United States Patent [19]

Clinton et al.

[11] **3,779,798**

[45] **Dec. 18, 1973**

[54] **CORROSION RESISTANT TINPLATE**

[75] Inventors: **Margaret A. Clinton**, Pittsburgh; **Martin G. H. Wells**, Bethel Park, both of Pa.

[73] Assignee: **Jones & Laughlin Steel Corporation**, Pittsburgh, Pa.

[22] Filed: **July 17, 1972**

[21] Appl. No.: **272,609**

Related U.S. Application Data

[63] Continuation of Ser. No. 730,669, April 12, 1968, abandoned, which is a continuation-in-part of Ser. No. 560,315, June 24, 1966, abandoned.

[52] **U.S. Cl.** ..... **117/131**, 29/196.4, 117/160 R

[51] **Int. Cl.** **C23c 35/00**

[58] **Field of Search** ..... 117/130 R, 131, 160 R, 117/114 B; 29/196.4, 183.5

[56] **References Cited**

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Primary Examiner—Ralph S. Kendall
Assistant Examiner—M. W. Ball
Attorney—G. R. Harris

[57] **ABSTRACT**

Tinplate of improved corrosion resistance comprises a steel base with a microstructure between the limits of martensitic-ferritic and fully martensitic provided with a coating of tin and an interfacial tin-iron alloy layer.

1 Claim, 11 Drawing Figures

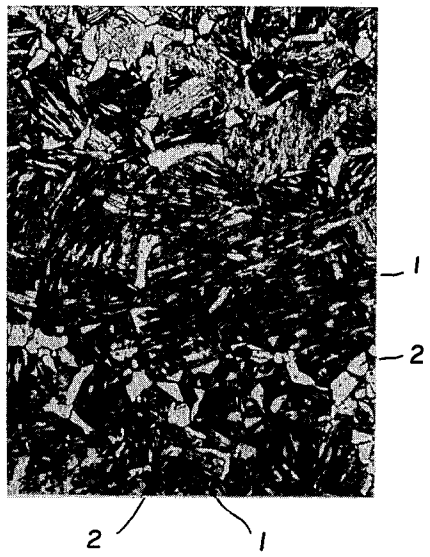


FIG. 1

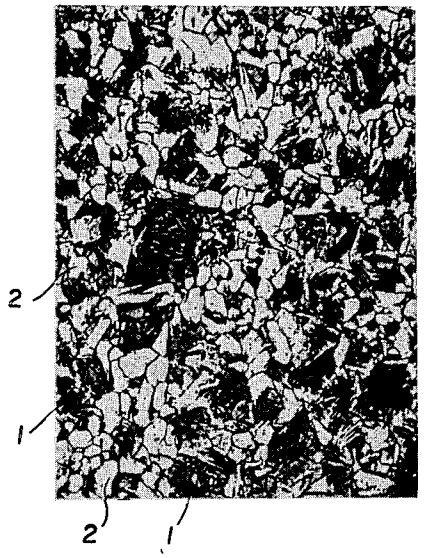


FIG. 2

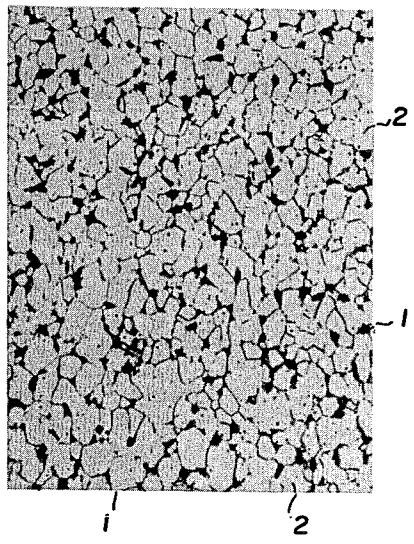


FIG. 3

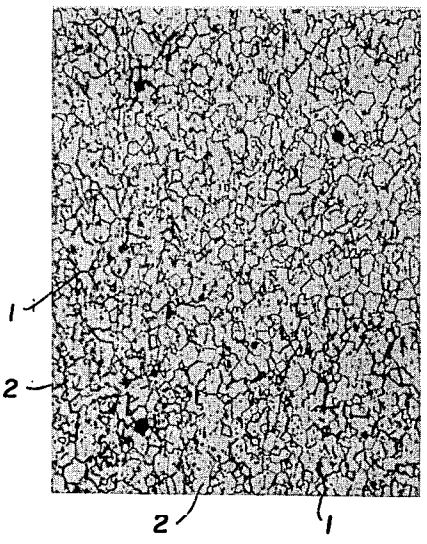


FIG. 4

INVENTORS
MARGARET A. CLINTON
MARTIN G. H. WELLS

ATTORNEY

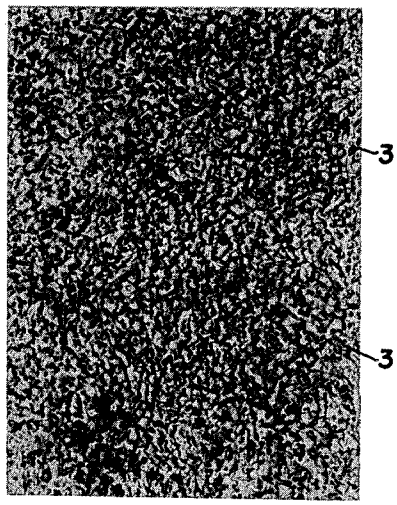


FIG. 5

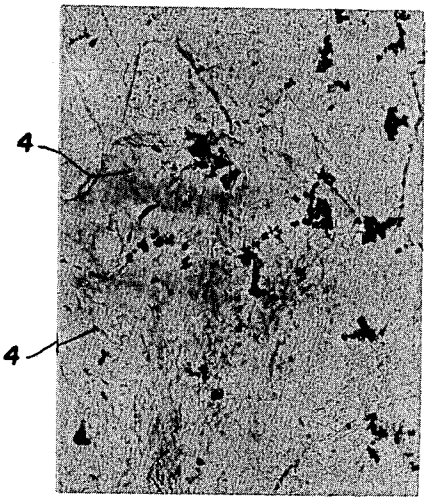


FIG. 6

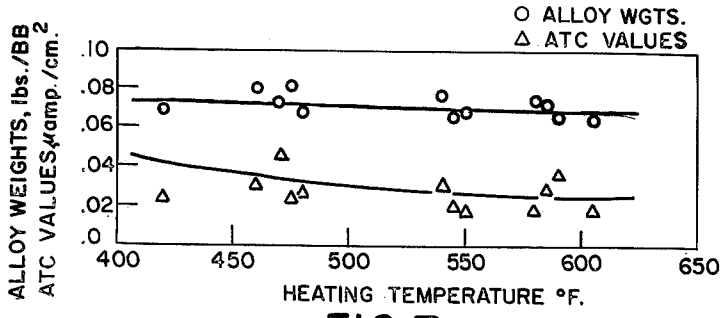


FIG. 7.

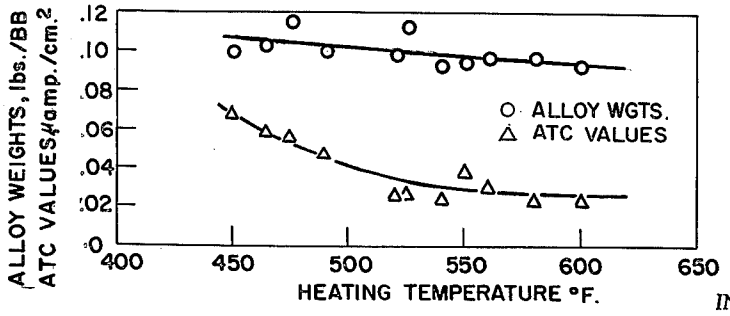


FIG. 8.

INVENTORS
MARGARET A. CLINTON
MARTIN G.H. WELLS

ATTORNEY

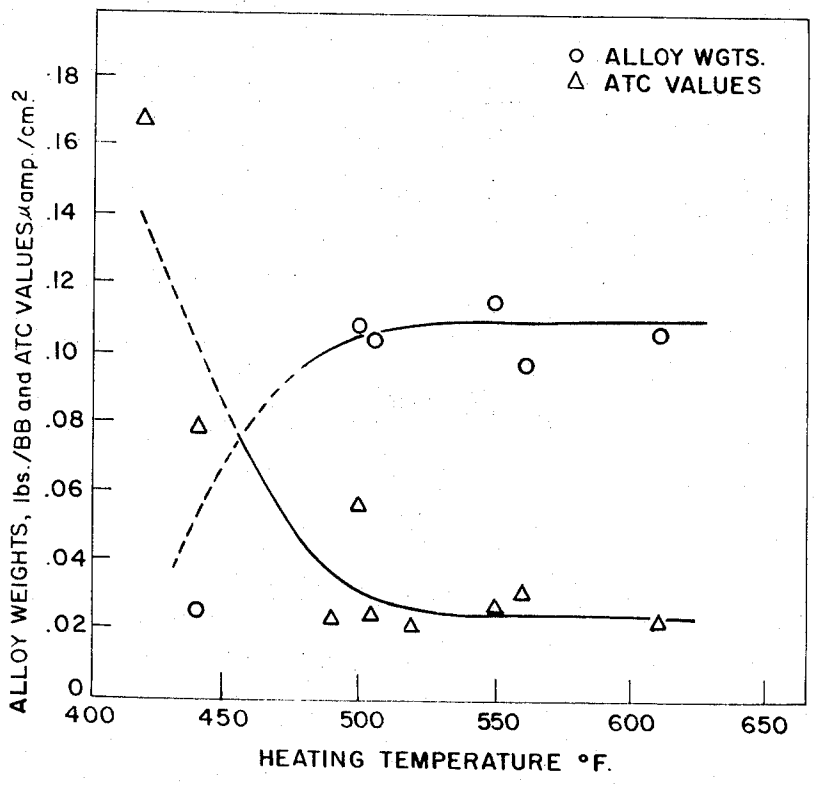


FIG. 9.

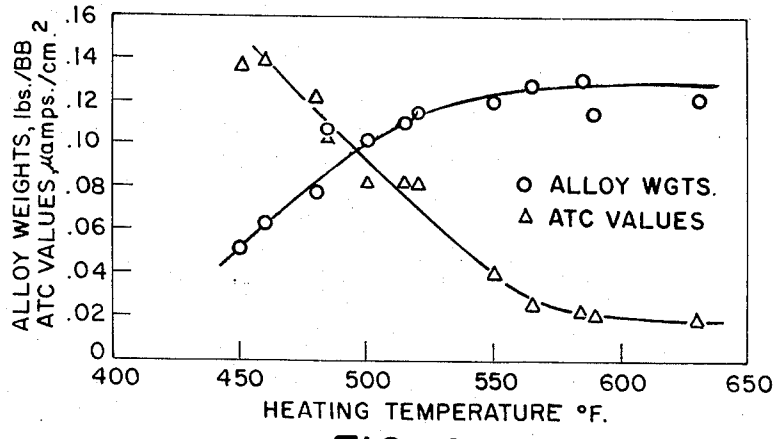


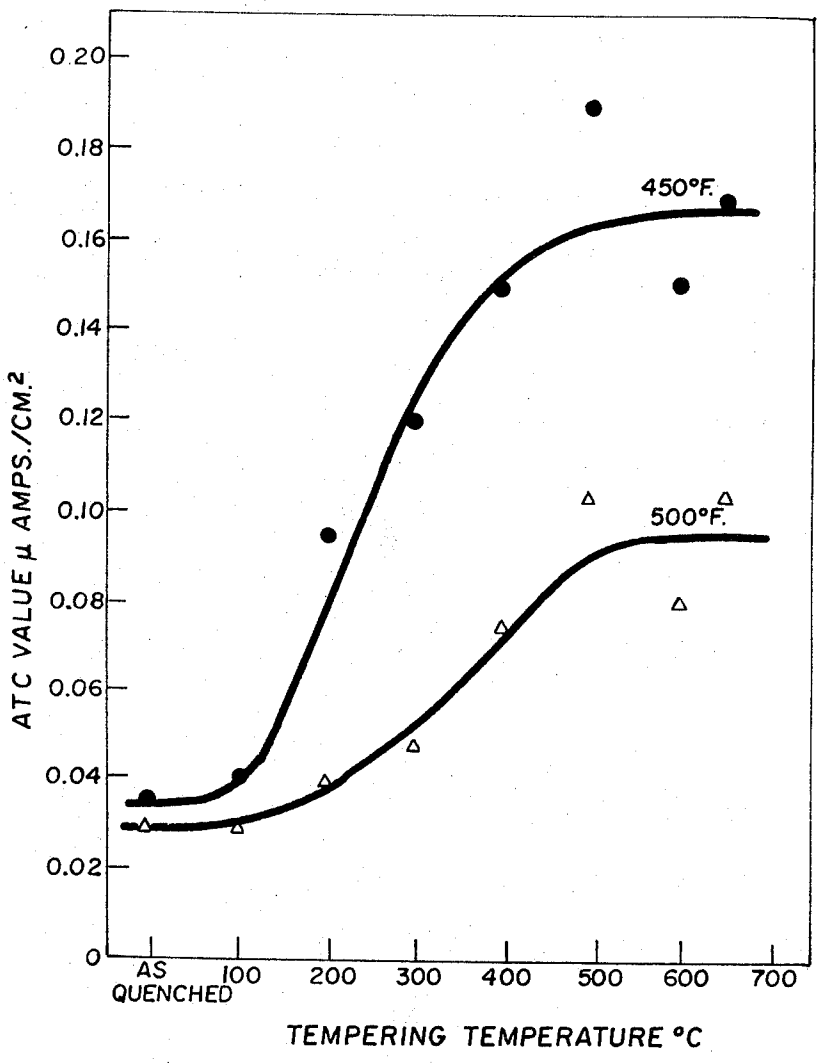
FIG. 10.

INVENTORS.
MARGARET A. CLINTON
MARTIN G. H. WELLS

BY

ATTORNEY

Fig. II.



INVENTORS
MARGARET A. CLINTON
MARTIN G. H. WELLS

CORROSION RESISTANT TINPLATE

This application is a continuation of copending U.S. Pat. Application Ser. No. 730,669, filed Apr. 12, 1968, now abandoned, which is a continuation-in-part of U.S. Pat. Application Ser. No. 560,315, filed June 24, 1966, now abandoned.

This invention relates to tinplate of improved corrosion resistance and its method of manufacture. It is more particularly concerned with tinplate comprising a steel base of substantially martensitic character, a tin coating and an intermediate tin-iron alloy layer of novel form.

Most tinplate in commercial use has its coating applied by an electrolytic process. Several variations of these processes are in general use, all of which permit the plating of a relatively thin coating which is relatively uniform in thickness. Because the thickness of tin on conventional tinplate is a small fraction of an inch, the amount of coating is expressed in terms of its weight. The term "base box" is a measure of tinplate area or surface and amounts to 31,360 square inches. The bulk of electrolytic tinplate is produced in the range of one-fourth to 1 pound of tin per base box of tinplate.

The corrosion resistance of tinplate, especially that used for food packs, is conventionally determined by a galvanic test, known as the alloy-tin couple test. Such a test comprises stripping or removing the tin from the sample of tinplate down to the tin-iron alloy surface and measuring the current density developed by a galvanic couple consisting of a tin electrode and the sample immersed in grapefruit juice containing 100 ppm of soluble stannous tin at a temperature of 79° F. The current density after 20 hours is measured in microamperes per square centimeter and the figures are referred to as ATC values. Low ATC values indicate good corrosion resistance and high ATC values represent poor corrosion resistance. The ATC test is described in the paper "The Alloy-Tin Couple Test — A New Research Tool" by G. G. Kamm, A. R. Willey, R. E. Beese and J. L. Krickl, published in "Corrosion," Volume 17, February, 1961, pages 106–112.

Commercial electrolytic tinplate as produced under varying conditions has ATC values ranging from very low figures of about 0.01 up to perhaps 0.5 microamperes per square centimeter. The ATC value of 0.05 has been arbitrarily selected as representing superior quality tinplate, although as we have mentioned, it is possible to produce tinplate having lower ATC values.

It is an object of our invention to produce tinplate with corrosion resistance superior to that which has heretofore been available. It is another object to produce tinplate with a tin-iron alloy layer having novel characteristics. It is another object to produce matte surface tinplate having superior corrosion resistance. It is another object to provide a method of making a tinplate of superior corrosion resistance without heating the tinplate above the melting point of tin. It is still another object to provide a method of making electrolytic tinplate of superior corrosion resistance without heating the tinplate to the melting point of tin. Other objects of our invention will appear in the course of the description thereof which follows.

We have found that the corrosion resistance of tinplate is greatly improved if its substrate is steel containing a significant amount of martensite, and that the best corrosion resistance is obtained when the steel substrate is substantially fully martensite. We have also found that the corrosion resistance of these substrates is better when the martensite is substantially untempered. We define the substrate structure as ranging from martensitic-ferritic (containing both martensite and ferrite) to substantially fully martensitic (containing substantially only martensite) steel. We have also invented a novel electrolytic tinplate of superior corrosion resistance having a matte surface and a tin-iron interfacial alloy layer.

Our invention is best understood with reference to the attached figures. FIG. 1 is a photomicrograph showing the microstructure of substantially fully martensitic tinplate substrate of our invention. FIG. 2 is a photomicrograph showing the microstructure of a substrate of our invention of martensitic-ferritic character comprising about 50 percent martensite. FIG. 3 is a photomicrograph showing the microstructure of another martensitic-ferritic substrate of our invention comprising about 20 percent martensite. FIG. 4 is a photomicrograph showing the ferritic microstructure of conventional tinplate substrate. FIGS. 1–4 were taken at a magnification of 500 diameters.

FIG. 5 shows the microstructure of the tin-iron alloy formed when the substrate of FIG. 1 is electrotinned and heated to a temperature of 460° F. FIG. 6 shows the microstructure of the unique iron-tin alloy formed when the substrate of FIG. 1 is electrotinned and heated to a temperature of 400° F. FIGS. 5 and 6 were taken at a magnification of 5,000 diameters.

FIG. 7 is a graph of two properties of substantially fully martensitic electrolytic tinplate heated to various temperatures. ATC values and weights of the tin-iron alloy layer are plotted against the temperatures to which the tinplate was heated. FIG. 8 is a similar graph of about 50 percent martensitic tinplate, and FIG. 9 is a similar graph of about 20 percent martensitic tinplate. FIG. 10 is a graph of the same properties of conventional ferritic electrolytic tinplate. FIG. 11 is a graph showing the effect tempering of martensitic tinplate has on ATC values at various reflow temperatures.

The martensitic steel substrate of our tinplate is produced from ordinary low carbon tinplate grade steel having the following typical analysis:

Carbon	Manganese	Phosphorus	Sulfur	Silicon
0.10 %	0.48 %	0.013 %	0.02 %	0.01 %

The steel in the form of continuous strip is heated to a temperature of about 1,700° F. and is continuously water quenched. Oils, brine and air can also be employed as quenching media. The martensitic steel so produced displays tensile strengths on the order of 125,000 psi and elongations of about 5 percent.

The substantially fully martensitic structure of FIG. 1 exhibits islands of ferrite, the light colored constituent **2-2**, surrounded by a matrix of martensite, the dark colored constituent **1-1**. We consider a structure comprising less than about 10 percent ferrite as being substantially fully martensitic. In the structure of FIG. 2 the aggregate amounts of martensite **1-1** and of ferrite **2-2** are about equal. In the structure of FIG. 3 the martensitic constituent **1-1** comprises only about 20 percent of the total, being surrounded by a matrix of ferrite **2-2**. This structure is about the lower limit of the martensitic-ferritic structure referred to herein. The structure of FIG. 4 is fully ferritic.

The heated and quenched steel strip is electroplated with tin in the conventional way. The tinplate described herein was tinned by the so-called halogen process, but processes employing other types of electrolytes are also satisfactory. Unbrightened electrolytic tinplate has a dull or matte surface and includes no interfacial tin-iron alloy layer. It is conventional to brighten the surface by heating the tinplate for a very short time to a temperature above the melting point of tin and then quenching it. This treatment leaves the tin in a bright or specular form and also produces a relatively thin tin-iron alloy layer intermediate the tin and the steel base. The effects of heat treatments of this type on tinplate of our invention comprising various proportions of martensite and on conventional ferritic tinplate are shown graphically in FIGS. **7** through **10.**

Samples of tinplate of those types previously indicated, as well as conventional tinplate, were heated to the various temperatures indicated on the graphs and the weight of the tin-iron alloy was determined in each case, as well as the ATC value of the tinplate. The graphs of the Figures show that the weight of the tin-iron alloy and the ATC values of the substantially fully martensitic tinplate of FIG. **7** are not greatly influenced by the heating temperature, as long as it is above about 400° F. As the percentage of martensite is decreased, however, the critical heating temperature increases. It is about 500° F. for the 20 percent martensitic tinplate of FIG. **9** and rises to between 550° F. and 575° F. for the conventional ferritic tinplate of FIG. **10.**

The tin-iron alloy layer of FIG. **5** is seen to be comprised of small columnar crystals **3-3** with their long axes oriented in seemingly random manner. This structure is somewhat similar to that which can be obtained in conventional halogen ferritic tinplate by various special processing steps generally requiring heating the matte tinplate appreciably above the melting point of tin. However, the individual crystals of FIG. **5** are considerably smaller than those observed in ferritic tinplate.

Samples of the heated and quenched steel strip previously identified were temper annealed at various temperatures for one hour, electroplated with tin in the conventional way and reflowed at 450° C. and 500° F. The ATC values of these samples were then determined, and the data so obtained are plotted in FIG. **11.** For both reflow temperatures of 450° F. and 500° F. the minimum ATC values are exhibited by the as-quenched or untempered materials, i.e., the materials which were not temper annealed. The curves of FIG. **11** show that as the tempering temperature is increased, the ATC values increase above the minimum value of the untempered materials.

Most interesting are the properties of the fully martensitic tinplate heated to temperatures of 400° F. or so, which temperatures are below the melting point of tin. The ATC values are excellent and a tin-iron alloy layer was formed, presumably by solid state diffusion. The tin surface of this specimen displayed the matte appearance of conventional unbrightened electrolytic tinplate, but its corrosion resistance was superior to all but the best brightened conventional tinplate. The nature of the tin-iron alloy layer formed by solid state diffusion is shown in FIG. **6** which is a photomicrograph of that layer. Very small columnar crystals **4-4** can be observed, but they are not nearly as well defined as those in FIG. **5.** The morphology of the alloy layer was determined in the electron microscope using the direct carbon replication technique as described generally in the paper, "Direct Carbon Replicas From Metal Surfaces," published in the "British Journal of Applied Physics," Volume 7, June, 1956, page 214.

The tin-iron alloy layer of the martensitic tinplate of our invention is appreciably thinner than that of conventional ferritic tinplate having comparable ATC values. From FIG. **7** it is seen that the weight of the alloy layer for fully martensitic tinplate is in the neighborhood of 0.07 pounds per base box regardless of the temperature at which the tinplate is heated and that the ATC values for such tinplate are of the order of 0.04 microamperes per square centimeter or less. FIG. **8** discloses that the weight of the alloy layer for 50 percent martensitic tinplate having an ATC value of about 0.04 is about 0.10 pounds per base box and FIG. **9** shows that the same is true for 25 percent martensitic tinplate. Conventional ferritic tinplate, however, with an ATC value of about 0.04 has an alloy layer weight of about 0.12 pounds per base box as appears from FIG. **10.**

The corrosion resistance and alloy layer weight of martensitic tinplate of our invention do not appear to be influenced significantly by the weight of the tin coating. The data graphed in the Figures were obtained from tinplate having a coating weight of 1 pound per base box, but we have observed almost identical properties in martensitic tinplate with a tin coating weight of only one-fourth pound per base box.

We claim:

1. The method of making matte surface tinplate of improved corrosion resistance comprising depositing tin on a steel base having a substantially fully martensitic microstructure and heating the tinplate to a temperature above about 400°F., but below the melting point of tin.

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