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[54] **ALUMINUM COATED STEEL**

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[51] **Int. Cl.** **B32b 15/00**

[58] **Field of Search** ..... 29/196.2; 117/114 C, 71 M; 148/31.5

[56] **References Cited**

UNITED STATES PATENTS

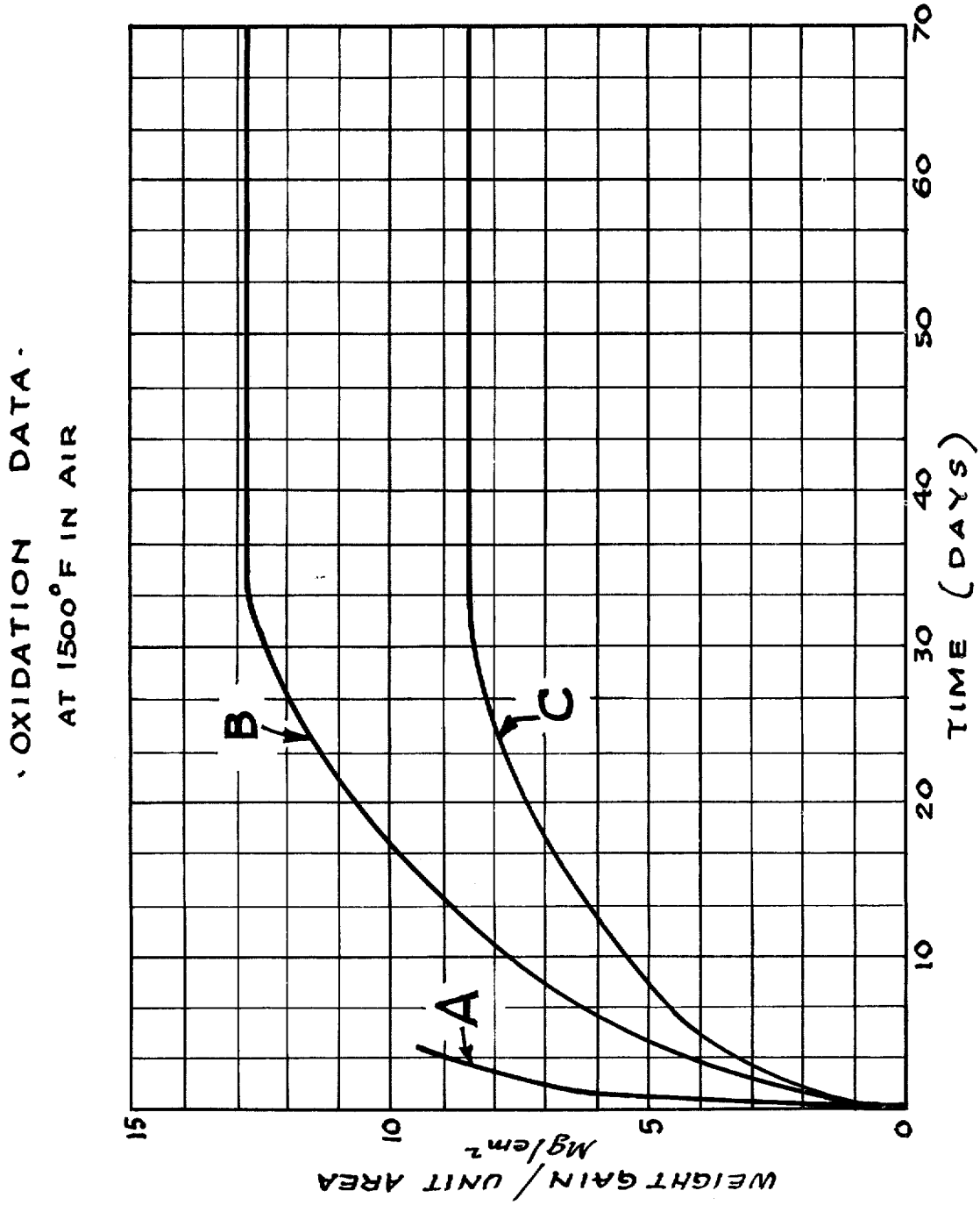
3,705,023	12/1972	Fister	75/123 B X
3,754,874	8/1973	Anderson	29/196.2 X

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[57] **ABSTRACT**

An aluminum coated low alloy low-carbon steel sheet material having increased resistance to oxidation at elevated temperatures of about 1,500 F which is formed by incorporating in a low-carbon steel before rolling and hot-dip aluminum coating an amount of aluminum between about 0.5 and 2 percent by weight and silicon in an amount between about 0.5 and 2 percent by weight, with the ratio of aluminum of silicon being between about 0.5 to about 1.5. Metals which have strong carbide and oxide forming properties, particularly chromium and titanium, can also be used in combination with the low-carbon aluminumsilicon steel in an amount which preferably does not exceed about 2 percent by weight of the steel.

15 Claims, 1 Drawing Figure


OXIDATION DATA
AT 1500°F IN AIR
WEIGHT GAIN / UNIT AREA
mg/cm²
0
5
10
15
TIME (DAYS)
10
20
30
40
50
60
70
A
B
C

ALUMINUM COATED STEEL

The present invention relates generally to a low alloy steel article having a non-ferrous metal protective coating and more particularly to an aluminum coated low alloy steel strip or sheet having increased resistance against oxidation at elevated temperatures.

It is economically important to be able to increase the resistance of steel oxidation at elevated temperatures in an inexpensive manner and without employing large amounts of costly alloying elements in the steel or in a protective coating applied thereto, while at the same time using conventional apparatus and coating procedures.

One method of increasing the oxidation resistance of steel has been to provide an aluminum surface coating, such as by continuously hot-dip aluminum coating a steel strip or sheet. However, when an aluminum coating containing silicon (Type I aluminum) is applied to steel and heated, excessive subsurface oxidation of the steel (i.e., oxidation of the steel below the aluminum coating) occurs at temperatures above 1,300°F, so that such aluminum coated steels are unsuited for prolonged service at temperatures above 1,300°F. Also, a typical aluminum coated mild steel, such as AISI 1008 steel, having a substantially pure aluminum coating (Type II aluminum) is not recommended for continuous usage at temperatures above about 1,300°F.

Previously, efforts have been made to improve the oxidation resistance and other properties of aluminum coated steel bases by incorporating various alloying elements in the steel base to be aluminum coated. Thus, U.S. Pat. No. 2,752,268 teaches that the adherence of an aluminum coating on a steel base is improved by incorporating minor amounts of molybdenum or tungsten in the steel base. It has also been disclosed in U.S. Pat. application Ser. No. 438,791, filed Feb. 1, 1974 that a mild steel base containing a small amount of free titanium when aluminum coated exhibits markedly improved high termperature oxidation resistance. U.S. Pat. No. 3,059,326 teaches that in order to impart significant, high temperature oxidation resistance to the steel aluminum should be incorporated in the steel in an amount between about 3 percent and 12 percent by weight and thereafter aluminum coating the shaped steel and heating to diffuse the aluminum coating into the steel and form an iron-aluminum alloy outer layer or casing on the aluminum alloy steel. However, the poor mechanical properties of the iron-aluminum alloy surface layer having a high aluminum content seriously limits formability and thus restricts the use of such diffusion coated aluminum alloy steel bases as an engineering material for high temperature operations. Production difficulties are also encountered with alloys containing as little as 4 percent by weight aluminum, and the surface of the aluminum alloy steel having such a high aluminum content is not readily wetted by molten aluminum in a hot-dip aluminum coating process.

It is, therefore, an object of the present invention to provide an aluminum coated low alloy steel article which is readily formable and has increased resistance to oxidation when heated to an elevated temperature.

It is a further object of the present invention to provide an improved process of producing an aluminum coated low alloy steel strip having increased resistance to oxidation of the steel when heated to an elevated temperature.

It is also an object of the present invention to provide a continuous hot-dip aluminum coated low alloy steel product having good formability and increased resistance to oxidation when heated at an elevated temperature which can be produced economically by conventional procedures and apparatus.

Other objects of the invention will be apparent to those skilled in the art from the detailed description and claims to follow when read in conjunction with the accompanying drawing.

It has been found that an aluminum coated low alloy steel sheet having good formability and increased resistance to oxidation when heated at an elevated temperature in an oxidizing atmosphere can be provided economically without using large amounts of expensive alloying elements in either the aluminum coating or in the steel base by incorporating in the steel before aluminum coating small amounts of both aluminum and silicon each in an amount less than about 2 percent by weight of the steel and with the ratio of aluminum to silicon being between about 0.5 and about 1.5. In addition, the said low alloy aluminum and silicon containing steel can have incorporated therein small amounts of one or more metals which have strong carbide forming properties and which preferably are also strong oxide formers selected from the group consisting of titanium, molybdenum, zirconium, hafnium, vanadium and chromium.

In accordance with the above described invention it has been found that high temperature oxidation resistance can be imparted to a mild steel, such as a low-carbon steel preferably having a maximum of about 0.1 percent by weight carbon, by incorporating in the steel before aluminum coating an amount of aluminum and silicon which, respectively, preferably does not exceed about 2 percent by weight. By incorporating the combination of aluminum and silicon in a mild steel and thereafter aluminum coating the resulting low alloy steel base or sheet greater high temperature oxidation resistance is imparted to the aluminum coated steel than is provided when only aluminum is incorporated in the steel. The surface coating which is formed when coating the steel with aluminum, such as a Type I aluminum coating, will contain oxides of both aluminum and silicon and form a protective surface coat which is more resistant to penetration by oxygen than a coating which contains only oxides of aluminum. And, by providing a reservoir of silicon as well as aluminum in the steel base, it is possible to replenish and maintain the integrity of the more dense aluminum-silicon oxide surface coating during service in a high temperature oxidizing atmosphere. In the event the surface coating is broken, silicon as well as aluminum diffuse from the base steel to the surface and reform the desired dense protective silicon and aluminum oxide surface film. The silicon and aluminum in the steel being strong oxide formers, also have the important property of preventing the formation of a continuous subsurface barrier layer containing iron oxide which is normally formed below the surface of an aluminum coated carbon steel on heating for prolonged periods at an elevated temperature of about 1,500°F in an oxidizing atmosphere.

The addition of small amounts of a strong carbide forming metal selected from the group consisting of titanium, molybdenum, zirconium, hafnium, vanadium and chromium to a mild steel containing aluminum and

silicon in accordance with the present invention serves the dual function of improving the metallurgical strength of the steel and further improving the oxidation resistance of the aluminum coating. Thus, the above metals by combining with the residual carbon in the steel reduce the amount of carbon available for combining with oxygen present or diffusing through the aluminum surface caoting and forming carbon monoxide gas which has a disruptive effect on the aluminum surface coating. Furthermore, it appears that free carbon in steel significantly blocks the diffusion of silicon and aluminum into the base steel, resulting in the formation of a thick intermetallic layer which remains for a considerable period of time below the surface of an aluminum coating during exposure in a high temperature oxidation atmosphere. When the aluminum coated product cools down rapidly, as when it is subjected to cyclic oxidation, the thick intermetallic layer cracks due to the difference in the thermal expansion coefficient between the steel base and the intermetallic layer, thereby reducing the oxidation resistance of the coated product. The metals of the above specified group, such as titanium and chromium, appear to improve the oxidation resistance of an aluminum coated product by significantly increasing the rate of diffusion of both aluminum and silicon into the steel base, as a result of the added metals combining with the carbon in the steel, and the intermetallic layer does not remain for an extended period as a thick fragile subsurface layer. It should be apparent from the foregoing that the added metals are preferably used in an amount sufficient to combine with all the free carbon in the steel, but having the said metals present in an amount sufficient to have one or more of the said metals in the free or uncombined form can provide additional benefits due to their strong oxide forming properties. In general, the metals added to the aluminum-silicon low alloy mild steel base will be between about 0.5 to 2.0 percent by weight of the steel.

A preferred method of aluminum coating a steel strip containing aluminum and silicon in accordance with the present invention is by a hot-dip coating process generally known in the art as a Sendzimir-type process, wherein a continuous steel sheet or strip which is free of scale and rust is fed continuously from a coil through a furnace containing an oxidizing atmosphere maintained at a temperature between about 330°F and 930°F which burns off any oil residue on the surface of the strip and forms a thin surface oxide film. The oxide coated steel sheet then passes through a furnace containing a reducing atmosphere, such as the hydrogen-containing HNX atmosphere, having a temperature between about 1,500°F and 1,800°F; whereby the oxide coating on the strip is reduced to form a surface layer of metal free of non-metallic impurities to which molten aluminum readily adheres. Following the reducing step, the strip is fed into a hot-dip aluminum coating bath through a protective hood which prevents the reduced metal surface being oxidized before entering the coating bath. The aluminum coating bath, for example, can be substantially pure aluminum (Type II aluminum coating), but preferably is an aluminum rich silicon alloy containing up to 11 percent by weight silicon (Type I aluminum coating). After leaving the hot-dip aluminum coating bath, the coating thickness on the strip is regulated by a pair of oppositely disposed thickness-regulating jet wipers or rolls which produce a uniform thin aluminum coating, and the strip is cooled by any suitable means. The aluminum coated strip is then wound into a coil. Conventional Sendzimir-type process apparatus can be used in each of the processing steps.

The step of burning off the oil and oxidizable combustible material on the surface of the steel strip before the strip is subjected to the reducing atmosphere can be omitted, if desired, provided the strip is otherwise thoroughly cleaned, immediately prior to the reducing step, as by conventional alkaline cleaning and pickling.

The steel base of the type generally used in the present invention, before incorporating any aluminum, silicon, or carbide forming element, is a low-carbon steel which has a carbon content of about 0.25 weight percent maximum and preferably has from about 0.03 weight percent to about 0.1 weight percent carbon. The low-carbon steel generally used in the present invention before the addition of the alloying elements will contain from about 0.2 weight percent to about 1.0 weight percent manganese, a maximum of about 0.05 weight percent sulfur, a maximum of about 0.04 weight percent phosphorus, about 0.002 weight percent silicon, a maximum of about 0.090 weight percent aluminum, and the balance being iron with the usual amount of impurities and residuals.

A typical low-carbon steel suitable for hot or cold rolling into sheets and hot-dip aluminum coating in which the silicon, aluminum and the added carbide forming elements are incorporated in accordance with the present invention has the following approximate composition:

	Percent by Weight
C	0.03–0.05
Mn	0.30–0.50
S	0.030
P	0.02
Si	0.002
Al	0.030–0.090
Fe	balance

The composition of the resulting steel base after addition of the alloying elements remains unchanged except for the increased concentration of aluminum, silicon, and added carbide forming elements.

The following Table I shows the amount of alloying elements which when added in accordance with the present invention to the above typical low-carbon steel and hot-dip aluminum coated in any conventional manner but preferably in accordance with the herein described procedures impart improved oxidation resistance when the hot-dip aluminum coated product is heated in air at 1,500°F:

TABLE I

Example No.	Amounts of Alloying Elements Added To Typical Low-Carbon Steel
1	0.60% Al + 1.20% Si
2	1.31% Al + 1.03% Si
3	0.66% Al + 1.09% Si
4	1.25% Al + 1.03% Si + 1.15% Cr
5	0.90% Al + 0.80% Si + 0.41% Ti
6	0.90% Al + 0.80% Si + 1.20% Cr + 0.45% Ti

The low alloy steel having the composition of Example 1 when hotdip aluminum coated with Type I alumi-

num and heated in an oxidizing atmosphere at 1,500°F for 64 days exhibited a weight gain of 8.55 mg. per cm. sq. as compared with a weight gain of 12.58 mg. per cm. sq. for a low-carbon aluminum alloy steel containing 0.05 percent C and 2 percent aluminum coated with the same Type I hot-dip aluminum coating.

The graphs in the accompanying drawing show the total weight gain per square centimeter due to both surface and subsurface oxidation of (1) a typical low-carbon steel (rimmed steel) sheet of the type used for hot-dip aluminum coating (Curve A), (2) a typical low-carbon steel sheet containing 2 percent by weight aluminum (Curve B), and (3) a low alloy low-carbon steel sheet containing 0.66 percent by weight aluminum and 1.2 percent by weight silicon and otherwise having the composition of a typical lowcarbon steel (Curve C), all having a Type I aluminum coating with a thickness of 2 mils and being heated cyclically in air at 1500°F over the indicated period of time. The data show that the aluminum coated low alloy low-carbon steel sheet containing Si and Al exhibits a much lower rate of oxidation than the aluminum coated conventional rimmed steel sheet significantly lower than the aluminum coated 2 percent aluminum alloy low-carbon steel product.

While the foregoing disclosure relates primarily to improving the oxidation resistance of an endless strip and sheet of steel of the type conventionally used for continuous hot-dip coating, it should be understood that the invention is not limited to steel strips and sheets, and the term "steel material" or "steel article" includes any steel material regardless to size or shape, including both hot and cold rolled steel strip material and steel wire, suitable for coating with aluminum. It will also be understood that the term "aluminum" as used in the claims is intended to cover pure aluminum which contains only traces of other elements as well as aluminum rich alloys. The term "low alloy low-carbon steel" designates a steel containing a maximum of about 0.25 percent by weight carbon and containing a maximum of about 5 percent by weight alloying elements chosen from among the elements aluminum, silicon and strong carbide and oxide formers in accordance with the herein described invention. Other methods and means for applying the aluminum coating to the steel article can also be used, as the invention is not limited to applying the aluminum by the hot-dip coating procedure specifically disclosed.

I claim:

1. An aluminum coated low alloy steel article having good formability and resistance to oxidation at elevated temperatures consisting essentially of a low alloy low-carbon steel base having incorporated therein as essential alloying elements a quantity of silicon and aluminum with each being present in an amount ranging between about 0.5 percent to about 2.0 percent by weight of said steel and the ratio of aluminum to silicon being between about 0.5 and about 1.5, and said base having on the surface thereof a coating of aluminum.

2. An aluminum coated low alloy steel article as in claim 1, wherein said steel base comprises about 0.6 percent by weight aluminum and about 1.2 percent by weight silicon.

3. An aluminum coated low alloy steel article as in claim 1, wherein said steel base comprises about 1 percent by weight aluminum and about 1 percent by weight silicon.

4. An aluminum coated low alloy steel article as in claim 1, wherein said steel base has a maximum carbon content of about 0.1 percent by weight.

5. An aluminum coated low alloy steel article as in claim 4, wherein said steel base contains not substantially in excess of about 2 percent by weight of a strong carbide former selected from the group of metals consisting of titanium, molybdenum, zirconium, hafnium, vanadium and chromium.

6. An aluminum coated low alloy steel article as in claim 5, wherein said carbide and oxide former comprises chromium in an amount of about 1 percent by weight of said steel.

7. An aluminum coated low alloy steel article as in claim 6, wherein said steel contains a maximum of about 0.5 percent by weight titanium.

8. An aluminum coated low alloy steel article as in claim 1, wherein said coating is aluminum containing up to about 11 percent by weight silicon.

9. In a method of coating a low alloy steel to form an article having good formability and high temperature oxidation resistance, the improvement comprising; coating a low alloy low-carbon steel base with aluminum to provide a surface layer of aluminum, and said steel base having incorporated therein a quantity of silicon and aluminum with each being present in an amount ranging between about 0.5 percent to about 2.0 percent by weight of said steel and the ratio of aluminum to silicon being between about 0.5 and about 1.5.

10. A method as in claim 9, wherein said steel base is coated with aluminum by immersing in a molten aluminum bath which contains up to about 11 percent by weight silicon.

11. A method as in claim 9, wherein said steel base is a low carbon steel containing a maximum of 0.1 percent by weight carbon.

12. A method as in claim 11, wherein said steel base has incorporated therein a maximum of about 2 percent by weight of a strong carbide forming metal selected from the group consisting of titanium, molybdenum, zirconium, hafnium, vanadium and chromium.

13. A method as in claim 11, wherein said steel base contains a maximum of about 0.05 percent by weight carbon, about 1 percent by weight aluminum, about 1 percent by weight silicon, and about 0.5 percent by weight titanium.

14. A method as in claim 13, wherein said steel base contains about 1.25 percent by weight chromium.

15. A method as in claim 11, wherein said steel base contains a maximum of about 0.05 percent by weight carbon, about 0.6 percent by weight aluminum and about 1.2 percent by weight silicon.

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