

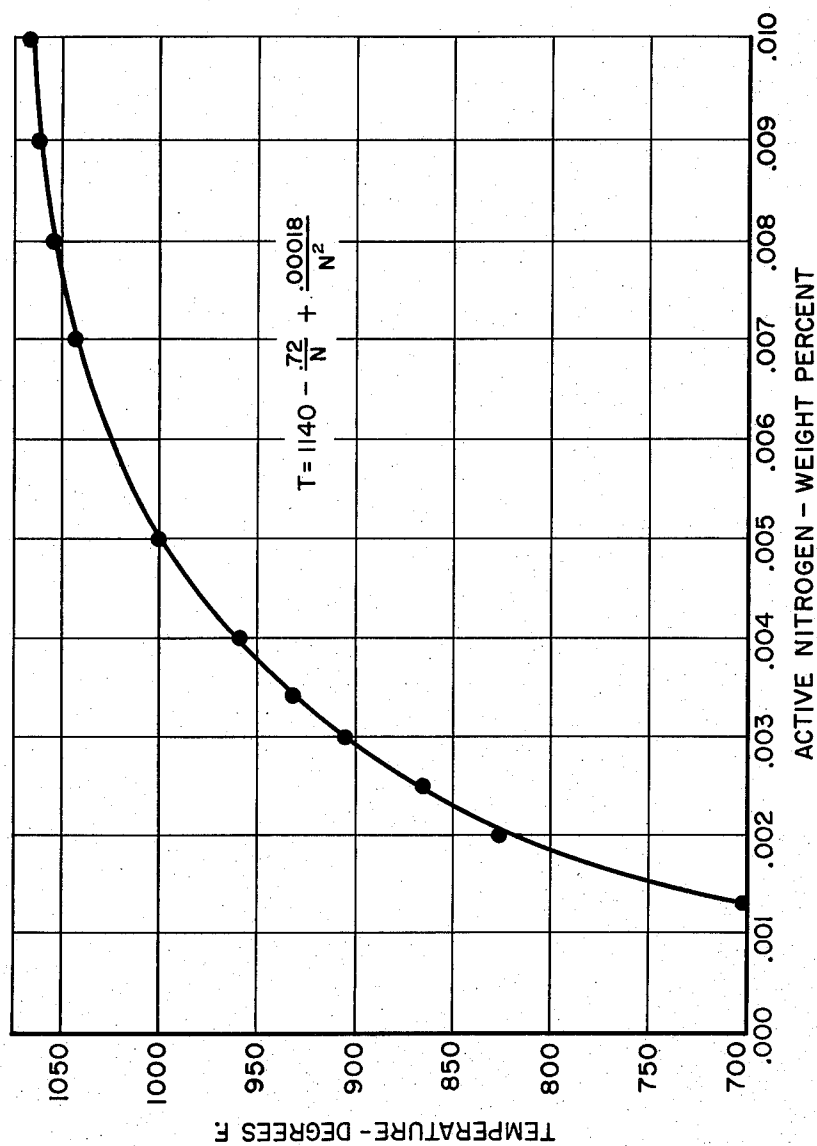
Dec. 27, 1960

W. BATZ ET AL

2,965,963

ALUMINUM CLADDING OF STEEL

Filed Sept. 21, 1956



INVENTORS
WALTER BATZ
JAMES W. THURMAN

BY *J.R. Harris*
ATTORNEY

1

2,965,963

ALUMINUM CLADDING OF STEEL

Walter Batz, Hopewell Township, Beaver County, and James W. Thurman, Pittsburgh, Pa., assignors to Jones & Laughlin Steel Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

Filed Sept. 21, 1956, Ser. No. 611,322

4 Claims. (Cl. 29—487)

This invention relates to a process for producing aluminum clad steel and is more particularly concerned with a process for producing such steel with a high degree of ductility.

For many purposes it would be desirable to employ aluminum coated sheets of steel, both in place of solid aluminum sheets and of steel sheets coated with other metals, for example, tin plate. Because of the difficulty of obtaining a strong bond between aluminum and a ferrous base, no commercially successful aluminum coated steel or process for the production of aluminum coated sheets was known prior to our invention. A number of processes for producing a hot dipped coating of aluminum on ferrous base metals have been advanced, and a certain amount of aluminum coated sheets so produced have been sold commercially, but these sheets all exhibit to a greater or less degree the defect that the aluminum coating tends to crack or peel off when the sheet is deformed. It is believed that this undesirable characteristic is a result of a brittle alloy of aluminum and iron which forms at the interface between these metals during the hot dipping operation. Some degree of control over the formation of this iron-aluminum alloy may be achieved by control of the chemical composition of the aluminum coating. For example, the addition of silicon or beryllium to the aluminum coating metal appears to be beneficial in this respect. However, it does not appear to be possible to provide by the hot dipping process a coating of commercially pure aluminum which will adhere to steel when the latter is deformed. Furthermore, it is very difficult, if not impossible, to produce by hot dipping a thin aluminum coating without pin holes.

Attempts have been made to produce aluminum coated steel sheets by cladding; that is uniting a sheet of aluminum to one of steel by subjecting them to rolling pressure followed in some cases by heat treating. None of these has produced a fully successful product. The mechanical bond created by rolling alone will not withstand deformation, and when the mechanically bonded product is heat treated in an attempt to improve the bond, the previously mentioned brittle alloy of iron and aluminum is formed.

The physical properties of alloys of aluminum and iron have been investigated by C. Sykes and J. W. Bampfyld and reported by them in the journal of the Iron and Steel Institute, volume CXXX, page 389, 1934. It appears that alloys of iron containing from 0 to 34% of aluminum consist of a homogeneous solid solution. The above mentioned investigators found, however, that alloys containing more than 17% of aluminum could not be worked in any way; that alloys containing from 5% to 16% of aluminum could be worked hot but were quite brittle when cold; and that only alloys containing less than 5% of aluminum were sufficiently ductile to be worked cold. Although iron and aluminum can alloy in any proportion, all such alloys containing more than about 5% aluminum are seen to be brittle

2

when subjected to cold deformation and therefore undesirable in aluminum coated steel sheets or similar articles intended to be cold formed.

It is an object of our invention, therefore, to provide a process for producing steel clad with an aluminum coating of uniform controlled thickness which will adhere to the base metal when the clad material is deformed. It is another object of our invention to provide a process for producing aluminum clad steel having a minimum amount of brittle iron-aluminum alloy. Other objects will appear in the course of the following description of our invention.

It is well-known to those skilled in the art that all steels made by conventional processes contain small amounts of nitrogen. The nitrogen content may be quite low—on the order of .001% to .002%—or, in some Bessemer steels, it may exceed .015%. Nitrogen can be deliberately added to steel by known methods, but it is quite generally considered to be an undesirable constituent of steel, and, where its control is practicable, it is usually held to a value as low as is feasible.

We have discovered that when a steel base is mechanically clad with an aluminum coating, the composite material so formed may be heat treated to bring about a strong metallurgical bond between the aluminum and the steel without the formation of brittle iron-aluminum alloy if the heat treating temperature is controlled in accordance with the active nitrogen content of the steel base.

We have found that the permissible heat treating temperature varies directly, although not linearly, with the active nitrogen content of the steel base. We have determined this relation by experiments upon numbers of specimens of steel base of predetermined nitrogen contents and upon other like specimens treated by known means to remove substantial proportions of that nitrogen. We also find that all the nitrogen which may be analytically determined to be present in a steel specimen is not necessarily active nitrogen for the purposes of our invention.

It is our theory that nitrogen which is dissolved interstitially in the iron atomic lattice at the temperature of heat treatment acts in some fashion to inhibit the formation of brittle iron-aluminum alloy and it is this dissolved or uncombined nitrogen which we denominate "active" nitrogen. We have found that nitrogen can combine with certain elements which may be added to steel in small amounts, and that the compounds so formed, presumably nitrides, are stable at the temperature of heat treatment required by the process of our invention. We have found that nitrogen in this form is not active nitrogen as contemplated by our invention. Elements forming stable nitrides of this type include aluminum, vanadium, niobium, zirconium, silicon, boron, and titanium. It is, therefore, necessary to the practice of our invention that the active nitrogen content of the steel base to be clad be determined analytically.

We have found that the active nitrogen content of the steel cannot be more than its so-called "soluble" nitrogen content and, for steels containing the stable nitride forming elements above-mentioned the active nitrogen content may be determined by subtracting from the "soluble" nitrogen content the nitrogen in the form of stable nitrides. This latter nitrogen content is known as the "ester-halogen" nitrogen content. The terms above-mentioned are familiar to those skilled in the art of the analytical determination of the constituents of steel and are defined and the analytical methods they indicate described in the paper "Behavior of Nitrogen and Some of Its Compounds in Steel," by H. F. Beeghly, published in Analytical Chemistry, volume 24, pp. 1095–1100, July 1952, and the references there listed.

Soluble nitrogen includes nitrogen from compounds which are decomposed either on solution of the specimen in an inorganic acid, such as hydrochloric acid, or subsequently during distillation from an alkaline solution, such as sodium hydroxide. Ester-halogen nitrogen includes nitrogen from compounds which remain after the steel matrix is dissolved in bromine and methyl acetate, or equivalent reagents, as described in the reference above-mentioned.

The steel base contemplated by our invention is ordinary low carbon steel, a representative analysis of which is:

	Percent
Carbon	.07
Manganese	.35
Phosphorus	.008
Sulphur	.030
Iron	Balance

If such a steel is rimmed, it normally contains no other deliberately added elements in significant amount and substantially its entire nitrogen content will appear as soluble nitrogen and is active nitrogen. If the steel above-mentioned is deoxidized with aluminum, its soluble nitrogen content will be the same as before but a very appreciable portion of its nitrogen content will be combined as aluminum nitride and can be determined as ester-halogen nitrogen. This ester-halogen figure must be subtracted from the soluble nitrogen figure to determine its active nitrogen content. The same is true if the steel contains other elements previously mentioned as acting the same way as aluminum with respect to nitrogen.

Our invention may best be described in terms of a present preferred process for producing aluminum coated steel sheets comparable to tin plate. We prefer to use as base metal either hot rolled low-carbon steel strip or cold rolled and annealed steel strip. The active nitrogen content of the steel strip is determined in the manner we have described. The steel base is prepared for cladding by a roughening operation, preferably shot blasting with steel grit. The aluminum for cladding is provided in the form of thin sheet or strip of commercially pure aluminum of uniform thickness, thereby insuring uniformity of thickness of the coating of the finished product. The cladding is accomplished by applying the aluminum sheet or strip to the surface of the roughened steel base and cold reducing the composite article by rolling it to a substantial degree of reduction. This cold reduction effects a mechanical bonding of aluminum to steel, but this bond will not withstand any substantial deformation. The composite article is therefore heat treated for a time sufficient to bring about metallurgical bonding between the steel and aluminum. As we have mentioned, the heat treating operation, in the absence of precautions to the contrary, may cause the formation of a brittle iron-aluminum alloy above-mentioned. The process of our invention, therefore, includes the novel step of controlling the temperature of the heat treating operation in accordance with the active nitrogen content of the steel base in a manner to be described.

Reference is now made to the attached figure which is a graph of heat treating temperatures for which brittle alloying between iron and aluminum begins plotted against active nitrogen content of the steel base in percentage by weight. The heat treating temperature at which alloying commences was experimentally determined for two or more samples each of steels having nitrogen contents ranging from slightly more than .001% to about .010%. The temperatures so obtained, which range from about 700° F. to about 1070° F., were plotted as shown. The curve drawn through them is expressed with sufficient accuracy by the empirical equation

$$T = 1140 - \frac{.72}{N} + \frac{.00018}{N^2}$$

where N represents active nitrogen content in percent by weight and T represents temperature in degrees F. It is reasonable to believe that a finite heat treating temperature exists for steels with active nitrogen contents of zero, and that it could be determined if very small active nitrogen contents could be determined. Those skilled in the art are aware, however, that the difficulty of obtaining representative samples, and the limits of error in analytical technique are such that active nitrogen determinations below about .001% are not of much practical significance.

We determine the maximum heat treating temperature for a steel base of any given active nitrogen content from the graph of the attached figure and, as has been mentioned, heat the steel at or below the temperature so determined for a time sufficient to bring about metallurgical bonding between the aluminum coating and the steel base. The time required at the higher temperatures will be only a few minutes if the material is heat treated in the form of a thin strand. It will be understood by those familiar with the art of heat treating sheet and strip that if the clad material is heat treated in the form of coils or piles of sheets the over-all time required to bring the mass of metal to temperature, to soak it, and then cool it to a temperature below the scaling point will be measured in tens of hours or in days, and will, in fact, be comparable with the time required to anneal sheet and strip in the conventional manner. The heat treatment contemplated by our process will also modify the physical properties of the clad material in a manner similar to conventional annealing and may be adjusted to obviate any further annealing treatment. The coated strip after heat treatment may be given the conventional "skin rolling" or like reduction in a cold rolling mill, if desired.

It will be understood that if the heat treatment required by our process is to serve as an anneal, the time required at the temperature selected from the graph of the figure will be longer for lower temperatures than it will be for higher temperatures. For this reason it is generally desirable to heat treat at a temperature as high as is permissible. We have found, however, that the effect of time of heating on the formation of brittle iron-aluminum alloy at the temperatures shown on the attached figure is not of much significance. The time of heating for each point plotted on the attached figure was about six hours and this could be multiplied or divided by a figure of two or three without changing the temperature at which alloying began by more than about 20°. We find that when an article of steel mechanically clad with aluminum is heat treated at a temperature substantially that determined from the active nitrogen content of the steel in accordance with the graph of the attached figure, a tenacious metallurgical bond is formed between aluminum and steel sufficient to withstand severe deformation of the article.

It is well-known that the nitrogen content of steel has a pronounced effect upon its aging and its response to cold working. In general, the higher the active nitrogen content of the steel, the greater the increase in hardness and the decrease in ductility as the steel is cold worked or allowed to age. For this reason, it is generally not desirable to utilize steel of too high an active nitrogen content for the process of our invention, even though such steel permits heat treating at a relatively high temperature, because such steel itself displays properties which are unsuitable for the desired product.

Although the attached figure indicates the heat treating temperatures at which brittle iron-aluminum alloy formation begins for steels of the nitrogen contents plotted, it will be understood that the temperature values so determined are only approximate. The beginning of the formation of brittle iron-aluminum alloy was determined by visual and metallographic examination of samples, and those skilled in the metallographic art are aware that the determination of such critical temperatures is not inde-

pendent of the judgment of the observer. Furthermore, the active nitrogen content of a coil of steel strip is not a unique value, as those skilled in the art of steelmaking know. For any given steel, therefore, it may be possible to heat treat at a temperature somewhat in excess of the specific temperature obtained from the graph corresponding to a specific active nitrogen content determination without unduly harmful effects, or it may be found that the maximum temperature of heat treatment may have to be held somewhat below the value shown by the graph.

As has been mentioned, our invention may be practiced by determining the active nitrogen content of the steel base to be used for cladding and controlling the maximum temperature of heat treatment in accordance therewith, or it may be practiced by selecting or manufacturing the steel strip to have an active nitrogen content within a range corresponding to the heat treating temperature which it is desired to employ. In some cases it may be desirable deliberately to add nitrogen to the steel base to obtain a high active nitrogen content.

The aluminum cladding metal is applied, as has been mentioned, in the form of thin sheet or strip which may be foil as thin as .0005". The aluminum coating provided by our process is thus a preformed aluminum coating, and may be inspected for pin holes in advance of its application. The aluminum is cut to the same dimensions as the base metal sheet or strip or preferably slightly narrower, and laid thereon on one or both sides as desired. The composite strip or sandwich so formed is then cold reduced in a rolling mill, or by other appropriate means, a substantial amount which we prefer to be at least about 35%. In this reducing operation both the aluminum coating and the steel base are reduced in thickness, and the roughened surface of the steel prevents the aluminum from crawling or creeping over the steel base so that it is reduced in thickness as uniformly as is the steel. This cold reduction effects mechanical bonding between the aluminum and the steel, as has been mentioned.

As we have mentioned, we prefer to roughen the surface of our steel base by blasting with steel grit. The size of grit employed is governed by the thickness of the aluminum to be applied so that the ridges and projections formed on the steel surface by the grit blasting do not puncture the aluminum coating upon cold rolling. For very thin aluminum foil, such as that of .0005" thickness previously mentioned, we prefer to grit blast with grit not larger than 120 mesh. When thicker foils are used, correspondingly larger particles of grit may be employed. For foil .002" in thickness, for example, we find 60 mesh grit satisfactory.

It will be understood that the thickness of aluminum sheet or foil used to produce a clad product having an aluminum coating of a desired thickness will depend upon the amount of cold reduction to which the clad strip is subjected. In our process the aluminum and the steel are reduced in the same degree so that if 50% cold reduction, for example, is contemplated, the aluminum sheet or foil should be about twice the thickness of the aluminum coating desired.

Methods of providing the steel base with a mechanically adherent aluminum coating other than the preferred method we have described may be employed in the practice of our invention.

We claim:

1. The process of producing a bimetallic article having a ferrous metal base and a tightly adherent aluminum coating, comprising providing a ferrous metal base of ordinary low-carbon steel with a predetermined active

nitrogen content in the range from about .001% to about .010%, coating the metal base at atmospheric temperature with a mechanically adherent aluminum coating, and heat treating the article at a temperature in the range between about 700° F. and about 1070° F. for a time sufficient to effect metallurgical bonding between metal base and aluminum coating, the temperature being adjusted with respect to the active nitrogen content of the article so as to be directly proportional thereto but below the temperature at which substantial amounts of brittle iron-aluminum alloy are formed at the ferrous metal-aluminum interface.

2. The process of producing a bimetallic article having a ferrous metal base and a tightly adherent aluminum coating, comprising providing a ferrous metal base of ordinary low-carbon steel with a predetermined active nitrogen content in the range from about .001% to about .010%, cladding the metal base at atmospheric temperature with aluminum, and heat treating the article at a temperature in the range between about 700° F. and about 1070° F. for a time sufficient to effect metallurgical bonding between metal base and aluminum coating, the temperature being adjusted with respect to the active nitrogen content of the article so as to be directly proportional thereto but below the temperature at which substantial amounts of brittle iron-aluminum alloy are formed at the ferrous metal-aluminum interface.

3. The process of producing a bimetallic article having a ferrous metal base and a tightly adherent aluminum coating, comprising providing a ferrous metal base of ordinary low-carbon steel with a predetermined active nitrogen content, coating the metal base at atmospheric temperature with a mechanically adherent aluminum coating, and heat treating the article for a time sufficient to effect metallurgical bonding between metal base and coating, at a temperature above about 700° F. and not exceeding that which may be determined from the equation

$$T = 1140 - \frac{.72}{N} + \frac{.00018}{N^2}$$

where N represents active nitrogen content in percent by weight and T represents temperature in degrees F.

4. The process of producing a bimetallic article having a ferrous metal base and a tightly adherent aluminum coating, comprising providing a ferrous metal base of ordinary low-carbon steel with a predetermined active nitrogen content in the range from significant amounts to about .010%, coating the metal base at atmospheric temperature with a mechanically adherent aluminum coating, and heat treating the article at a temperature not exceeding about 1070° F. for a time sufficient to effect metallurgical bonding between metal base and aluminum coating, the temperature being substantially that which may be determined from the equation

$$T = 1140 - \frac{.72}{N} + \frac{.00018}{N^2}$$

where N represents active nitrogen content in percent by weight and T represents temperature in degrees F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,444,422	Bradford	July 6, 1948
2,753,623	Boessenkool et al.	July 10, 1956
2,767,467	Siegel	Oct. 23, 1956
2,782,498	Mushovic et al.	Feb. 26, 1957