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[54] **ALUMINUM COATED STEEL**

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

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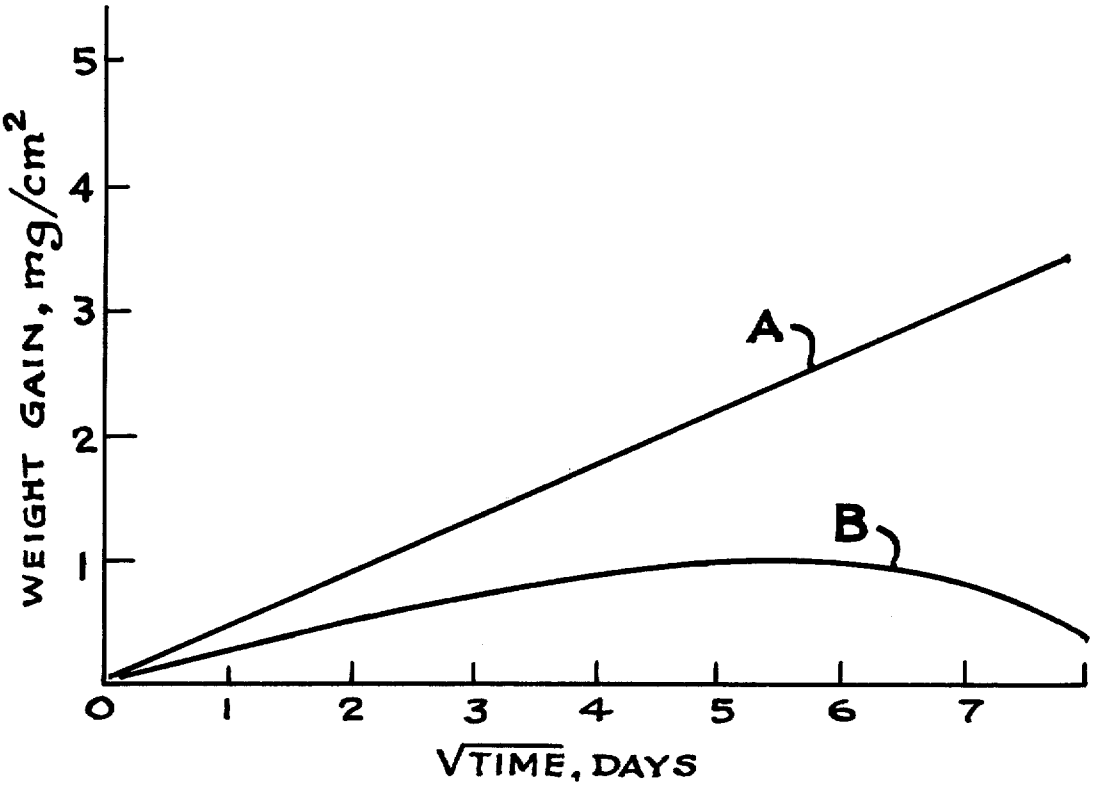
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[57] **ABSTRACT**

An aluminum coated low alloy mild steel sheet material and a method of making said material which contains a small amount of titanium sufficient to precipitate all the carbon in the low carbon steel and provide a slight excess of uncombined titanium dissolved in the steel and containing molybdenum in an amount less than 1 percent by weight with the balance being mainly iron and incidental impurities. The aluminum coated material exhibits extraordinarily high creep resistance and rupture strength for a low carbon steel material at a service temperature above 1,250 F (i.e. 1,300 F) in an oxidizing atmosphere.

11 Claims, 1 Drawing Figure

- CYCLIC OXIDATION TO 1500°F -



ALUMINUM COATED STEEL

The present invention relates generally to a steel article suitable for service at an elevated temperature above 1,250°F, and more particularly to an aluminum coated low alloy mild steel sheet which has good resistance to oxidation at temperature of 1,500°F and which also has unusually high creep resistance and rupture strength at temperatures of 1,300°F while at the same time having good formability at room temperature.

It is important to provide a steel sheet or the like which can be used at an elevated temperature of about 1,500°F in an oxidizing atmosphere for extended periods without undergoing destructive oxidation and without resorting to the use of high alloy steels. One method of increasing the oxidation resistance of steel has been to provide an aluminum coating on the steel sheet. However, when an aluminum coating containing silicon (Type I aluminum) is applied to mild or low carbon steel and heated, excessive subsurface oxidation of the steel occurs at temperatures above 1,300°F. Such aluminum coated steels are unsuited for service of even a few days at temperatures above 1,300°F. Also, a typical aluminum coated mild steel such as AISI 1,008 steel having a substantially pure aluminum coating (Type II aluminum) is not recommended for extended use at temperatures above about 1,100°F.

A further very important requirement of a steel sheet or like article intended for service at elevated temperatures is that the article have good mechanical properties at the elevated service temperature (i.e. must be resistant to creep and rupture) and at the same time the article should have good formability at room temperature. The high temperature strength required is important to insure structural integrity of the article after prolonged service at the elevated temperature, and the room temperature formability is important in order to facilitate fabrication.

Heretofore, stainless steel alloys containing at least 12 percent chromium have generally been used where the extended service life is to be in an oxidizing atmosphere at temperatures of about 1,500°F and where good high temperature physical properties are required. Stainless steel alloys, however, are relatively expensive to produce and are often too expensive for many applications.

It is therefore an object of the present invention to provide an aluminum coated low alloy steel article which is suitable for long term service in an oxidizing atmosphere at elevated temperatures and which is less expensive to produce than stainless steel.

It is a further object of the present invention to provide an aluminum coated low carbon steel sheet having good resistance to oxidation at 1,500°F and high creep resistance at elevated temperatures without using a high percentage of alloying elements in the steel.

It is another object of the present invention to provide an aluminum coated low alloy mild steel sheet having resistance to oxidation at 1,500°F and good rupture strength at elevated temperatures which also exhibits good room temperature formability.

Other objects of the present invention will be apparent to those skilled in the art from the detailed description and claim to follow when read in conjunction with the accompanying drawing which shows the weight gain of a mild steel panel embodying the present invention and a stainless steel panel over a prolonged period of cyclic oxidation at an elevated temperature.

It has been found that a steel article having good mechanical properties and high resistance to surface and subsurface oxidation when heated at an elevated temperature in an oxidizing atmosphere can be provided economically without using large amounts of expensive alloying elements in the steel by applying a thin aluminum coating to a low carbon steel (0.03 to 0.10 percent by wt. C) containing both a small amount of molybdenum (i.e. less than 1 percent by wt.) and an amount of titanium which is sufficient to precipitate all of the carbon and nitrogen contained in the steel and leaving a small excess of uncombined metallic titanium in solution in the steel. Preferably the excess of uncombined titanium remaining in the steel is an amount between about 0.1 and 0.3 percent by weight of the steel. Since the weight percent of titanium must be approximately four times the weight percent of carbon in the steel (i.e. the amount of nitrogen present being relatively small) in order to precipitate essentially all the carbon in the steel, the titanium content of the substrate steel sheet in the present invention preferably is at least four times the carbon content of the steel plus an additional amount of titanium sufficient to provide about 0.1 to 0.3 percent by weight uncombined titanium. The titanium content can be as much as ten times the weight percent of carbon in the steel, but an amount of titanium greater than that specified herein gives no increased benefits and merely adds unnecessarily to the cost. Since the total amount of carbon and nitrogen in a low carbon steel of the type conventionally used for producing aluminum coated steel sheet material is small, generally less than 0.1 percent, the total amount of titanium required in the present invention is also small, comprises less than 1 percent by weight of the steel, and will generally fall between about 0.35 percent and 0.70 percent by wt. of the steel.

It has been found that when a small amount of molybdenum is also combined with the low carbon steel containing sufficient titanium to combine with all of the carbon and nitrogen in the steel and leaving a small excess of uncombined titanium in solution in the steel, the resulting low alloy steel exhibits good formability properties at room temperature and has extraordinarily good high temperature strength properties, including good resistance to creep and high rupture strength. These high temperature strength properties are very unusual in a low carbon steel. The amount of molybdenum used in the titanium alloy steel which is devoid of free carbon preferably ranges between about 0.1 and 0.70 percent by weight of the steel.

A preferred method of aluminum coating a low carbon steel strip having the molybdenum and 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 and preferably between 1,600°F

– 1,750°F; whereby the oxide coating on the strip is reduced to form a surface layer of metal free of nonmetallic 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 steep 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 two graphs in the accompanying drawing show the total weight gain per square centimeter of exposed area due to surface and subsurface oxidation of a (A) hot dip aluminum content steel sheet embodying the present invention and containing 0.05 percent by weight carbon, 0.50 percent molybdenum, and 0.35 percent by weight titanium having a Type I aluminum coating of a thickness of 2 mils and (B) a panel of stainless steel 409 (SAE 51409), both heated in air at 1,500°F over the indicated period of time. The aluminum coated molybdenum-titanium containing low alloy steel sheet (Curve A) exhibits no weight loss due to spalling, retained its integrity and continue to show a uniform oxidation rate throughout the total length of the test period. The stainless steel panel (Curve B) shows a loss of weight due to spalling of the iron-chromium oxide film.

The improved oxidation resistance is obtained as a result of the uniform gradual diffusion of aluminum of the coating into the surface of the steel when heated at an elevated temperature, either during a treating step or in use. The heating at the elevated temperature can and normally does take place in air or in a like oxidizing atmosphere, since there is no continuous subsurface barrier layer of oxide formed on prolonged heating in an oxidizing atmosphere, as in the usual aluminum coated low carbon steel sheet, and only discreet particles of metallic oxide are formed below the surface of the steel in the form of a discontinuous subsurface stratum which does not impede the uniform diffusion of the aluminum into the steel surface.

A low alloy mild (i.e. low carbon) steel suitable for hot or cold rolling into sheets and aluminum hot-dip coating in accordance with the present invention falls within the following approximate composition:

	Percent by Weight
C	0.035 – 0.10
N	.010
Mn	0.30 – 0.70
Ti	0.30 – 0.70
Mo	0.10 – 0.70
Al	0.03 – 0.09
Fe and incidental impurities	Balance

In order to further characterize the article of the present invention panels of steel having the composition indicated in the following Tables were tested to determine their mechanical properties at room temperature and at a temperature of 1,300°F. In Tables I and II each of the test panels of low alloy aluminum killed low carbon steel having the indicated chemical analysis was subjected to a preheating cycle identical to that which a steel sheet would be subjected to in the course of continuous hot-dip aluminum coating in a Sendzimir-type coating process, and thereafter the panels were subjected to standard tensile strength tests with the following results:

TABLE I

Properties of Experimental Alloys

Alloy Steels	Composition*					Preheat Temp. (°F)	LYS or 0.2 PS (ksi)	UTS (ksi)	0.2 PS / UTS	E_t (%)	E_T (%)
	C	Ti	Mn	Al	Mo						
Ti-1	0.045	0.34	0.32	0.036	—	1600	22.1	51.6	0.43	21.3	35.1
						1750	21.8	48.0	0.45	20.3	35.6
Ti-1 + Mo(0.50)	0.06	0.35	0.35	0.036	.50	1600	26.1	54.5	0.48	18.3	29.8
						1750	22.0	51.8	0.42	21.2	33.9
MF-1 (SAE 51409)						—	40.0	68.0	0.66	—	30.0

*Containing in addition the normal amounts of impurities: N, S, P, Si

TABLE II

Tensile Properties of Experimental Alloys at 1300°F

Alloy	Composition*					Preheat Temp. (°F)	0.2 PS (ksi)	UTS (ksi)	0.2 PS / UTS	E_T (%)
	C	Mn	Ti	Al	Mo					
Ti-1	0.045	0.34	0.32	0.036	—	1600	7.8	9.5	0.82	77.5
						1750	9.8	11.2	0.88	53.0
Ti-1 + Mo	0.06	0.35	0.35	0.036	0.50	1600	10.5	13.8	0.76	42.0
						1750	11.5	14.8	0.78	38.0
MF-1 (SAE 51409)							11.0	12.0	0.92	36.0

*Containing in addition the normal amounts of impurities: N, S, P, Si

It will be evident from the foregoing data that the low alloy mild steel base of the present invention containing 0.35 percent by wt. titanium and 0.50 percent by wt. molybdenum exhibits no significant loss of room temperature ductility as compared with a like low alloy steel without molybdenum while exhibiting substantially improved high temperature tensile strength. The tensile strength properties of the low alloy titanium-molybdenum low carbon steel compares favorably with the muffler grade stainless steel (SAE 51409) used as a reference standard. By adjustment of the carbon, titanium and molybdenum content within the herein disclosed ranges, it is possible to provide a steel which has good high tensile strength while retaining adequate room temperature ductility for forming purposes and which has the further advantage of being produced by a standard hot-dip aluminum coating procedure, such as on a conventional Sendzimir continuous hot-dip coating line.

Test hot-dip aluminum coated low alloy mild steel panels embodying the present invention and having the composition indicated in Table I were subjected to standard stress rupture and creep strength tests at 1,300°F in air, and the results obtained are shown in the following Tables III and IV:

TABLE III

Creep Data for ALUMINIZED TITANIUM AND TITANIUM-MOLYBDENUM ALLOY STEELS at 1300°F IN AIR

Steel	Stress Level (psi)	Time to Creep (hrs.) 0.5%	1.0%	5%	Minimum Creep Rate (% Hr.)	Elongation at Rupture %
Titanium (Ti-1)	3000	30	65	375	.013	17
	4000	10	20	104	.044	28
	5000	2.5	4.0	18.5	.26	65
Titanium + Molybdenum (Ti-1 + Mo)	4000	5	40	740	.0048	25
	4500	15	40	310	.012	28
	5000	10	27	175	.033	37
	6000	—	1.5	2.3	.195	46

TABLE IV

Stress Rupture Data For ALUMINIZED Alloy Steels at 1300°F in Air

Stress Level (psi)	Rupture Life (hrs.) Titanium Alloy Steel (Ti-1)	Titanium-Molybdenum Alloy Steel (Ti-1 + Mo)
2,000	5,100	60,100
2,500	2,500	27,000
3,000	1,200	12,300
3,500	562	5,600
4,000	272	2,500
4,500	130	1,120
5,000	63	509
5,500	—	231
6,000	—	105

The data in Tables III and IV indicate that the aluminum coated low alloy titanium-molybdenum mild steel panels of the present invention have the rupture life thereof at 1,300°F in air improved by a factor of 10, as compared with aluminum coated low titanium alloy mild steel panels. The creep data also show the extraordinary beneficial effect of adding a small amount of molybdenum to a low titanium mild steel, as evidenced by the greatly reduced creep rate at the selected stress levels at 1,300°F. These improvements in the high temperature strength properties are extraordinary in a low carbon steel and are very important in expanding the utility and applications of the low carbon steels.

We claim:

1. An aluminum coated low alloy mild steel article adapted for service at an elevated temperature comprising, a low-alloy aluminum killed low carbon steel sheet which contains uniformly distributed throughout as an essential combination of alloy elements titanium in an amount up to a maximum of 1% by wt. which combines with all the carbon and nitrogen and leaving uncombined titanium throughout the steel and molybdenum in an amount between about 0.10 percent and 0.70 percent by wt. of said steel, a uniform thin coating of metallic aluminum directly on a surface of said steel sheet which is free of surface oxides and non-metallic impurities, said article in the as coated condition exhibiting good formability at room temperature and high creep resistance and rupture strength at an elevated temperature of 1300°F – 1500°F, and said article after heating in an oxidizing atmosphere at a temperature of 1500°F and said article having aluminum uniformly diffused into the surface of steel sheet with only discrete particle of metallic oxide formed below the surface of said steel as a discontinuous subsurface stratum; whereby said aluminum coated low alloy mild steel article exhibits increased oxidation resistance, high creep resistance and increased rupture strength on heating the said elevated temperature in an oxidizing atmosphere.

2. An article as in claim 1, wherein an excess of titanium remains uncombined in said steel in an amount between about 0.1 and 0.3 percent by weight of said steel.

3. An article as in claim 1, wherein said low-alloy low-carbon steel contains a maximum of about 0.10 wt. percent carbon, a maximum of about 0.01 wt. percent nitrogen, a maximum of about 0.70 wt. percent manganese, and a maximum of about 0.09 wt. percent aluminum with the balance being essentially iron with the normal amount of incidental impurities contained in a mild steel.

4. An article as in claim 1, wherein said coating of aluminum is substantially pure aluminum.

5. An article as in claim 1, wherein said coating of aluminum contains silicon up to about 11 percent by weight silicon.

6. A method of providing an aluminum coated low alloy mild steel sheet which has good formability at room temperature and high creep resistance and rupture strength at an elevated temperature which comprises, applying a uniform thin coating of metallic aluminum directly to a surface of a steel sheet which is free surface oxides and non-metallic impurities and which is formed of a low-alloy aluminum killed low carbon steel having distributed uniformly throughout said steel as an essential combination of alloy element titanium in an amount up to 1% which combines with all the carbon and nitrogen in the said steel and molybdenum in an amount between about 0.10 and 0.70 percent by weight.

7. A method as in claim 6, wherein an excess of titanium remains uncombined in said steel in an amount between about 0.1 percent and 0.3 percent by weight of said steel base.

8. A method as in claim 6, wherein said steel base contains a maximum of about 0.10 wt. percent carbon, a maximum of about 0.01 wt. percent nitrogen, a maximum of about 0.70 wt. percent manganese, and a maximum of about 0.09 wt. percent aluminum with the balance being essentially iron with the normal amounts of impurities contained in a low carbon steel.

9. A method as in claim 6, wherein said aluminum is applied to said steel article by immersing said steel article (material) in a bath of molten aluminum.

10. A method as in claim 9, wherein said molten aluminum bath is substantially pure aluminum.

11. A method of providing an aluminum coated low alloy steel sheet which has good formability at room temperature and high creep resistance and rupture strength at an elevated temperature which comprises, adjusting the composition of an aluminum killed low-carbon steel which contains a maximum of about 0.10 wt. % carbon, a maximum of about 0.01 wt. % nitrogen, a maximum of about 0.70 wt. % manganese, and a maximum of about 0.09 wt. % aluminum with the balance being essentially iron with the normal amount of incidental impurities contained in a low-carbon aluminum killed steel by adding to said steel while said steel is in a molten condition as an essential combination of alloy elements titanium in an amount up to 1% by wt. which combines with all the carbon and nitrogen in the steel and leave an excess of uncombined titanium distributed throughout the steel and molybdenum in an amount between about 0.10 percent and 0.70 percent by weight to form a low-alloy aluminum killed low carbon steel and applying directly to a surface of a sheet of said low-alloy aluminum killed low-carbon steel while said surface is free of oxides and non-metallic impurities a thin uniform coating of molten metallic aluminum, and cooling said coating to provide an aluminum coated low-alloy steel sheet having good formability at room temperature and having high creep resistance and rupture strength at elevated temperatures up to 1500°F.

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