METHOD OF COATING LOW ALLOY STEELS

Inventors: Charles Flinchum, Trenton; F. Curtiss Dunbar, Monroe; Jerry L. Arnold, Franklin, all of Ohio

Assignee: Armco Steel Corporation, Middletown, Ohio

Filed: May 24, 1974

References Cited

UNITED STATES PATENTS

2,197,622  4/1940  Sendzimir ......................... 117/51

3,295,199  1/1967  Schrader............................. 117/51 X
3,320,085  5/1967  Turner.................................. 117/51

Primary Examiner—Ralph S. Kendall
Assistant Examiner—John D. Smith
Attorney, Agent, or Firm—Melville, Strasser, Foster & Hoffman

ABSTRACT

A method of fluxless hot dip metallic coating of low alloy steel strip and sheet containing aluminum, titanium, silicon, chromium, and/or mixtures thereof. A surface readily wettable by molten coating metal is obtained by heating the steel to a temperature of about 1100° to 1675° F in an atmosphere oxidizing to iron, then further treating under conditions which will reduce the iron oxide, whereby to form a surface layer comprising a substantially pure iron matrix containing a uniformly distributed fine dispersion of oxides of the alloying elements.

16 Claims, 4 Drawing Figures
A ORIGINAL SURFACE
B SURFACE CONDITION AFTER PRETREATMENT
C SURFACE CONDITION JUST PRIOR TO ENTERING THE COATING BATH
D GRAPHICAL REPRESENTATION OF Me CONTENT OF MATERIAL IN CONDITION C

CONVENTIONAL PROCESSING OF STEEL WITH Me < CRITICAL LEVEL

CONVENTIONAL PROCESSING OF STEEL WITH Me > CRITICAL LEVEL

MATERIAL PROCESSED ACCORDING TO PRESENT INVENTION
1

METHOD OF COATING LOW ALLOY STEELS

BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates to improvements in the process of hot dip metallic coating of low alloy steel sheet and sheet material whereby to enhance the wettability of the surfaces thereof by molten coating metals such as zinc, zinc alloys, aluminum, aluminum alloys and ternes, and to insure good adhesion of the coating. Low alloy steels which may be treated by the process of the present invention include those containing up to about 3% aluminum, up to about 1% titanium, up to about 2% silicon, or up to about 5% chromium, and mixtures thereof, with the remainder of the composition typical of a carbon steel, as defined by Steel Products Manual, Carbon Sheet Steel — page 7 (May 1970) — published by American Iron and Steel Institute.

2. Description of the Prior Art
In the hot dip metallic coating of steel strip and sheet material without a flux, it is necessary to subject the sheet and strip to a preliminary treatment which provides a clean surface free of iron oxide scale which is readily wettable by the molten coating metal and to which the coating metal will adhere after solidification thereof. Two types of seal-in-line preliminary treatments are commonly used in this country, one being the so-called Sendzimir process and the other so-called Selas process. Detailed descriptions of these two types of processes may be found in U.S. Pat. No. 2,110,893, issued Mar. 15, 1938 to T. Sendzimir, and U.S. Pat. No. 3,320,085, issued May 16, 1967 to C. A. Turner, Jr., respectively.

Briefly, the conventional Sendzimir process for preparation of carbon steel strip and sheet material for hot dip metallic coating involves passing the material through an oxidizing furnace heated, without atmosphere control, to a temperature of about 1600°F, by combustion, electric resistance, electric induction, or other conventional means, the residence time being sufficient to cause the material to reach a temperature of about 700° to 900°F, withdrawing the material from the furnace into air, forming a controlled surface oxide layer varying in appearance from light yellow to blue, introducing the material into a reducing furnace containing a hydrogen and nitrogen atmosphere, the residence time being sufficient to bring the material to a temperature of about 1350° to 1700°F. The controlled oxide layer is completely reduced, and the material is then cooled to approximately the temperature of the molten metal coating bath and led beneath the surface of the bath while surrounded by the hydrogen-nitrogen protective atmosphere.

In the conventional Selas method of treating carbon steel strip and sheet material, the steps comprise passing the material through a furnace heated to a temperature of at least about 2200°F by direct combustion of fuel and air therein, the furnace containing an atmosphere of gaseous products of combustion having no free oxygen and at least about 3% excess combustibles, the residence time of the material being sufficient to cause it to reach a temperature of about 800° to 1300°F, while maintaining bright steel surfaces completely free from oxidation, withdrawing the material from the furnace while still surrounded by gaseous products of combustion, introducing the material directly into a reducing section having a hydrogen and nitrogen atmosphere, in which the material may be further heated from 800° to 1700°F and/or cooled to approximately molten coating metal bath temperature, and then leading the material beneath the surface of the bath while surrounded by the hydrogen-nitrogen protective atmosphere.

It has been found that the above-conventional processes, while satisfactory for treatment of carbon steel strip and sheet material, may not satisfactorily prepare the surfaces of low alloy steel and sheet material for hot dip metallic coating. More specifically, it has been found that low alloy steels containing aluminum, titanium, silicon, chromium and/or mixtures thereof in appreciable amounts are not wettable by molten coating metals such as aluminum and zinc when treated under the above-described conditions. The final product is thus completely unacceptable since large areas have no coating whatever or a coating which does not adhere to the base metal.

Moreover, in carbon steel containing relatively small amounts of alloying elements, e.g., about 0.05% acid-soluble aluminum, it has been found that poor adherence of the solidified coating metal to the base metal occasionally occurs even though the material appears to have been wetted by the molten coating metal. In other words, although the metallic coating is continuous, adherence is poor in some areas thereof, thus resulting in high rejection rates.

It is thus apparent that a definite need exists for a reliable process of fluxless hot dip metallic coating of low alloy steels which avoids the problems described above.

SUMMARY

It is a principal object of the present invention to provide a method for the hot dip metallic coating of low alloy strip and sheet material which enhances the wettability of the surface of the material by molten coating metal and which insures good adhesion of the coating metal to the base material after solidification thereof.

In low alloy steels of the type defined above, the alloying element aluminum (in uncombined form) is most easily oxidized, followed in order by titanium, silicon, chromium, and iron. Conversely, iron oxide is the most easily reduced of these elements followed in order by the oxides of chromium, silicon, titanium and aluminum.

While not wishing to be bound by theory, it is applicants' belief that conditions can exist in the conventional processing which would first result in the formation of an external skin of aluminum oxide, a refractory compound, which is not wettable either by molten zinc or by molten aluminum. If other elements such as titanium, silicon and chromium are present instead of aluminum, these may also diffuse or migrate to the surface and be oxidized to form a stable oxide layer which may not be wetted by the molten coating metal. Since aluminum oxide is extremely difficult to reduce, any subsequent treatment under conventional carbon steel reducing conditions is ineffective in producing a reduced surface layer which is wettable by the molten coating metal.

The present invention constitutes a discovery that subjecting the surface of a low alloy steel containing alloying elements more readily oxidizable than iron to strongly oxidizing conditions in the pretreatment processing results in formation of a surface layer of iron oxide containing a dispersion of oxides of the alloying elements either in the form of relatively small, uniformly dispersed precipitates, or in solid solution. This
is followed by subjecting the steel to a conventional re-
ducing treatment in a hydrogen-containing atmosphere
which reduces the surface layer to a substantially pure
iron matrix containing a uniformly distributed fine dis-
persion of oxides of the alloying elements.

As used herein, the term "internal oxidation" will be
understood to designate the formation of a dispersion
of oxides of alloying elements in an iron matrix adja-
cent the surface, when processed conventionally. The
term "external oxidation" will be used to designate the
formation of an external skin or layer of stable oxides
of alloying elements more readily oxidizable than iron,
when subjected to conventional processing. However,
these terms will not be applied to the process of the
present invention.

In current commercial in-line-annal hot dip metallic
coating lines, the required high degree of oxidizing po-
tential may be achieved as follows:

When practising the Sendzimir process, the tempera-
ture of the strip and sheet material upon exiting the ox-
dizing furnace is increased to a range of about 1100°
to about 1400°F (rather than the conventional 700°
to 900°F). In the Selas process, the temperature of the
strip and sheet material exiting the direct fired preheat
furnace is increased to about 1400° to 1675°F (rather
than the conventional 800° to 1300°F). Moreover, the
atmosphere in the direct fired preheat furnace is modi-
fied so as to contain 0 to 6% excess oxygen and no ex-
cess combustibles.

The present application discloses that an external
skin of unreducible oxide will form in the reducing sec-
tions of both the conventional Selas-type and Send-
zimir processes if a critical level of oxidizing elements
is exceeded. As hereinafter explained in detail, Auger
analysis showed that this external oxidation also takes
place in the pretreatment furnace of the conventional
Selas process. In the conventional Sendzimir pretreat-
ment processing the maximum temperature reached
(900°F) is believed to be too low for significant diffu-
sion of the oxidizing element to occur. Many of the
alloy steels mentioned in this invention are very resis-
tant to oxidation, and, in fact, when a steel containing
approximately 2% Al, 1.2% Cr, 1% Si, 0.5% Ti is sub-
jected to the conventional Sendzimir pretreatment prac-
tice, the maximum recommended temperature of
900°F is insufficient to produce a visible oxide film.

The process of the present invention is unsuitable for
a carbon steel which does not contain substantial
amounts of the more easily oxidized alloying elements
because the iron surface would be scaled to such an ex-
tent that a conventional reducing treatment would not
convert all of the thickness of the scale surface, and
poor coating adherence would result. It would likewise
follow that a treatment for alloy levels considerably
lower than the above-mentioned 2% Al, 1.2% Cr, 1%
Si, 0.5% Ti steel, but yet beyond the carbon steel level,
would require preoxidation treatment conditions be-
tween the maximum tolerable for carbon steel and that
required for the above cited example of a low alloy
steel.

The above theory also explains the previously-dis-
cussed problem of poor adherence of coating metal to
a carbon steel base metal containing relatively small
amounts of acid-soluble aluminum, e.g., as little as
0.03% in some instances. Here again the diffusion of
aluminum to the surface accompanied by oxidation
thereof, while not forming an aluminum oxide layer of
sufficient thickness or continuity to prevent complete
wetting of the surface by the molten coating metal, nev-
evertheless sometimes prevents good adherence of the
coating metal after solidification by reason of the re-
fractory nature of the aluminum oxide areas on the sur-
face.

In its broadest aspect, the method of the invention
can be relied upon to enhance to wettability by a mol-
ten coating metal of, and to insure adherence of the
coating metal (after solidification thereof) to, the sur-
face of a low alloy steel containing one or more alloying
elements more readily oxidizable than iron. This is ef-
fected by first heating the steel to a temperature of
about 1100° to about 1675°F in an atmosphere oxidiz-
ing to iron, and subjecting the steel to further treatment
under conditions which reduce the iron oxide, whereby
to reduce the surface layer to a substantially pure iron
matrix containing a uniform dispersion of oxides of the
alloying elements.

BRIEF DESCRIPTION OF THE DRAWINGS

Reference is made to the accompanying drawing
wherein:
FIGS. 1A, 1B and 1C are diagrammatic representa-
tions of surface conditions at indicated processing
stages of an iron alloy containing an element Me, which
forms an oxide more stable than iron oxide, in an
amount less than the critical content under conven-
tional Selas-type pretreatment conditions;
FIG. 1D is a graphic representation of the surface
condition of the alloy of FIG. 1C;
FIGS. 2A, 2B and 2C are diagrammatic representa-
tions of surface conditions at indicated processing
stages of an iron alloy containing an element Me, which
forms an oxide more stable than iron oxide, in an
amount greater than the critical content under conven-
tional Selas-type pretreatment conditions;
FIG. 2D is a graphic representation of the surface
condition of the alloy of FIG. 2C;
FIGS. 3A, 3B and 3C are diagrammatic representa-
tions of surface conditions at indicated stages of the
process of the present invention of an iron alloy con-
taining an element Me, which forms an oxide more sta-
ble than iron oxide, in an amount greater than the criti-
cal content as calculated for conventional Selas-type
pretreatment;
FIG. 3D is a graphic representation of the surface
condition of the alloy of FIG. 3C;
FIG. 4 is a graphic representation of the relation be-
tween the critical aluminum content of a low alloy steel
and the hydrogen content and dew point of the treat-
ment atmosphere.

DESCRIPTION OF THE PREFERRED
EMBODIMENTS

As stated above, according to applicants' theory, in
conventional pretreatment of a low alloy steel contain-
ing an element which forms an oxide more stable than
iron oxide, a surface layer of this more stable oxide is
formed which is not reduced in the reducing section
nor in the molten coating bath. Hence, very little wet-
ting of the surface of the low alloy steel occurs. In the
following discussion, it should be kept in mind that it is
necessary to qualify the term oxidizing to indicate
whether it means oxidizing to iron. On the other hand,
when the term reducing is used, this will mean that it is
reducing to iron unless otherwise specified.

As indicated above, the manner in which aluminum
oxide is formed in a low alloy steel is of great signifi-
cance. With low aluminum concentrations, e.g., less than about 0.05% acid-soluble aluminum, and a relatively high oxidizing potential (such as that obtained by heating to about 1800°F in a 20% hydrogen atmosphere having a dew point of about 120°F) internal oxidation of the aluminum has been observed. Under these circumstances a precipitate of aluminum oxide is dispersed uniformly in a relatively pure iron matrix, and the surface of the alloy remains predominantly pure iron. However, as the concentration of aluminum is increased, or as the oxidizing potential is decreased, the rate of penetration of the internal oxide is decreased. At some combination of aluminum content and relatively low surface oxidizing potential, a transition from internal to external oxidation will occur. This external oxidation results in the formation of the previously mentioned aluminum oxide layer or skin which acts as a barrier to prevent wetting by a molten coating metal. Calculations will be set forth hereinafter showing the relation between aluminum contents and oxidizing potential which causes the formation of such an aluminum oxide layer, but which can be avoided successfully in accordance with the present invention.

As explained above, the essential feature of the present invention is to conduct the "oxidizing" treatment under conditions which are highly oxidizing to iron. This results in the formation of a surface layer or scale on the low alloy steel strip and sheet which is primarily iron oxide (Fe₂O₃) in which oxides of alloying elements such as aluminum, titanium, silicon and chromium are present either as finely dispersed precipitates or in a solid solution with iron oxide. In either event these stable oxides of the alloying elements are present as a minor volume fraction of the surface layer and are uniformly dispersed throughout the layer. In other words, diffusion or migration of the alloying elements to the surface is avoided. When material having a surface layer in this form is passed through the reducing furnace, the iron oxide portion is readily reduced. The more stable oxides of the alloying elements are not reduced and remain uniformly dispersed in a substantially pure iron matrix. In this condition the low alloy steel surface is readily wettable by a molten coating metal such as zinc or aluminum.

It is unlikely that a layer of aluminum oxide could subsequently form on the outer surface of the steel in the reducing section since this could occur only if aluminum diffuses from the unreacted matrix out through the freshly formed substantially pure iron layer to the surface. Reaction kinetics would dictate against such an occurrence.

After reduction of the iron oxide the hot dip coating process is conducted in conventional manner with the strip and sheet material being led beneath the surface while surrounded by a protective atmosphere. Coating and finishing are effected by any conventional method. A sample from a heat of a low alloy steel having a nominal composition of about 0.05% carbon, 2% chromium, 2% aluminum, 1% silicon, 0.5% titanium, about 0.3% manganese and remainder substantially iron, was subjected to a conventional Selas-type process of heating to about 1200°F with an atmosphere containing 3% excess combustibles, followed by treatment in a reducing section at about 1600°F for three minutes in an atmosphere of 25% hydrogen and 75% nitrogen, having a dew point of −60°F. Another sample of the same heat was treated in accordance with the method of the present invention by heating to a temperature of 1500°F in a direct fired furnace having no combustibles and 2% excess O₂, followed by the same treatment in the reducing furnace as that set forth above.

These samples were subjected to surface analysis by an Auger Spectrometer made by Physical Electronics, Inc. An Auger spectrum was obtained for each sample surface. Each sample was then sputter etched with an argon ion gun, and simultaneously the amounts of certain elements present were monitored using the multiplexing feature of the system. This gave an elemental concentration profile as a function of depth from the surface of each sample. After a certain period of sputter etching a second Auger spectrum was run for comparison with the initial surface spectrum.

The most marked difference between the two Auger spectra of the initial surfaces of each sample was that the surface of the conventionally treated sample showed about 10 times more aluminum, less iron and slightly more oxygen present than did the surface of the sample treated in accordance with the present invention. After sputter etching for 15 minutes at a nominal 80 A/min rate, the conventionally treated sample showed significantly less aluminum and oxygen and more iron than the initial surface of that sample. After sputter etching the sample treated in accordance with the method of the invention for 12 minutes at a nominal 25 A/min rate, this sample showed little change in the aluminum content as compared to its initial surface, although iron increased and oxygen decreased substantially.

Reference is made to FIG. 2C, which represents diagrammatically, and to FIG. 2D, which represents graphically, the surface condition of the above sample subjected to conventional Selas-type treatment, derived from the data of the Auger spectra. It will be noted that a layer of oxides of the alloying elements is formed on the surface of the sample (i.e., external oxidation), whereas the alloy content drops sharply to a lower value of short distance inwardly from the surface (FIG. 2D). This shows the diffusion or migration of alloying elements to the surface. Thereafter, as distance from the surface increases, the content of the alloying elements gradually increases, thus showing some tendency for alloying elements in the internal lattice of the steel to diffuse to the surface. This is to be contrasted with FIGS. 1C and 1D showing the behavior of a sample containing less than a critical content and thus exhibiting internal oxidation.

Reference is made to FIG. 3B representing diagrammatically the surface condition of the above sample after heating in an atmosphere oxidizing to iron in accordance with the process of the invention. A surface layer is formed comprising iron oxide and oxides of the alloying elements uniformly dispersed, or in solid solution, in the iron oxide layer. FIG. 3C represents diagrammatically, and FIG. 3D represents graphically, the surface condition after the reducing treatment, derived from the data of the Auger spectra. FIG. 3D shows that the concentration of alloying elements at the surface is substantially less than in the corresponding stage of the conventional treatment shown in FIG. 2D.

The mathematics for internal oxidation have been established in the following articles:

C. Wagner, "Zeit. Elektrochem.", 63, pp 772-790 (1958)
R. A. Rapp, "Corrosion", 21, pp 382-401 (1965)
In order to permit simplification in the mathematics, a special case will be assumed in which aluminum is the alloying element and in which:

$$\frac{N_a}{N_f} << \frac{D_f}{D_0} << 1$$

where

- $N_a$ = oxygen mole fraction established at the surface
- $N_f$ = original mole fraction soluble Al
- $D_f$ = diffusivity of Al
- $D_0$ = diffusivity of O

The rate of internal oxidation is given by

$$\xi = 2y(D_0)^{1/2}$$

where

- $\xi$ = depth of penetration of internal oxide
- $t$ = time

$$\gamma = \frac{(\pi/4)^{1/2} \times D_0^{1/2} \times N_a^{1/2}}{2 \nu \times D_0^{1/2} \times N_f^{1/2}}$$

with

- $\nu$ = stoichiometric ratio of oxygen to aluminum atoms in $\text{Al}_2\text{O}_3$, i.e., $\nu = 3/2$

It has been determined experimentally in the above-mentioned article by Rapp that when the volume fraction of aluminum oxide is less than 0.3 internal oxidation results, but when the volume fraction of aluminum oxide is greater than this value, external oxidation occurs with formation of an aluminum oxide layer on the surface. The final working equation which determines the critical content of aluminum tolerable without the occurrence of external oxidation is as follows:

$$N_t = \left(\frac{0.3 \times \pi \times D_0 \times N_a^{1/2} \times V_{Al}}{2 \times \nu \times D_0^{1/2} \times V_{Al/2}}\right)^{1/2}$$

where

- $V_{Al}$ = molar volume of body-centered-cubic iron,
- $V_{Al/2}$ = molar volume of Al $\text{O}_3$ (i.e. one half of molar volume of $\text{Al}_2\text{O}_3$).

Assuming a temperature of 1600°F and an atmosphere of 25% hydrogen and 75% nitrogen with a dew point of -60°F the oxygen partial pressure is calculated to be 1.08 x 10^-24 atmosphere. Using results published in an article by J.H. Swisher and E.G. Turkdogan in Trans. Met. Soc. AIME, 239, pp. 426-431 (1967) on the solubility of oxygen in body-centered-cubic iron, a value of equilibrium oxygen solubility ($N_a^{1/2}$) of 2.73 x 10^-9 is obtained. Using published data* for $D_0$, $D_f$, $V_{Fe}$, and $V_{Al}^{1/2}$, a value of 0.05% aluminum is calculated which represents the critical level for the above operating conditions. More than 0.05% aluminum would result in an external aluminum oxide layer or scale, while less than 0.05% aluminum would produce an internal oxide of aluminum precipitated uniformly in an iron matrix.


As will be apparent from the above equation, an increase in the dew point of the gas (which would increase $N_a^{1/2}$) would result in an increase in the critical aluminum content which could be tolerated and still avoid formation of an external aluminum oxide scale. In other words, a higher oxidizing potential raises the critical aluminum content.

Reference is made to FIG. 4 which is a graphic representation of the relation of hydrogen content and dew point to the critical aluminum content in body-centered-cubic iron at a temperature of 1600°F. An aluminum content in the area beneath each curve results in internal oxidation, while an aluminum content above each curve results in external oxidation with consequent formation of a difficulty reducible oxide layer or scale. The curves of FIG. 4 are plotted from equation (1) above. It is apparent that relatively slight increases in the hydrogen content sharply reduce the critical aluminum content at the lower hydrogen levels.

It is desired to emphasize at this point that the above equation and the graph of FIG. 4 are not a definition of or limitation on the present invention. Rather, these make it possible to predict in a quantitative manner when and why external oxidation may occur in conventional fluxless hot dip metallic coating operations. The present invention makes it possible to avoid external oxidation when the critical aluminum content exceeds that which could be tolerated under conventional or normal conditions. In other words, the equation and graph of FIG. 4 can be used to ascertain whether a steel of any given composition may be processed in conventional manner or whether it must be processed in accordance with the present invention in order to obtain good wettability by the molten coating metal and good adherence of the coating.

The above equation, while not exact, can also be utilized (with appropriate substitutions) to calculate the concentrations of other elements such as titanium, silicon and chromium, which form oxides more stable than iron oxide. If more than one of such elements is present, the critical content of the element which forms the most stable oxide (aluminum) should first be calculated, followed in order by calculations of the critical contents of titanium, silicon and chromium. If none is present in an amount near the critical content, external oxidation should not occur under conventional processing conditions unless two or more elements exhibit a synergistic or cumulative effect, with the fractions of critical contents adding up to a total greater than the critical content of any one element.

A coil of strip of the above 2% Cr - 2% Al - 1% Si - 0.5% Ti steel treated in accordance with the method of the invention was coated in a Selas-type commercial aluminum coating line. The strip surface was readily wetted by the molten aluminum, and the solidified coating exhibited excellent adherence to the base metal strip.

For comparison, another coil of the same low alloy steel was subjected to conventional pretreatment followed by coating in the same commercial aluminum coating line. This strip was not wettable by the molten aluminum, and the final product was thus unacceptable. The treatment conditions for these coils are summarized in Table I.

3,925,579
A series of nine laboratory heats was prepared with pure iron as a base and to each of which a different amount of aluminum or silicon was added. These samples were then rolled to strip thickness and coated with molten aluminum in a Selas-type continuous coating line. Furnace conditions were in accordance with conventional practice in that the direct fired preheat furnace atmosphere contained 6% combustibles and the temperature to which the strips were heated in the preheat furnace was 1275°F. Critical contents of aluminum and silicon were calculated from equation (1) above for the furnace conditions.

Metallographic examination of the coated samples showed that in all instances where the aluminum or silicon content was less than the theoretical critical amount, as determined from equation (1), the materials were completely wetted by the molten aluminum of the coating bath. In all cases where the aluminum or silicon content was equal to or greater than the theoretical critical content, metallurgical examination showed a lack of wetting as evidenced by areas which did not contain an iron-aluminum intermetallic alloy layer.

Additional samples from all nine heats were then coated on the same Selas-type coating line under furnace conditions contemplated in the process of the present invention. The preheater was adjusted to provide 3% excess \( O_2 \) and no combustibles in the furnace atmosphere and samples were heated to slightly above 1500°F, thereby creating conditions strongly oxidizing to iron. These furnace conditions resulted in complete wetting by molten aluminum of all heats, even those which exhibited uncoated areas under conventional processing conditions. The results of these tests are summarized in Table II.

It is apparent from these tests that merely heating a steel to a temperature above that used in conventional processing is not effective if the atmosphere is not oxidizing to iron at the temperature involved. It is further evident from the Auger spectra reported above that the process is equally effective for aluminum-and/or-silicon-killed steels and for steels containing greater amounts of alloying elements, e.g., up to about 3% aluminum, up to about 5% chromium, up to about 2% silicon, up to about 1% titanium, and mixtures thereof. Moreover, although the process of the invention has particular utility in alumining steels containing the specific alloying elements cited above, it is not so limited and is effective for fluxless hot-dip coating by any commonly-used coating metal of a ferrous metal strip or sheet containing an alloying element or elements more readily oxidizable than iron.

Coating metals which may be used include, but are not limited to, those described in U.S. Pat. No. 2,784,122 issued Mar. 5, 1957 to N. Cox et al., at column 2, lines 9–33; and in U.S. Pat. 2,839,455, issued June 17, 1958 to H. La Tour et al., at column 1, lines 68–72 and column 2, lines 1–7. The disclosures of these patents are incorporated herein by reference.

### Table I

<table>
<thead>
<tr>
<th>Pretreatment Conditions</th>
<th>Present Invention</th>
<th>Conventional Practice</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st Trial</td>
<td>2nd Trial</td>
</tr>
<tr>
<td>(1) Combustion Ratios</td>
<td>2.6% excess ( O_2 )</td>
<td>2.8% excess ( O_2 )</td>
</tr>
<tr>
<td>preheat section</td>
<td>1550°F</td>
<td>1500°F</td>
</tr>
<tr>
<td>(2) Strip Temp. after</td>
<td>1800°F</td>
<td>1750°F</td>
</tr>
<tr>
<td>preheater</td>
<td>1800°F</td>
<td>1750°F</td>
</tr>
<tr>
<td>(3) Radiant Tube Zones</td>
<td>150 fpm</td>
<td>145 fpm</td>
</tr>
<tr>
<td>(4) Line Speed</td>
<td>1750°F</td>
<td>1500°F</td>
</tr>
<tr>
<td>(5) Strip Temp. after</td>
<td>5000 cfh</td>
<td>5000 cfh</td>
</tr>
<tr>
<td>Radiant Tube</td>
<td>+15°F</td>
<td>-20°F</td>
</tr>
<tr>
<td>(6) Hydrogen in</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reducing Section</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7) Dew Point at bottom</td>
<td></td>
<td></td>
</tr>
<tr>
<td>of Slow Cool Zone</td>
<td></td>
<td></td>
</tr>
</tbody>
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### Table II

#### Aluminum-Coated Low Alloy Steels

<table>
<thead>
<tr>
<th>Samples</th>
<th>% Al</th>
<th>CONDITION I</th>
<th>CONDITION II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(0.15% Al Critical)*</td>
<td></td>
</tr>
<tr>
<td>A-1</td>
<td>0.008</td>
<td>Good coating**</td>
<td>Good coating</td>
</tr>
<tr>
<td>A-2</td>
<td>0.036</td>
<td>Good coating</td>
<td>Good coating</td>
</tr>
<tr>
<td>A-3</td>
<td>0.22</td>
<td>Uncoated areas*** (0.41% Si Critical)*</td>
<td>Good coating</td>
</tr>
<tr>
<td>B-1</td>
<td>1.28</td>
<td>Uncoated areas**</td>
<td>Good coating</td>
</tr>
<tr>
<td>B-2</td>
<td>0.18</td>
<td>Good coating</td>
<td>Good coating</td>
</tr>
<tr>
<td>B-3</td>
<td>0.027</td>
<td>Good coating</td>
<td>Good coating</td>
</tr>
<tr>
<td>C-1</td>
<td>0.70</td>
<td>Uncoated areas**</td>
<td>Good coating</td>
</tr>
<tr>
<td>C-2</td>
<td>0.12</td>
<td>Good coating</td>
<td>Good coating</td>
</tr>
<tr>
<td>C-3</td>
<td>0.003</td>
<td>Good coating</td>
<td>Good coating</td>
</tr>
</tbody>
</table>

#### Treatment Conditions

<table>
<thead>
<tr>
<th>STRIP TEMP. AFTER</th>
<th>Preheater</th>
<th>% EXCESS ( O_2 )</th>
<th>% ( H_2 )</th>
<th>D.P.</th>
<th>MAXIMUM STRIP TEMP.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREHEATER</td>
<td>COMBUSTIBLES</td>
<td>1275°F</td>
<td>6</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

#### Critical Contents

- **Table I:**
  - Low Alloy Strip .050 in thickness x 48 in Width - nominal 2% Cr, 2% Al, 1% Si, 0.5% Ti, 0.5% C, 0.3% Mn, balance Fe
  - Pretreatment Conditions:
    - Combustion Ratios preheat section: 2.6% excess \( O_2 \), 2.8% excess \( O_2 \) for both 1st and 2nd Trial.
    - Strip Temp. after preheater: 1550°F for 1st Trial, 1500°F for 2nd Trial.
    - Hydrogen in Reducing Section: 5000 cfh.
    - Dew Point at bottom of Slow Cool Zone: +15°F, -20°F.

- **Table II:**
  - Aluminum-Coated Low Alloy Steels: Metallographic Examination For Coating-Base Metal Diffusion Layer
  - Samples: A-1, A-2, A-3, B-1, B-2, B-3, C-1, C-2, C-3
  - Condition I: % Al, % Si
  - Condition II: Good coating, Good coating, Uncoated areas, Good coating, Good coating, etc.
  - Treatment Conditions: Strip Temp. after Preheater: 1275°F, Combustibles: 6, % Excess \( O_2 \): 0, % \( H_2 \): 100, D.P.: +15°F, Maximum Strip Temp.: 1500°F, % Al: 0.15, % Si: 0.41
As indicated above, in its broadest aspects, the method of the invention comprises heating a low alloy steel containing alloying elements more readily oxidizable than iron in an atmosphere oxidizing to iron under conditions which form on the steel a surface layer of iron oxide containing a dispersion of oxides of the alloying elements, then further treating the steel under conditions reducing to iron oxide. When the initial heating step is carried out in accordance with the Selas-type process, the steel is preferably heated to a temperature of about 1400°F to about 1600°F in an atmosphere of gaseous products of combustion containing 0% to 6% excess O₂, preferably about 2% excess O₂, and no combustibles. In the subsequent reducing section the steel is preferably brought to a temperature of about 1500°F to about 1700°F in an atmosphere containing hydrogen, preferably at least about 20% hydrogen. The steel is then cooled to appropriate bath entry temperature while still protected by the hydrogen-nitrogen atmosphere, the dew point of which must be consistent with carbon steel practice.

It will be understood that the strip bath entry temperature and maximum dew point of the hydrogen-nitrogen atmosphere in the furnace are dependent on the type of coating metal (i.e., the minimum strip temperature prior to bath entry). In general the strip is brought to a temperature ranging from slightly less than to slightly higher than that of the coating metal bath. When coating with aluminum a dew point not higher than about 50°F should be observed. When galvanizing, a maximum dew point of about 15°F should be observed because of the lower strip temperature. For aluminizing, typical strip bath entry temperatures are about 1250°F to 1350°F, while for galvanizing, typical strip bath entry temperatures are about 850°F to 950°F.

In a new installation the advantages of rapid strip heating, adaptability to processing different types of steel, and furnace pressure control clearly favor the use of a Selas-type installation. However, as indicated above, the method of the invention is equally applicable to a Sendzimir-type process, and existing installations of this type can be readily adapted for operation in accordance with the method of this invention. Basically, the only difference is to heat the steel in the oxidizing furnace to a temperature of 1100°F or greater, preferably to 1300°F. The conditions in the reducing section remain unchanged.

The lower strip preheat oxidizing temperature range for the Sendzimir-type process as compared to the Selas-type process is accounted for by the differences in atmosphere composition to which the strip is exposed. Thus, to produce a given thickness of surface oxide, a lower temperature is required when strip is heated in the Sendzimir oxidizing furnace and exposed to air than with the Selas-type system where the strip is exposed only to oxidizing products of combustion prior to direct entry into the reducing furnace.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of enhancing the wettability by a molten coating metal of the surface of a low alloy steel strip and sheet stock containing alloying elements more readily oxidizable than iron, chosen from the group consisting of aluminum, titanium, silicon, chromium, and mixtures thereof, said alloying elements being present in amounts greater than the critical contents thereof as calculated from the following equation wherein aluminum and aluminum oxide are used as illustrative of the alloying element:

\[
N_R = \left( \frac{0.3 \times \pi \times D_v \times N_{O_2} \times V_{\text{org}}}{2 \times \pi \times D_v \times V_{AIO_3/2}} \right)^{\frac{1}{3}}
\]

where

- \(N_{O_2}\) = initial mole fraction soluble at
- \(D_v\) = diffusivity of oxygen
- \(N_{O_2}\) = oxygen mole fraction established at the surface
- \(V_{\text{org}}\) = molar volume of body-centered-cubic iron
- \(V_{AIO_3/2}\) = molar volume of AIO₃/2

comprising the steps of passing said stock continuously through a furnace in which said stock is heated to a temperature of about 1100°F to 1675°F in an atmosphere oxidizing to iron whereby to form on said stock a surface layer of iron oxide containing oxides of said alloying elements, dispersed or in solid solution therein, and subjecting said stock to further heat treatment in a hydrogen-containing atmosphere having a dewpoint which makes said atmosphere reducing to iron oxide within the temperature range of 800°F to 1700°F whereby to reduce said surface layer to a substantially pure iron matrix containing a uniform fine dispersion of said oxides of said alloying elements.

2. The method claimed in claim 1, wherein said furnace is heated by direct combustion of fuel and air therein to produce an atmosphere of gaseous products of combustion containing 0 to 6% excess oxygen and no excess combustibles, and wherein said stock is withdrawn from said furnace while still surrounded by said atmosphere at a temperature of about 1400°F to about 150°F.

3. The method claimed in claim 2, wherein said coating metal is aluminum, zinc, or alloys thereof, and wherein said steel, after withdrawal from said furnace, is brought to a temperature of about 1500°F to about 1700°F in a hydrogen-nitrogen atmosphere comprising at least about 20% hydrogen.

4. The method claimed in claim 3, wherein said coating metal is aluminum or alloys thereof, wherein said steel is cooled approximately to the temperature of the molten coating metal bath and introduced into said bath while still surrounded by said hydrogen-nitrogen atmosphere, said atmosphere having a maximum dew-
point of about 50° F.

5. The method claimed in claim 3, wherein said coating metal is zinc or alloys thereof, wherein said steel is cooled approximately to the temperature of the molten coating metal bath while still surrounded by said hydrogen-nitrogen atmosphere, said atmosphere having a maximum dewpoint of about 15° F.

6. The method claimed in claim 1, wherein said furnace is heated without atmosphere control, and wherein said stock is withdrawn from said furnace into air at a temperature of about 1100° to about 1400° F.

7. The method claimed in claim 6, wherein said coating metal is aluminum, zinc, or alloys thereof, and wherein said steel, after contacting air, is brought to a temperature of about 1500° to about 1700° F in a hydrogen-nitrogen atmosphere comprising at least about 20% hydrogen.

8. The method claimed in claim 7, wherein said coating metal is aluminum or alloys thereof, wherein said steel is cooled approximately to the temperature of the molten coating metal bath and introduced into said bath while still surrounded by said hydrogen-nitrogen atmosphere, said atmosphere having a maximum dewpoint of about 50° F.

9. The method claimed in claim 7, wherein said coating metal is zinc or alloys thereof, wherein said steel is cooled approximately to the temperature of the molten coating metal bath while still surrounded by said hydrogen-nitrogen atmosphere, said atmosphere having a maximum dewpoint of about 15° F.

10. The method of claim 1, wherein said low alloy steel contains up to about 3% aluminum, up to about 1% titanium, up to about 2% silicon, and up to about 5% chromium.

11. The method of claim 10, wherein said furnace is heated by direct combustion of fuel and air therein to produce an atmosphere of gaseous products of combustion containing 0% to 6% excess oxygen and no excess combustibles, and wherein said stock is withdrawn from said furnace while still surrounded by said atmosphere at a temperature of about 1400° to about 1675° F.

12. The method claimed in claim 10, wherein said furnace is heated without atmosphere control, and wherein said stock is withdrawn from said furnace into air at a temperature of about 1100° to about 1400° F.

13. The method claimed in claim 10, wherein said coating metal is aluminum, zinc, or alloy thereof.

14. In the method of fluxless hot dip metallic coating of low alloy steel strip and sheet stock containing at least one alloying element in uncombined form chosen from the group consisting of up to about 3% aluminum, up to about 1% titanium, up to about 2% silicon, up to about 5% chromium, and mixtures thereof, said alloying element being present in an amount greater than the critical content thereof as calculated from the following equation wherein aluminum and aluminum oxide are used as illustrative of the alloying element:

\[
N_{Al} = \left[ \frac{0.3 \times \pi \times D_{O} \times N_{Al}^{0.8} \times V_{Fe}}{2 \times \nu \times D_{Al} \times V_{AlO_{2/3}}} \right]^{1/2}
\]

where

- \( N_{Al} \) = original mole fraction soluble Al
- \( D_{O} \) = diffusivity of oxygen
- \( N_{Al}^{0.8} \) = oxygen mole fraction established at the surface
- \( V_{Fe} \) = molar volume of body-centered-cubic iron
- \( \nu \) = stoichiometric ratio of oxygen to aluminum atoms in Al, O
- \( D_{Al} \) = diffusivity of Al
- \( V_{AlO_{2/3}} \) = molar volume of AlO_{2/3}

wherein the surface of said stock is prepared for coating by a continuous preliminary treatment involving heating under conditions producing an oxide coating on said surface, followed by further heat treatment under conditions reducing to iron oxide, and wherein the stock is thereafter passed into a molten metal coating bath while surrounded by a protective atmosphere, the improvement which comprises heating said stock in the first said heating step to a temperature of about 1100° to about 1675° F in an atmosphere oxidizing to iron whereby to produce a surface layer of iron oxide containing a uniform dispersion or solid solution of oxides of said alloying elements.

15. The method of claim 14, wherein said first heating step is conducted in a furnace heated by direct combustion of fuel and air therein and in an atmosphere of gaseous products of combustion containing 0 to 6% oxygen and no excess combustibles, and wherein said stock is withdrawn from said furnace while still surrounded by said atmosphere at a temperature of about 1400° to about 1675° F.

16. The method claimed in claim 14, wherein said first heating step is conducted in a furnace without atmosphere control, and wherein said stock is withdrawn from said furnace into air at a temperature of about 1100° to about 1400° F.