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Gomersall

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[54] **ALUMINUM COATED STEEL**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 205,569, Dec. 7, 1971, abandoned.

[52] **U.S. Cl.** ..... **29/196.2;** 117/71 M; 117/114 C

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

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

[56] **References Cited**

UNITED STATES PATENTS

3,059,326	10/1962	Jominy	29/196.2
3,250,611	5/1966	Lula	75/126 D

FOREIGN PATENTS OR APPLICATIONS

1,391,659	11/1965	France	75/124

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[57] **ABSTRACT**

An aluminum coated steel article, particularly steel sheet or strip material, having increased resistance to subsurface oxidation at elevated temperatures of about 1500°F is formed by incorporating in a carbon steel substrate before hot-dip aluminum coating an amount of titanium sufficient to combine with or precipitate all of the carbon in the steel and provide an excess of uncombined titanium dissolved in the steel.

19 Claims, 5 Drawing Figures

FIG.1

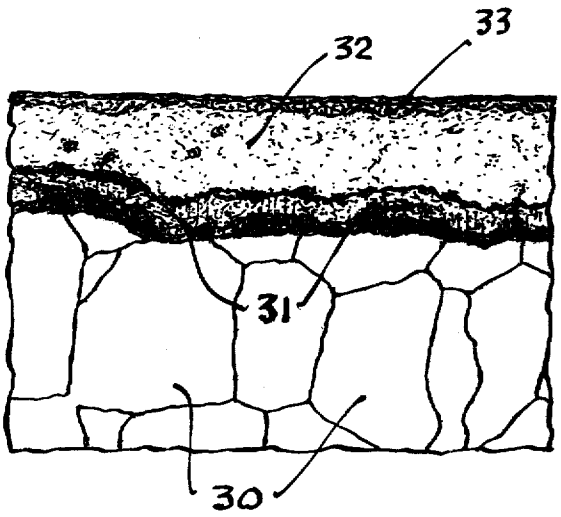
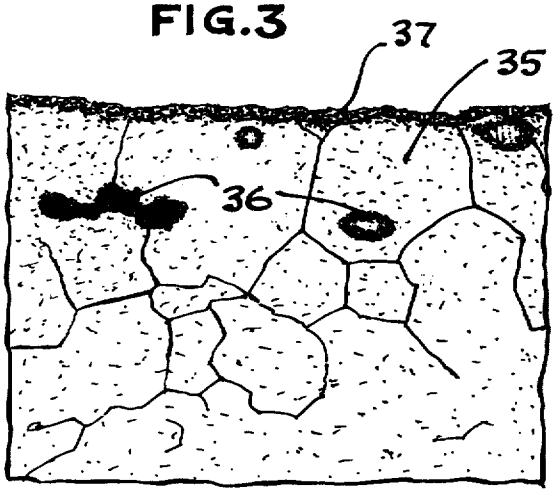


FIG.2



FIG.3



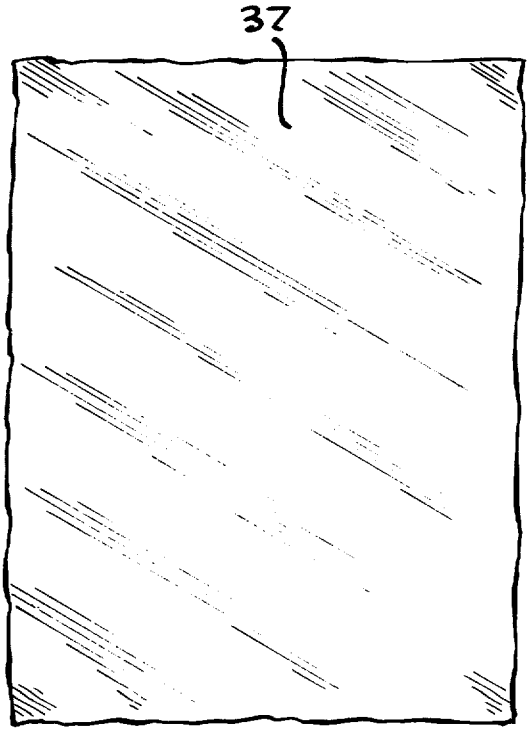
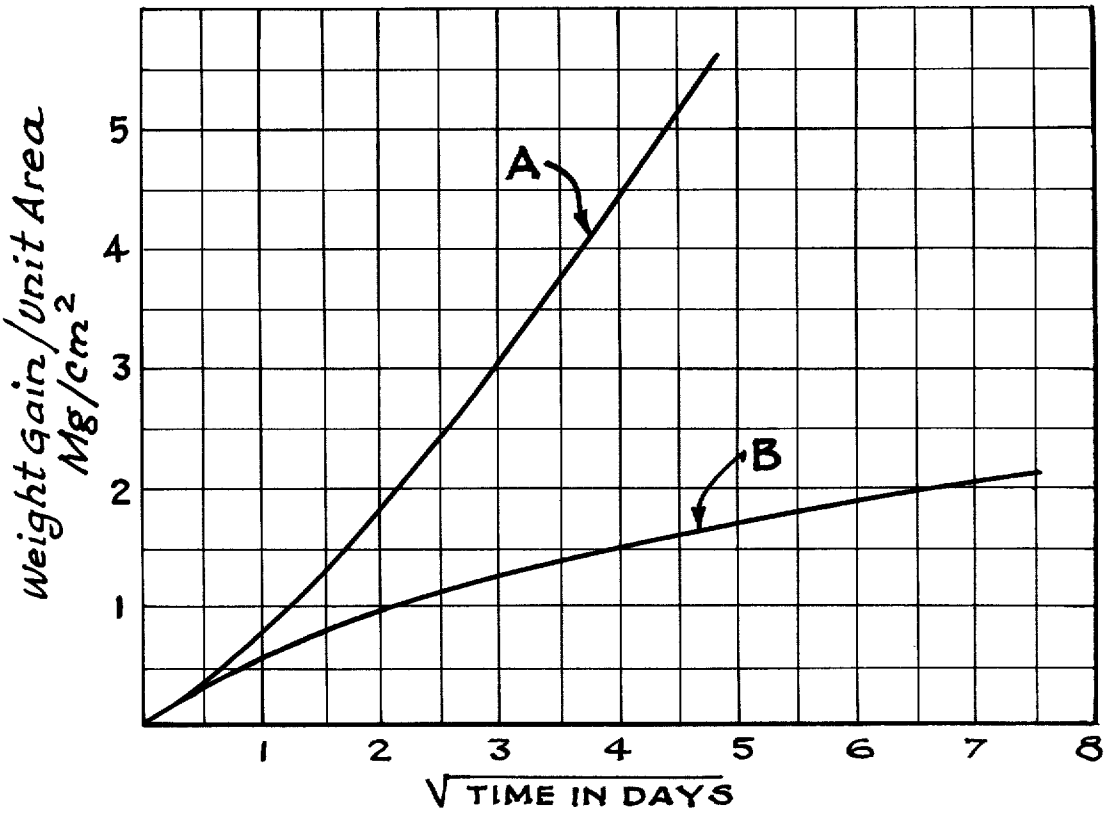


FIG.4

FIG. 5



ALUMINUM COATED STEEL

This application is a continuation-in-part of my prior application Ser. No. 205,569, filed Dec. 7, 1971, now abandoned.

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 steel strip or sheet having increased resistance against oxidation at elevated temperatures. The aluminum coated steel of the present invention is particularly suitable for use in automotive exhaust systems, e.g. an exhaust muffler.

It is important to be able to increase the resistance of steel to oxidation at elevated temperatures in an inexpensive manner and without employing large amounts of costly alloying elements, 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 plain carbon steel strip or sheet. However, when an aluminum coating containing up to about 11 wt. percent silicon (Type I) is applied to plain carbon steel and the coated product is heated while exposed to air, 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.

The piror art has also resorted to the use of special alloy steel compositions in order to provide the high temperature oxidation resistance and other physical properties required in steels to be used in fabricating components of automotive exhaust systems. Typical of such steels is a stainless steel designated in the trade as MF-1 steel. As described in the Lula et al U.S. Pat. No. 3,250,611, this material is a ferritic stainless steel containing 10.0 to 12.5 wt. percent chromium and 0.20 to 0.75 wt. percent titanium. The aluminum coated steel of the present invention is a vast improvement over MF-1 steel since it provides equal or better high temperature oxidation resistance at a much lower cost by avoiding the use of expensive chromium-containing stainless steels.

Jominy et al U.S. Pat. No. 3,059,326 discloses the use of relatively ductile iron-aluminum alloys containing 3 to 12 wt. percent aluminum for fabricating gas turbine burner liners. After fabrication, an aluminum coating is applied to the article and the coated article is subjected to a diffusion anneal to impart the required high temperature oxidation resistance. Other alloying ingredients may be used as optional additives to the ferrous base alloy in addition to the essential aluminum, but according to Jominy et al there is no beneficial effect on high temperature oxidation resistance and the effect may even be detrimental. The present invention is a substantial improvement over Jominy et al since it provides a coated steel product in sheet or strip form which has both the desired high temperature oxidation resistance and the desired fabrication characteristics and does not require the expensive and inconvenient two-step procedure of Jominy et al.

It is also suggested in the prior art to incorporate titanium in either the aluminum coating (Sprowl et al U.S. Pat. No. 3,180,716) or in a flux applied to the steel base before aluminum coating (Lundin et al U.S. Pat. Nos. 2,686,354, 2,686,355, and 2,708,304). However, the use of titanium in the aluminum coating composition does not provide the desired high temperature oxidation resistance in the coated product. Moreover, the use of a titanium-containing flux is an inconvenient and expensive procedure, and the resultant coated product does not possess the desirable combination of properties obtained with the present invention.

Accordingly, one object of the present invention is to provide a more economical aluminum coated steel article, particularly steel sheet or strip, which has improved resistance to oxidation at elevated temperatures and which avoids the need to add substantial amounts of expensive alloying elements to the base steel.

Another object of the present invention is to provide a Type I and Type II aluminum coated steel article which has increased resistance to oxidation when heated to a temperature of about 1,500°F.

A further object of the present invention is to provide a continuous process of hot-dip aluminum coating a steel sheet or strip to obtain a coated product which exhibits increased resistance to subsurface oxidation of the steel when heated to a temperature of about 1,500°F.

Still another object of the invention is to provide an improved corrosion resistant article of manufacture for use in an automotive exhaust system, such as an exhaust muffler or the like.

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, wherein:

FIG. 1 is a diagrammatic illustration of a vertical section of a rimmed steel sheet with a Type I aluminum coating after heating at an elevated temperature in an oxidizing atmosphere;

FIG. 2 is a diagrammatic illustration of a plan view of the surface of the Type I aluminum coated rimmed steel sheet of FIG. 1 after further heating at an elevated temperature in an oxidizing atmosphere;

FIG. 3 is a diagrammatic illustration of a vertical section of a titanium-containing mild steel sheet with a Type I aluminum coating, in accordance with the present invention, after heating at an elevated temperature in an oxidizing atmosphere;

FIG. 4 is a diagrammatic illustration of a plan view of the surface of the aluminum coated steel sheet of FIG. 3 after further heating at an elevated temperature in an oxidizing atmosphere; and

FIG. 5 is a graph showing the total weight gain per square centimeter of surface area by an aluminum coated conventional rimmed steel sheet and an aluminum coated titanium-containing steel sheet of the present invention when the sheets are heated in air at 1,500°F.

It has been found that the foregoing objects can be achieved and that a low alloy steel article, particularly steel sheet or strip, having an increased resistance to subsurface oxidation when heated at an elevated temperature in an oxidizing atmosphere can be provided economically without using large amounts of expensive alloying elements by incorporating in a plain carbon steel base before aluminum coating a small amount of

titanium sufficient to combine with or precipitate essentially all of the carbon in the steel base and leave an excess of uncombined titanium in solution in the steel base.

The titanium-containing plain carbon steel base used in the present invention is a low carbon steel or mild steel having a carbon content of up to about 0.25 wt. percent max., usually from about 0.03 wt. percent to about 0.25 wt. percent and preferably from about 0.03 wt. percent to about 0.10 wt. percent, and having titanium added thereto in an amount which is sufficient to combine with all the carbon in the steel base and leave an excess of uncombined titanium. Typically, the plain carbon steel base will consist essentially of from about 0.03 wt. percent to about 0.25 wt. percent carbon (preferably, 0.03 wt. percent to 0.10 wt. percent), from about 0.20 wt. percent to about 0.50 wt. percent manganese, about 0.05 wt. percent max. silicon, titanium in an amount sufficient to combine with all the carbon in the steel base and leave an excess of uncombined titanium, and the balance iron with the usual amounts of impurities and residuals. Preferably, the steel is a killed steel, and particularly an aluminum killed steel, in which case the residuals or impurities present will include the usual amounts of aluminum or other deoxidizers characteristic of killed steel. Although, as explained hereinafter, titanium is the essential alloying element to be added to the plain carbon base steel to obtain the advantages of the present invention, it is also within the scope of the invention to add small amounts of other metallic alloying elements to improve the physical properties of the base steel. However, the amount of such other metallic alloying elements should not exceed about 1 percent by weight and preferably should not exceed about 0.5 percent by weight. Thus, the steel articles of the present invention are, in any case, low alloy steel articles.

Preferably, the excess of uncombined titanium remaining in the steel is an amount between about 0.1 and about 0.3 per cent by weight. Since the weight per cent of titanium must be approximately four times the weight per cent of carbon in the steel in order to combine with or precipitate essentially all the carbon in the steel, the minimum titanium content of the substrate steel sheet in the present invention should be four times the carbon content of the steel plus an additional amount of titanium sufficient to provide from about 0.1 to about 0.3 per cent percent by weight uncombined titanium. While the titanium content can be as much as ten times the weight per cent of carbon in the steel, an amount of titanium greater than that specified herein gives no increased benefits and merely adds unnecessarily to the cost. And, since the amount of carbon in a steel conventionally used for producing aluminum coated steel is small, generally less than 0.10 wt. percent, the total amount of titanium required in the present invention is small. The inclusion of titanium in the steel in the aforementioned amounts also results inherently in stabilization of any nitrogen in the steel (usually not exceeding about 0.006 wt. percent so that both the carbon and nitrogen are stabilized, probably as titanium carbides or titanium carbo-nitrides.

A preferred method of aluminum coating a steel strip having the titanium content thereof 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) or an aluminum rich alloy, such as aluminum containing up to 11 percent by wt. 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.

FIG. 1 of the drawing shows diagrammatically a vertical section of a sheet of rimmed steel (e.g. AISI 1008 steel) hot-dip aluminum coated as herein described by the Sendzimir-type process with a Type I aluminum coating containing 8 per cent by wt. silicon after the coated strip has been exposed to oxidation by heating in air at 1,500°F for a period of 100 hours. The steel base **30** has a continuous subsurface oxide layer **31** which is formed between the surface of the steel base **30** and the hot-dip aluminum coating **32**. The subsurface oxide layer **31** is comprised essentially of two oxide components having different concentrations of aluminum and iron. A thin aluminum oxide coating **33** is formed on the surface of the aluminum coating **32**. The subsurface oxide layer **31** grows quite rapidly when the strip is held in an oxidizing atmosphere, such as air, at about 1,500°F, and the rate at which the oxide layer **31** grows increases as the silicon content of the aluminum coating increases. The subsurface oxide layer **31** prevents or substantially retards diffusion of aluminum from the surface coating **32** into the steel substrate **30**. When the aluminum coated steel sheet is held at an elevated temperature, such as 1,500°F, the subsurface oxide layer **31** continues to grow until eventually spalling or flaking of the aluminum coating **32** occurs and a portion of the oxide layer **31** along with the aluminum rich coating **32** falls away and exposes the steel base **30** to further oxidation, as best shown in FIG. **2**.

FIG. 2 is a diagrammatic illustration of a plan view of the rimmed steel sheet of FIG. 1 having the Type I aluminum coating after exposing the coated sheet to oxidation by heating in air at a temperature of 1,500°F for a period of 200 hours and shows that the aluminum rich

coating 32 has spalled badly, exposing the steel base 30 in some areas, and that a voluminous growth of ferrous metal oxide 34 has taken place in the areas where spalling has occurred. The same basic mechanism as above described was observed for the subsurface oxidation of a Type II aluminum coated rimmed steel exposed to oxidation in air at a temperature of 1,500°F.

When a steel strip having a titanium content in accordance with the present invention is hot-dip aluminum coated by the herein described Sendzimir-type process, or by any equivalent process which provides a clean oxide-free surface for hot-dip aluminum coating, and the coated strip is exposed to oxidation in air at a temperature of 1,500°F, the formation of a continuous subsurface oxide layer is avoided or substantially retarded. And, where a continuous layer of subsurface oxide is not formed, aluminum from the aluminum coating is free to diffuse and does diffuse into the substrate steel base when the strip is heated to an elevated temperature in an oxidizing atmosphere. The diffusion of aluminum into the steel base further increases the resistance of the steel base to subsurface oxidation.

FIG. 3 of the drawing is a diagrammatic illustration, in accordance with the present invention, of a vertical section through a titanium-containing aluminum killed steel sheet 35 containing 0.05 percent by wt. carbon and 0.35 percent by wt. titanium (the steel composition being otherwise comparable to the steel sheet of FIGS. 1 and 2) and having a hot-dip Type I aluminum coating (8 per cent by wt. silicon) which has substantially diffused into the steel as a result of heating sheet 35 in air at 1,500°F for 100 hours. The heating of the sheet 35 also forms a small amount of subsurface oxide as distinct isolated particles 36 which are dispersed in the titanium-containing steel forming a discontinuous subsurface stratum. The dispersed particles 36 are comprised essentially of oxides of iron, aluminum, and titanium in varying proportions. A continuous subsurface oxide layer of the type shown in FIG. 1 is not formed even after prolonged high temperature heating, and the hot-dip aluminum surface coating diffuses into the steel below the discontinuous subsurface stratum of metal oxides, thereby providing increased resistance to oxidation.

FIG. 4 illustrates disgrammatically a plan view of the uniform gray matte aluminum oxide surface 37 of the aluminum coated titanium-bearing steel sheet of FIG. 3, after the sheet has been heated in air for a period of 200 hours at a temperature of 1,500°F. The surface 37 is completely free of flaking or spalling.

FIG. 5 presents two curves showing the total weight gain per square centimeter due to both surface and subsurface oxidation of a conventional aluminum coated rimmed steel sheet (Curve A) and that of an aluminum coated sheet of aluminum killed steel in accordance with the present invention which contains 0.05 percent by weight carbon and 0.35 percent by weight titanium (Curve B), both coatings being a Type I aluminum coating having a thickness of 2 mils and both heated in air at 1,500°F over the indicated period of time. The aluminum coated titanium-containing steel sheet, which represents a preferred embodiment of the present invention (Curve B), exhibits a much lower rate of oxidation than the conventional aluminum coated rimmed steel sheet (Curve A).

A typical aluminum killed steel having a low carbon content suitable for hot or cold rolling into sheets and hot-dip aluminum coating and having a titanium content in accordance with the present invention has the following approximate chemical analysis:

	Percent by Weight
C	0.05
Mn	0.30 – 0.50
S	0.030
P	0.02
Si	0.002
Al	0.005 – 0.090
Ti	0.25 – 0.45
Fe	balance

While the mechanism by which the present invention retards or prevents the formation of an undesirable continuous barrier layer of subsurface oxides is not entirely understood, it is presently believed that the free or uncombined titanium which is present throughout the steel base acts preferentially as a "getter" for oxygen and thus inhibits the formation of iron and aluminum oxides below the surface. Since titanium is a strong carbide and nitride former, it is essential to have present in the steel sufficient titanium to provide the required amount of free or uncombined titanium after all of the carbon and nitrogen in the steel has combined with titanium. Although the amount of free or uncombined titanium required is relatively small (preferably from about 0.1 to about 0.3 wt. percent), it is present throughout the steel base and thus provides a reservoir of titanium for its protective and inhibiting effect during prolonged exposure of the aluminum coated steel to a high temperature oxidizing atmosphere. As oxygen penetrates through minute cracks in the surface region of the coated steel, free titanium is always available to react with the oxygen, thereby minimizing the formation of the undesirable subsurface oxides as a barrier layer. In the absence of a substantial reservoir of free titanium, the desired protective effect would soon be lost and the undesired oxide barrier would be formed.

As previously mentioned, the aluminum coated steel sheet or strip of the present invention is specially suited for use in fabricating components of an automotive exhaust system, particularly exhaust mufflers but also other parts of the exhaust train, such as inlet pipes, tail pipes, Y-pipe assemblies, and catalytic converters. Not only does the aluminum coated titanium-containing steel of the present invention have excellent high temperature oxidation resistance, as described above, but it also possesses good formability and other desirable physical properties, such as good high temperature tensile properties, which are required for fabricating mufflers and other automotive exhaust components.

While the foregoing disclosure relates primarily to improving the oxidation resistance of strips and sheets 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 in the claims which follow the term "steel material" or "steel article" includes any steel material regardless of 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 terms "aluminum coating" and "aluminum coated" as used in the claims are intended to cover pure aluminum which contains only traces of other elements as well as aluminum rich alloys containing added ingredients such as

zinc, magnesium, silicon, copper, beryllium, etc. Other methods and means for applying the aluminum coating to the steel article can also be used such as spraying, cladding, and the like, and 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 which has good formability and has good subsurface oxidation resistance and tensile properties when heated at an elevated temperature in an oxidizing atmosphere consisting essentially of an aluminum killed low carbon steel base which has titanium added to the said low carbon steel as the essential added alloy element with the titanium being uniformly distributed throughout the steel in an amount which combines with all of the carbon and nitrogen in the steel and providing an excess of between about 0.1 and about 0.3 weight percent of uncombined titanium throughout the steel, and a uniform thin coating of metallic aluminum directly on a surface of said steel base which is free of surface oxides and non-metallic material, said low alloy steel article in the as-coated condition exhibiting good formability and when heated in an oxidizing atmosphere at an elevated temperature of 1,500°F exhibiting good subsurface oxidation resistance and tensile properties.

2. The article of claim **1**, wherein said steel base is an aluminum killed steel containing from about 0.005 wt. percent to about 0.09 wt. percent aluminum.

3. The article of claim **1**, further characterized in that said steel base is devoid of other added metallic alloying elements in an amount exceeding about 1 percent by weight.

4. The article of claim **3**, wherein said steel base is devoid of other added metallic alloying elements in an amount exceeding about 0.5 percent by weight.

5. The article of claim **1**, wherein the carbon content of said steel base is from about 0.03 wt. percent to about 0.10 wt. percent.

6. The article of claim **1**, wherein said aluminum coating contains up to about 11 wt. percent silicon.

7. The article of claim **1**, wherein said aluminum coating is substantially pure aluminum.

8. The article of claim **1** further characterized in that upon exposure of said article to an oxidizing atmosphere at an elevated temperature, formation of a substantially continuous subsurface oxide layer in said steel base is avoided and diffusion of aluminum from said coating into said steel base is thereby facilitated.

9. An aluminum coated low alloy steel article which is resistant to surface and subsurface oxidation and exhibits high tensile properties when heated in an oxidizing atmosphere at an elevated temperature of about 1,500°F, consisting essentially of:

an aluminum killed mild steel base containing titanium added thereto in an amount between at least four times and not substantially in excess of about 10 times the amount of carbon in the steel base which effects precipitation of all of the said carbon and nitrogen and provides an excess of between about 0.1 and about 0.3 weight percent of chemically uncombined titanium distributed through the steel; and

a metallic aluminum surface coating directly on a clean oxide-free surface of said steel base;

said article possessing good formability and on heating in an oxidizing atmosphere at an elevated temperature forming a discontinuous subsurface stratum of discrete particles of oxides below the coating of aluminum, whereby said coating of aluminum diffuses into said steel base without being impeded by a continuous subsurface barrier layer of oxides between the said steel base and said aluminum coating when heated at said elevated temperature.

10. An aluminum coated steel article as in claim **9**, wherein said mild steel base is a low carbon steel containing a maximum of about 0.10 percent by weight carbon.

11. A method of producing an aluminum coated low alloy mild steel article characterized by having good formability and good high temperature oxidation resistance and tensile properties at elevated temperatures, comprising applying an aluminum coating directly to the surface of an aluminum killed plain carbon steel base having a carbon content of up to about 0.25 wt. percent max. and having titanium as an essential added alloying element present in an amount between about four times and about ten times the carbon content and which is sufficient to combine with all the carbon and nitrogen in the steel base and provide an excess of between about 0.1 and about 0.3 weight percent of uncombined titanium distributed throughout the steel.

12. The method of claim **11**, wherein said aluminum coating is applied by immersing said steel base in a bath of molten aluminum.

13. A corrosion resistant article of manufacture for use in an automotive exhaust system, such as an exhaust muffler, said article being formed from an aluminum coated steel sheet possessing good formability and consisting essentially of an aluminum killed plain carbon steel having a carbon content of up to about 0.25 wt. percent max. and having titanium added thereto as an essential added alloying element in an amount between about four times and about 10 times the carbon content of said steel and which is sufficient to combine with all the carbon and nitrogen in the steel and provide an excess of between about 0.1 and about 0.3 weight percent of uncombined titanium; and

an aluminum coating directly on the surface of said steel which is free of oxides and non-metallic material.

14. The article of claim **13**, wherein said steel is an aluminum killed steel containing from about 0.005 wt. percent to about 0.09 wt. percent aluminum.

15. An aluminum coated low alloy steel article as in claim **1**, wherein said aluminum killed low carbon steel base in which said titanium is incorporated has a maximum of about 0.25 wt. percent carbon, from about 0.02 to about 0.50 wt. percent manganese, a maximum of about 0.05 wt. percent silicon, and from about 0.005 to about 0.09 wt. percent aluminum.

16. A method of increasing the resistance of a formable aluminum coated low alloy carbon steel sheet to flaking and spalling due to subsurface oxidation when heated at an elevated temperature at 1,500°F comprising; adjusting the composition of a low alloy aluminum killed low carbon steel by adding titanium to said aluminum killed steel while said steel is in a molten condition in an amount sufficient to combine with all of the carbon and nitrogen in the steel and provide an excess of between about 0.1 and about 0.3 weight percent of uncombined titanium throughout said steel to form a low alloy steel, forming a sheet of said low alloy alumi-

num killed low carbon steel, applying directly to a surface of said sheet while said surface is free of oxides and non-metallic impurities a thin uniform coating of molten metallic aluminum, and cooling the aluminum coating to provide an aluminum coated low alloy mild steel sheet possessing good formability and having good resistance against surface and subsurface oxidation and good tensile properties when heated in an oxidizing atmosphere at an elevated temperature of 1,500°F.

17. A method as in claim **16** wherein said steel to which said titanium is added has a maximum of about 0.25 wt. percent carbon, from about 0.02 to about 0.50 wt. percent manganese, a maximum of about 0.05 wt. percent silicon, and between about 0.005 and about 0.09 wt. percent aluminum.

18. A method as in claim **17,** wherein no other alloying element is added to said low carbon steel in an amount greater than the wt. percent of titanium added to said steel.

19. A method as in claim **16,** wherein no other alloying element is added to said low carbon steel in an amount greater than 1 percent of the weight of said steel.

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