therefore, if these defects in the plated aluminum layer are eliminated, the blister defect is also eliminated.

This invention is based on this finding, and provides aluminum-coated steel sheets for enameling, the aluminum layer of which is of the rolled-and-recrystallized structure.

Disclosure of the Invention

According to the invention of this application, an aluminum-coated steel sheet for enameling comprising a base steel sheet characterized in that the aluminum coating layer has a rolled-and-recrystallized structure.

That is to say, the substrate sheet for enameling in accordance with this invention has a coated aluminum layer which has been rolled and annealed for recrystallization, and thus is free from pinholes and is provided with good ductility. Therefore, generation of cracks in the coated aluminum layer when the sheet is worked for shaping is prevented, and thus development of the blister defect in the stage of enameling is substantially prevented.

The aluminum-coated steel sheet for enameling according to the invention of this application is produced for instance by aluminum-plating a base steel sheet by the conventional process, rolling the sheet and annealing the rolled sheet for recrystallization.

As the base sheet, ordinary low carbon steel (usually about 0.2 % by weight of C or less) sheet is preferably used from the viewpoint of formability. The lower the C content is, the higher the temperature of formation of the Al-Fe intermetallic compound (simply referred to as "alloy" hereinafter) at the interface between the base steel sheet and the plated aluminum layer is. This fact is advantageous in that alloying of the coated aluminum layer in the course of the recrystallization annealing and the later firing is retarded and thus adhesion of the resulting enamel layer is improved. In this respect, the preferred C content is not more than about 0.02 %. Nitrogen (N) has an effect to raise the alloy formation temperature, too, and therefore it is preferred that base steel sheets contain about 0.001 - 0.02 % by weight N.

The aluminum coating layer can be formed by hot-dip plating, vacuum evaporation, powder coating, cladding, etc. When hot-dip aluminum plating of base steel sheets is carried out, the Al-Fe alloy is usually formed at the interface between the base steel sheet and the plated layer. If the alloy, which is hard and brittle, is produced in a large amount, it will cause cracking when the plated sheet is rolled. In order to prevent this, it is effective to use an Al-Si plating bath containing not less than about 1.0 % by weight of silicon (Si) instead of a neat Al bath. By the use of this bath, the thickness of the alloy layer formed during plating can be restrained to about 2 - 5 μm or less, and thus occurrence of cracking during rolling can be avoided. However, if the bath contains too much Si, hard and brittle plate-like crystals of Si appear spread throughout the plated layer and cause cracking during rolling. The Si content should preferably be not more than 15 % by weight.

After a required thickness of aluminum layer has been formed, the plated sheet is subjected to rolling. Either of cold rolling or warm rolling (at about 100 - 450°C, for instance) will do. About 10 % reduction is required in order to fill up pinholes and unplated portions of the cast structure of the plated layer, although the degree of reduction can be suitably selected in consideration of the thickness of the starting sheet and that of the finished sheet. Especially, if a sheet is rolled down by more than 20 %, not only the coated aluminum layer but also the base steel sheet is modified to rolled structure, and their recrystallization temperature is lowered. Thus recrystallization of base steel sheets is achieved at a lower temperature. This fact is also advantageous in that alloying of the coated aluminum layer in the course of annealing is inhibited. When the aluminum coating layer is formed by hot-dip plating, if rolling is carried out by more than 20 %, an alloy layer formed in the interface between the base steel sheet and the plated aluminum layer during plating is divided minutely. This fact contributes to prevention of separation of and/or cracking in the plated layer, which would be caused during the later shaping work. However, too high reduction again causes cracking in the plated aluminum layer, which induces the blister defect in the finished enamel. So the reduction is preferably limited to 70 %.

The rolled aluminum-plated steel sheet is now subjected to recrystallization annealing, since the plated aluminum layer is of a work-hardened rolled structure and is poor in ductility. Annealing is preferably carried out at about 250 - 480°C. The annealing will be required for about 10 min. to 3 hours, for instance. So, by this annealing the plated aluminum layer is provided with good ductility and the filled-in pinholes etc. are completely eliminated by recrystallization.

The structure of the plated aluminum layer of the thus obtained aluminum-plated steel sheet is similar to the forged structure rather than the initial cast structure. The plated layer is entirely free from pinholes, and has good mechanical properties, especially ductility. So this material can be used as the substrate for enameling as is or after shaping as desired, and gives excellent enameled products free from the blister defect.

In the substrate sheet of this invention which is manufactured by the process explained above, the temperature of alloy formation at the interface between the base steel sheet and the aluminum coating layer is high, and therefore, and the alloy is not easily formed when the substrate is subjected to high temperatures. This rise in alloy formation temperature is markedly exhibited when the recrystallization annealing is carried out at a rather high temperature within the above-mentioned range (about 250 - 480°C), preferably in the range of about 300 - 480°C. The fact that the alloy formation temperature is high is very significant in that a higher firing temperature can be employed in the step of enamel layer formation. Aluminum-coated steel sheets develop an alloy between the base steel sheet and the coated aluminum layer because of mutual diffusion of Fe and Al when they are subjected to a high temperature of about 500°C or higher. In an extremely case, the aluminum layer is alloyed up to the surface and becomes grayish black. If such alloy formation occurs during the enamel forming firing, the resulting enamel coating layer is poor in adhesion to the substrate and easily scales off. Therefore, high firing temperatures cannot be employed, and selection of usable glazes is strictly restricted. In contrast, the substrate sheets for enameling in accordance with this invention have high alloy formation temperatures, especially those which have been annealed at a temperature of about 300°C or higher, do not undergo practically no alloying even if they are subjected to a high firing temperature in excess of 500°C, about 550°C or higher. Thus glazes can be selected from a wide range of materials and enameling can be effected at higher temperatures without sacrificing the adhesion to the substrate. As the result, enamel products with excellent enamel layer characteristics such as chemical resistance, hardness, luster etc. can be obtained. As stated above, the alloy formation temperature is remarkably raised when the C content of the base steel sheet is lower and the Al coating layer contains Si.

When a substrate sheet of this invention is used after being strongly worked in accordance with the shape desired in the finished product, workability of the base steel sheet is often a problem. Because when an aluminum-coated steel sheet is rolled by 20 % or more in order to minutely divide the alloy layer formed at the interface between the substrate steel sheet and the coated aluminum layer during coating operation, or a higher rolling reduction is employed because of the difference in thickness between the base steel sheet and the finished product sheet, not only the coating layer but also the base steel sheet is changed to the rolled structure with work hardening. This work hardening is not eliminated by the annealing for recrystallization of the aluminum coating layer. Of course, no difficulty is encountered when such a substrate sheet is enameled as a flat sheet or after undergoing a light degree of shaping work such as bending or pressing. However, when strong working such as deep drawing is applied to the substrate sheet, the work hardening of the base sheet must be eliminated. In such a case, the annealing after the rolling should be carried out at a temperature higher than the recrystallization temperature of the base steel sheet. The temperature is preferably about 500 - 600°C. It must not exceed about 600°C in order to avoid melting of the coated aluminum layer. By this annealing the aluminum coating layer is simultaneously recrystallized and both the base sheet and the coating layer become rolled-and-recrystallized structure.

In this case, however, care must be taken not to cause alloying of the aluminum coating layer since the annealing is carried out at a higher temperature in comparison with the annealing intended for recrystallization of the aluminum coating layer only (about 250 - 480°C). In this respect, employment of a low carbon content base sheet and a Si-containing aluminum coating layer is effective as mentioned above. But it is very effective to carry out the annealing in two steps. That is, the first step annealing is effected at a rather low temperature, preferably in a range of about 300 - 480°C, and the second step annealing is effected at a higher temperature, preferably in a range of about 500 - 550°C, which is the temperature range in which the base steel sheet is recrystallized. The first step annealing is carried out over a range of about 3 - 10 hours for instance, and the second step annealing is carried out over a range of about 3 - 12 hours. By such a two step annealing, substrate sheets for enameling, which have good workability with the base steel sheet and the aluminum coating layer both recrystallized, are obtained without causing alloying at the interface. And substrate sheets obtained by this two step annealing can be fired for enameling at a temperature higher than about 500°C without suffering from alloying at the interface, since their alloying temperature is high. Therefore, the products are free from the problem of poor adhesion, and have far more excellent enamel coating than the conventional enamel products, and glazes can be selected from a wider range of sources.

In the invention of this application, there is essentially no restriction on the thickness of the base steel sheet and the aluminum coating layer. The reduction in rolling can be suitably selected within the above-mentioned range in accordance with the thickness of the aluminum-coated steel sheet and the thickness of the finished enamel product. In order to obtain a substrate sheet of a desired thickness, rolling and recrystallization annealing can be repeated as many times as required.

Brief Description of the Attached Drawings

Now the invention is specifically described with reference to the attached drawings, wherein:

Fig. 1 shows the shape of the test piece for the bending test of substrate sheets for enameling; and

Fig. 2 shows the shape of the test piece for the deep drawing test of substrate sheets for enameling.

Specific Description of the Invention

An aluminum-plated sheets for enameling was obtained by hot-dip plating a 0.8 mm thick cold rolled low carbon plain steel sheets, the surfaces of which had been degreased and cleaned by heating in a reduction atmosphere furnace, by passing them through an Al-Si plating bath (Si content: 9 % by weight; temperature: 670°C) in a Sendzimir apparatus. The obtained aluminum-coated steel sheets were rolled with reductions of 5 - 80 %, and annealed at temperatures of 250 - 500°C for 6 hours. Thus 20 aluminum coated steel sheet samples were obtained.

A commercially available enamel glaze for aluminum-coated steel sheets was made into a suitable slip and was applied by spraying onto the surfaces of the aluminum-coated steel sheets obtained as described above to a thickness of 80 μm, and were fired at 550°C for 7 minutes, to produce enameled products.

Properties of the aluminum coating layers of the substrates (pinholes, cracks, recrystallization and alloying) are summarized in Table 1 and the characteristics of the enameled products (blister defect and adhesion) are summarized in Table 2.

(A) Properties of aluminum coating layer.

i. Pinholes and cracks.

Microscopically observed. Results are summarized in the column "P". The symbols have the following meanings:

o : Neither pinholes nor cracks.

× : Pinholes or cracks observed.

ii. State of recrystallization.

Judged on the basis of Vickers hardness and observation by a metallographic microscope. Results are summarized in the column "R.C.".

o : Good recrystallization

× : Insufficient recrystallization

iii. State of alloying.

Microscopically observed. Results are summarized in the column "A".

o : No alloy formation

× : Alloy formed (grayish black surface)

(B) Characteristics of enamel layer.

i. Blister defect.

Observed with a 10 power loupe. Results are summarized in the column "F".

o : No blister defect

× : Blister defect

ii. Adhesion.

Adhesion was determined in accordance with the drop impact deformation test by measuring the amount of the residual enamel layer when a test piece was placed between a die with a 25.5 mm diameter hole and a punch 25 mm in diameter and a 1 kg weight was dropped thereupon so as to form a deformation recess 3 mm in maximum depth. The results are summarized in the column "AD".

o : Good adhesion (no scaling)

△ : Insufficient adhesion (1 - 50 % scaling)

× : Poor adhesion (more than 50 % scaling)

Table 1

No.	Base Steel Sheet C Content (wt%)	Rolling Reduction (%)	Recrystallization Annealing Temperature (°C)																	
			250			300			350			400			450			500		
			P	R.C.	A	P	R.C.	A	P	R.C.	A	P	R.C.	A	P	R.C.	A	P	R.C.	A
1	0.15	5	×	o	o	×	o	o	×	o	o	×	o	o	×	o	×	×	-	×
2		10	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
3		40	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
4		70	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
5		80	×	o	×	×	o	o	×	o	o	×	o	o	×	o	o	×	-	×
6	0.05	5	×	o	o	×	o	o	×	o	o	×	o	o	×	o	o	×	-	×
7		10	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
8		40	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
9		70	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
10		80	×	o	×	×	o	×	×	o	×	×	o	×	×	o	o	×	-	×
11	0.02	5	×	o	o	×	o	o	×	o	o	×	o	o	×	o	o	×	-	×
12		10	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
13		40	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
14		70	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
15		80	×	o	o	×	o	o	×	o	o	×	o	o	×	o	o	×	-	×
16	0.01	5	×	o	o	×	o	o	×	o	o	×	o	o	×	o	o	×	-	×
17		10	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
18		40	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
19		70	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	-	×
20		80	×	o	o	×	o	o	×	o	o	×	o	o	×	o	o	×	-	×

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Table 2

No.	Base Steel Sheet C Content (wt%)	Rolling Reduction (%)	Recrystallization Annealing Temperature (°C)											
			250		300		350		400		450		500	
			F	AD	F	AD	F	AD	F	AD	F	AD	F	AD
1	0.15	5	×	Δ	×	○	×	○	×	○	×	○	×	×
2		10	○	Δ	○	○	○	○	○	○	○	○	×	×
3		40	○	Δ	○	○	○	○	○	○	○	○	×	×
4		70	○	Δ	○	○	○	○	○	○	○	○	×	×
5		80	×	Δ	×	○	×	○	×	○	×	○	×	×
6	0.05	5	×	Δ	×	○	×	○	×	○	×	○	×	×
7		10	○	Δ	○	○	○	○	○	○	○	○	×	×
8		40	○	Δ	○	○	○	○	○	○	○	○	×	×
9		70	○	Δ	○	○	○	○	○	○	○	○	×	×
10		80	×	Δ	×	○	×	○	×	○	×	○	×	×
11	0.02	5	×	○	×	○	×	○	×	○	×	○	×	×
12		10	○	○	○	○	○	○	○	○	○	○	×	×
13		40	○	○	○	○	○	○	○	○	○	○	×	×
14		70	○	○	○	○	○	○	○	○	○	○	×	×
15		80	×	○	×	○	×	○	×	○	×	○	×	×
16	0.01	5	×	○	×	○	×	○	×	○	×	○	×	×
17		10	○	○	○	○	○	○	○	○	○	○	×	×
18		40	○	○	○	○	○	○	○	○	○	○	×	×
19		70	○	○	○	○	○	○	○	○	○	○	×	×
20		80	×	○	×	○	×	○	×	○	×	○	×	×

As seen in Tables 1 and 2, in the substrate sheets which were obtained by 10 - 70 % reduction rolling and recrystallization annealing at about 250 - 480°C, pinholes of the aluminum coating layer were completely filled up and eliminated and the layer had a good rolled-and-recrystallized structure. The resulting enamel layer was free from blister defect and had no problem regarding adhesion. Especially, there was observed an obvious trend that the recrystallization annealing temperature could be raised as the C content of the base steel sheet became lower. It will be noted that both in the case where the rolling reduction was less than 10 % and in the case where it was more than 70 %, blister defect developed. This is because, in the former, rolling reduction was insufficient and pinholes remained, and in the latter, rolling reduction was excessive and cracking occurred in the aluminum coating layer.

Experimental results pertaining to the relation between the Si content of the plating bath and the workability of the plated aluminum layer are shown in Table 3. Steel sheets (C content: 0.05 %) 1.2 mm in thickness were plated with Al to a thickness of 120 μm by passing them through plating Al-Si baths of different Si contents by the conventional method, and they were cold-rolled with reduction of 10 - 70 %. Cracking and scaling of the rolled sheets were microscopically observed. As seen in Table 3, when the Si content of the bath (accordingly the formed aluminum coating) was low, the alloy layer at the interface between the base steel sheet and the aluminum coating layer develops cracking and the coating layer developed cracking and scaling even if the rolling reduction was low. This is because a high degree of alloy formation occurred during plating. On the other hand, when the Si content was too high, cracking occurred. This is because hard and brittle plate-like crystals of Si were formed in the plated layer.

For this reason it is desirable that the bath contains about 1 - 15 % by weight Si.

Table 3

No.	Si Content (wt%)	Rolling Reduction (%)	State of Plated Layer After Rolling
1	0.5	10	Cracking in alloyed layer, scaling of plated layer
2		30	"
3		50	"
4		70	"
5	1	10	Good
6		30	"
7		50	"
8		70	"
9	9	10	"
10		30	"
11		50	"
12		70	"
13	15	10	"
14		30	"
15		50	"
16		70	"
17	17	10	Cracking in alloyed layer, local scaling of plated layer
18		30	"
19		50	"
20		70	"

Experimental results pertaining to the relation between the Si content of the plated aluminum layer and the adhesion of the resulting enamel layer are shown in Table 4. The experiments were carried out as follows. Steel sheets 1.2 mm in thickness (0.06 % by weight C) were passed through Al-Si plating baths (0.1 - 15 % by weight Si) by the conventional method so as to form a 120 μm thick plated layer and the plated sheets were cold-rolled with 20 % reduction. The sheets were annealed at 300°C in order to recrystallize the plated Al layer (6 hours). A commercially available glaze was applied onto the substrate sheets obtained as described above to a thickness of 80 μm, and the sheets were fired. The thus obtained enameled products were tested by the above-described drop impact deformation method and evaluated by the amount of the remaining enamel layer. The symbols in the table have the same meanings as explained above. It will be noted that adhesion was satisfactory when the Si content was 1 - 15 % by weight. This is because the alloy formation temperature was raised by the existence of Si and thus alloy formation during the firing was inhibited.

Concerning the rolled-and-recrystallized structure of both the aluminum coating layer and the base steel sheet, the following experiments were carried out.

Low carbon steel sheets 0.8 mm in thickness (C content: 0.15 - 0.01 % by weight) were degreased and heated in a reduction atmosphere furnace so as to clean the surfaces thereof, and then were passed through an Al-Si plating bath (Si content: 9 % by weight; temperature: 670°C; dipping time: 5 seconds). The thus obtained aluminum-plated steel sheets were cold-rolled by 10 - 80 %. Thereafter, they were heated at 350°C for 8 hours as the first step, and heated at 450 - 600°C for 10 hours as the second step.

A commercially available glaze for aluminum-coated steel sheets was made into a suitable slip and was applied onto the degreased surfaces of the substrate sheets obtained as described above to form a 80 μm thick glaze layer. The substrate sheets with the glaze layer were fired at 550°C for 7 minutes and enameled products were obtained.

Properties of the above substrates (state of recrystallization of both the base steel sheet and the plated aluminum layer, pinholes, cracking and alloy formation in the plated aluminum layer) are shown in Table 5. The carbon content of the base steel sheets was 0.15 % by weight. Evaluation and rating of the properties were the same as stated above.

(i) State of rolled-and-recrystallized structure of the base steel sheet and the plated aluminum layer. (Results are indicated in the column "C.R.".)

o : Good rolled-and-recrystallized structure
△ : Insufficient recrystallization
× : Insufficient rolling and recrystallization

(ii) Pinholes and cracks. (Results are indicated in the column "P".)

o : No defect
× : Pinholes and cracks observed

(iii) Alloy formation. (Results are indicated in column "A".)

o : No alloy formation
× : Alloy formation (grayish black surface)

Table 4

No.	Si Content (wt%)	Enameling (Firing) Temp. (°C)	Adhesion of Enamel Layer
1	0.1	470	×
2		500	×
3		550	×
4		600	×
5	0.5	470	o
6		500	△
7		550	×
8		600	×
9	1.0	470	o
10		500	o
11		550	o
12		600	△
13	9.0	470	o
14		500	o
15		550	o
16		600	o
17	15.0	470	o
18		500	o
19		550	o
20		600	o

As seen in Table 5, Samples No. 1 - 4 (rolling reduction 10 %) were insufficient in rolling reduction of the base steel sheet, Samples No. 5, 9, 13 and 17 (annealed at 450°C) were insufficient in recrystallization and Samples No. 17 - 20 (rolling reduction 80 %) were excessive in rolling reduction. In Samples No. 17 - 20, cracking developed. In contrast, the samples which underwent a 20 - 70 % reduction rolling and a second step annealing at 500 - 600°C had good rolled-and-recrystallized structure and were free from pinholes and cracks. None of the samples suffered from alloy formation. This was because all of them underwent a first step annealing at 350°C.

The relation between the conditions of the first annealing step and the workability of the plated aluminum layer is shown in Table 6. All the samples underwent a second step annealing at 550°C for 10 hours. Workability was judged by the close bending test as stipulated in JIS Z-2248 and the deep drawing cup test using a deep drawing tester for thin steel sheets marketed by Erichsen & Co. (punch diameter: 40 mm, punch shoulder radius of curvature: 1 mm, die diameter: 42 mm, die shoulder radius of curvature: 5 mm, blank diameter: 80 mm, depth of drawing: 20 mm) and test pieces which were formed by shaping substrate sheets into the shapes shown in Fig. 1 and Fig. 2. The surface appearance and the state of the plated layer of the worked portion (a) and (b) shown in the figures were observed, and the results are indicated in the table. The symbols have the following meanings:

o : Good workability (no cracking)
△ : Somewhat insufficient workability (light cracking)
× : Poor workability (heavy cracking)

Table 5

No.	Rolling Reduction (%)	Annealing Temp. (°C)	Properties of Substrate Sheets			
			Base Sheet C.R.	Plated Layer C.R.	P	A
1	10	450	×	o	o	o
2		500	o	o	o	o
3		550	o	o	o	o
4		600	o	o	o	o
5	20	450	Δ	o	o	o
6		500	o	o	o	o
7		550	o	o	o	o
8		600	o	o	o	o
9	40	450	Δ	o	o	o
10		500	o	o	o	o
11		550	o	o	o	o
12		600	o	o	o	o
13	70	450	Δ	o	o	o
14		500	o	o	o	o
15		550	o	o	o	o
16		600	o	o	o	o
17	80	450	Δ	o	×	o
18		500	o	o	×	o
19		550	o	o	×	o
20		600	o	o	×	o

As seen in Table 6, the samples which underwent a first step annealing at 330 - 450°C exhibited good workability of the plated aluminum layer. This is because the alloy formation temperature was raised by the first step annealing and alloy formation was avoided in the second step annealing. Also it is noted that with lower C content of the base steel sheet, alloy formation was inhibited and good workability of the plated aluminum layer was retained.

Enamel characteristics of the obtained enameled products (blister defect and adhesion) are shown in Table 7. In this test, the sample substrate sheets were rolled and annealed, whereby the second step annealing was carried out at 550°C. Enamel characteristics were judged with respect to the worked portions. The method of evaluation was the same as above.

(i) Blister defect (results indicated in the column "F").

o : No blister defect

× : Blister defect occurred

(ii) Adhesion (results indicated in the column "AD").

o : Good adhesion (no scaling)

△ : Insufficient adhesion (1 - 50 % scaling)

× : Poor adhesion (more than 50 % scaling)

Table 6

No.	Base Steel Sheet C (wt%)	Rolling Reduction (%)	Temp. of First Step Annealing (°C)									
			250		300		400		450		500	
			Bending	Deep Drawing	Bending	Deep Drawing	Bending	Deep Drawing	Bending	Deep Drawing	Bending	Deep Drawing
1	0.15	10	×	×	o	o	o	o	o	o	×	×
2		20	×	×	o	o	o	o	o	o	×	×
3		50	×	×	o	o	o	o	o	o	×	×
4		70	×	×	o	o	o	o	o	o	×	×
5		80	×	×	o	o	o	o	o	o	×	×
6	0.05	10	×	×	o	o	o	o	o	o	×	×
7		20	×	×	o	o	o	o	o	o	×	×
8		50	×	×	o	o	o	o	o	o	×	×
9		70	×	×	o	o	o	o	o	o	×	×
10		80	×	×	o	o	o	o	o	o	×	×
11	0.02	10	o	Δ	o	o	o	o	o	o	×	×
12		20	o	Δ	o	o	o	o	o	o	×	×
13		50	o	Δ	o	o	o	o	o	o	×	×
14		70	o	Δ	o	o	o	o	o	o	×	×
15		80	o	Δ	o	o	o	o	o	o	×	×
16	0.01	10	o	Δ	o	o	o	o	o	o	×	×
17		20	o	Δ	o	o	o	o	o	o	×	×
18		50	o	Δ	o	o	o	o	o	o	×	×
19		70	o	Δ	o	o	o	o	o	o	×	×
20		80	o	Δ	o	o	o	o	o	o	×	×

Table 7

No.	Base Steel Sheet C (wt%)	Rolling Reduction (%)	Temp. of First Step Annealing (°C)									
			250		300		400		450		500	
			F	AD	F	AD	F	AD	F	AD	F	AD
1	0.15	10	o	x	o	o	o	o	o	o	x	x
2		20	o	x	o	o	o	o	o	o	x	x
3		50	o	x	o	o	o	o	o	o	x	x
4		70	o	x	o	o	o	o	o	o	x	x
5		80	x	x	x	o	x	o	x	o	x	x
6	0.05	10	o	x	o	o	o	o	o	o	x	x
7		20	o	x	o	o	o	o	o	o	x	x
8		50	o	x	o	o	o	o	o	o	x	x
9		70	o	x	o	o	o	o	o	o	x	x
10		80	x	x	x	o	x	o	x	o	x	x
11	0.02	10	o	△	o	o	o	o	o	o	x	x
12		20	o	△	o	o	o	o	o	o	x	x
13		50	o	△	o	o	o	o	o	o	x	x
14		70	o	△	o	o	o	o	o	o	x	x
15		80	x	△	x	o	x	o	x	o	x	x
16	0.01	10	o	△	o	o	o	o	o	o	x	x
17		20	o	△	o	o	o	o	o	o	x	x
18		50	o	△	o	o	o	o	o	o	x	x
19		70	o	△	o	o	o	o	o	o	x	x
20		80	x	△	x	o	x	o	x	o	x	x

It is noted from Table 7, that when substrate sheets, which were rolled with a 20 - 70 % reduction and first annealed at 330 - 450°C and then annealed at 550°C, were used, enamel products free from blister defect and having good adhesion were obtained. In contrast, blister defect developed in Samples No. 5, 10, 15 and 20. This is because the rolling reduction was excessive and thus cracking occurred in the plated aluminum layer. The samples which underwent a first step annealing at 250°C and 500°C were poor in adhesion since the alloy formation temperature was not sufficiently raised by the first step annealing. Also there was noted a trend that with lower C content of the base steel sheet, alloy formation was more inhibited and thus adhesion of the enamel layer was retained or improved.

Merits of the Invention

The invention has been described specifically with respect to hot-dip aluminum-plated steel sheets in the above. However, it will be understood by those skilled in the art that enamel products having the same enamel characteristics will be obtained by treating in the same way aluminum-coated steel sheets prepared by powder coating, vacuum evaporation, cladding, etc.

The aluminum-coated steel sheets in accordance with this invention have excellent characteristics as the substrate for enameling, from which enameled products with an enamel layer free from blister defect and having good adhesion to the substrate can be obtained. The firing temperature can be raised without sacrificing adhesion of the enamel layer, and therefore the restriction on selection of glazes is eased and the resulting enamel layer can be improved in chemical resistance, and other properties of the enamel.

Claims

1. An aluminum-coated steel sheet for enameling comprising a base steel sheet characterized in that the aluminum coating layer has a rolled-and-recrystallized structure.

2. The aluminum-coated steel sheet for enameling as claimed in Claim 1, wherein the aluminum coating layer contains 1 - 15 % by weight silicon.

3. The aluminum-coated steel sheet for enameling as claimed in Claim 1, which is further characterized in that the base steel sheet also has a rolled-and-recrystallized structure.

4. The aluminum-coated steel sheet for enameling as claimed in Claim 3, wherein the aluminum coating layer contains 1 - 15 % by weight silicon.

Fig. 1

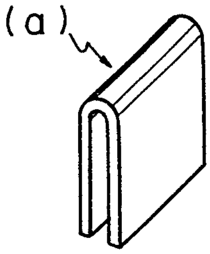
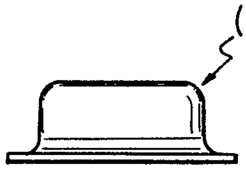


Fig. 2



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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	DE - A1 - 2 909 418 (FURUKAWA ALUMINIUM CO., LTD.) * Claims; examples *	1-4	C 23 C 1/08 C 23 C 5/00 C 23 C 9/00 C 23 D 3/00
X	DE - B2 - 2 553 051 (POLITECHNIKA SLASKA IM. WINCENTEGO PSTROWSKIE-GO) * Claim; column 2, lines 9-40; example *	1-4	
X	DE - A - 1 521 197 (CLEVITE CORP.) * Claims; column 2, lines 21-56 *	1-4	
X	US - A - 4 150 178 (T. YAGI et al.) * Claims; column 3, lines 46-66; example 1 *	1-4	**TECHNICAL FIELDS SEARCHED (Int. Cl. 3)**
X	US - A - 4 148 942 (A. GIEREK et al.) * Claims; column 3, lines 26-44; examples *	1-4	C 23 C C 23 D
X	US - A - 4 079 157 (T. YAGI et al.) * Fig. 1-3; claims *	1-4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	17-02-1983	SLAMA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 6, no. 7, January 16, 1982 THE PATENT OFFICE JAPANESE GOVERNMENT page 49 C 87 * Kokai-no. 56-130 461 (NITSUSHIN SEIKOU K.K.) * --	1-4	
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A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 4, no. 151, October 23, 1980 THE PATENT OFFICE JAPANESE GOVERNMENT page 96 C 28 * Kokai-no. 55-97 474 (MATSUSHITA DENKI SANGYO K.K.) * --	1	
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A	PATENT ABSTRACTS OF JAPAN, unexamined applications, field C, vol. 4, no. 61, May 8, 1980 THE PATENT OFFICE JAPANESE GOVERNMENT page 73 C 9 * Kokai-no. 55-28 381 (MATSUSHITA DENKI SANGYO K.K.) * --	1	
Y	PATENT ABSTRACTS OF JAPAN, unexamined applications, field C, vol. 4, no. 46, April 10, 1980 THE PATENT OFFICE JAPANESE GOVERNMENT page 57 C 6 * Kokai-no. 55-18 521 (FURUKAWA ALUMINUM KOGYO K.K.) * --	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
Y	PATENT ABSTRACTS OF JAPAN, unexamined applications, field C, vol. 3, no. 14, February 8, 1979 THE PATENT OFFICE JAPANESE GOVERNMENT page 72 C 36 * Kokai-no. 53-138 933 (MITSUBISHI JUKOGYO K.K.) * ----	1-4	