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ALUMINUM COATED STEEL ARTICLE AND METHOD OF PRODUCING IT

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3 Sheets-Sheet 1

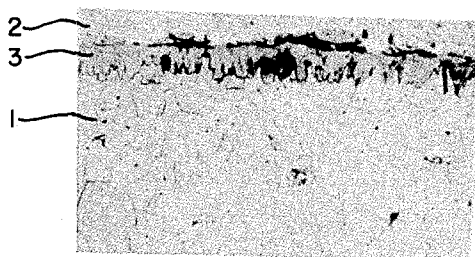


Fig. 1



Fig. 2

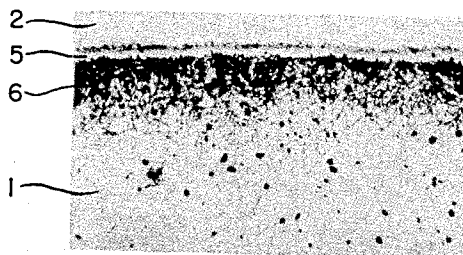


Fig. 3

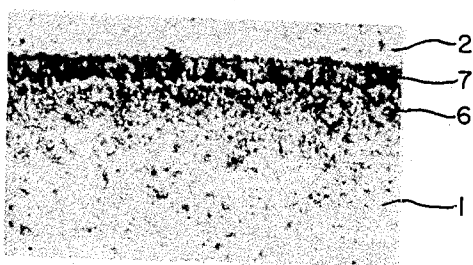


Fig. 4

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3 Sheets-Sheet 2

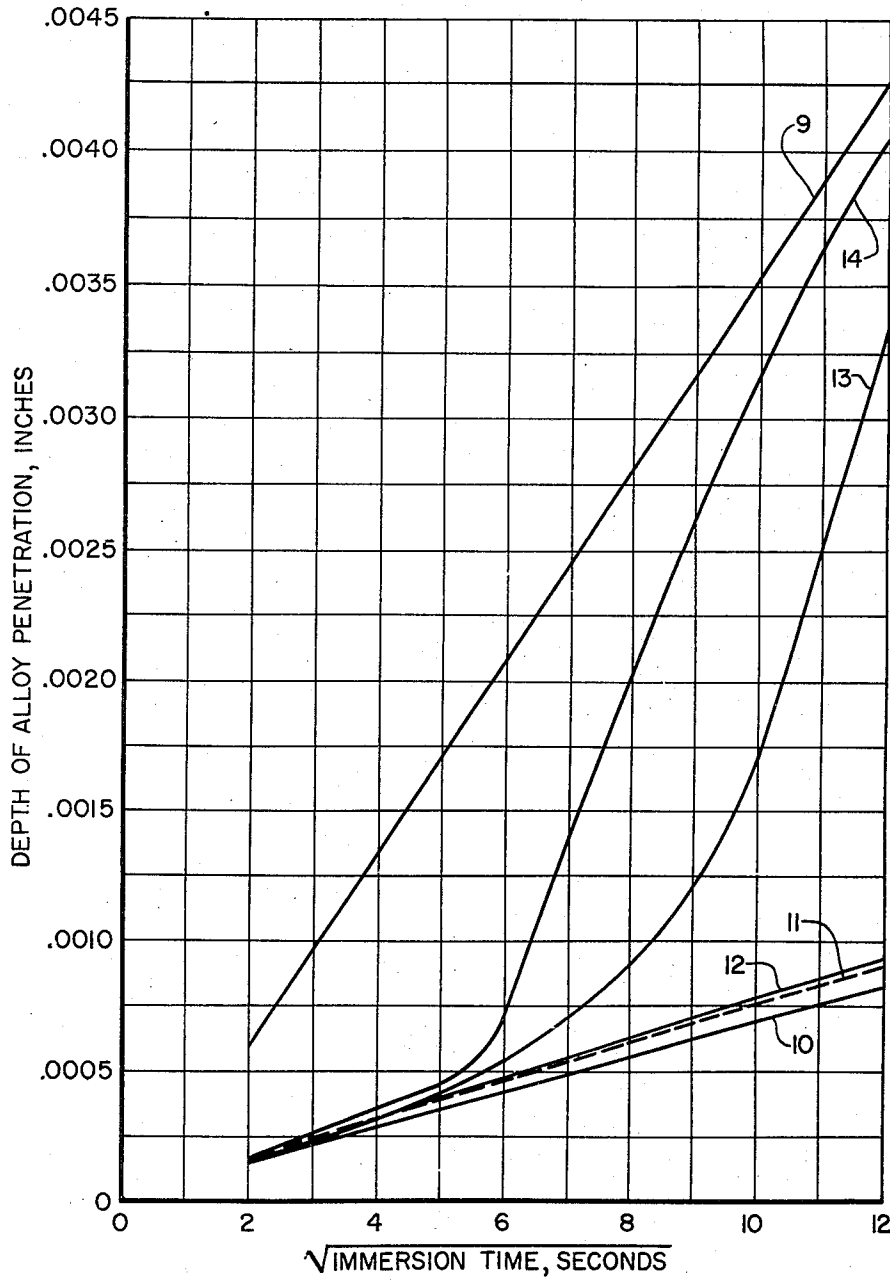


Fig. 5

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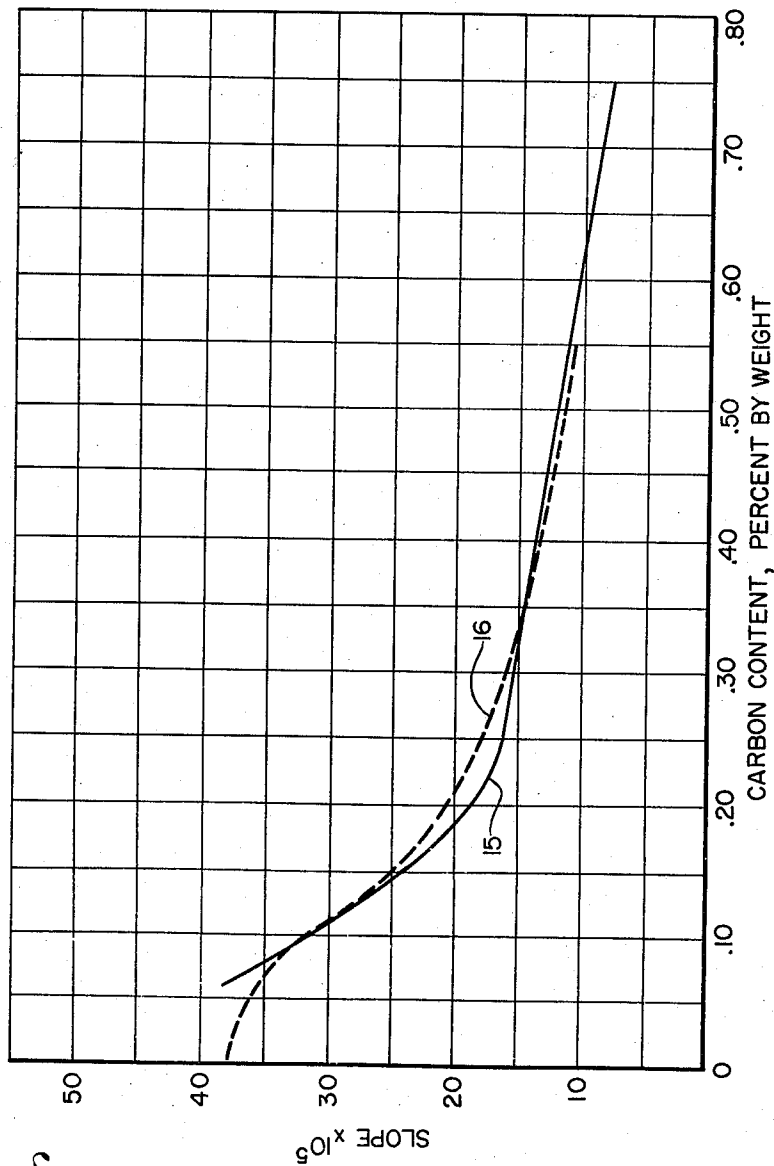


Fig. 6

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ALUMINUM COATED STEEL ARTICLE AND METHOD OF PRODUCING IT

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14 Claims. (Cl. 148—6.35)

This invention relates to a bimetallic article having a ferrous base and a strongly adherent aluminum coating, and to a method of producing such articles.

For many purposes it would be desirable and economical to employ aluminum coated steel articles both in the form of sheet or strip and wire or rod. Because of the difficulty of obtaining a strong bond between aluminum and a ferrous base, no process of making aluminum coated steel has attained any considerable degree of commercial success prior to our invention. A considerable amount of work has been done toward the production of ferrous articles having aluminum coatings produced by hot dipping, and efforts have been made to produce ferrous articles in sheet form having aluminum coatings clad thereon. In general, however, these articles nearly always exhibit to a greater or less degree the defect that the aluminum coating tends to crack or peel off when the article is deformed. It is believed that this undesirable characteristic is caused by a brittle alloy of aluminum and iron which forms at the interface between these metals at temperatures reached in the production of hot dipped articles or in the annealing of clad articles. Some degree of control over the formation of this iron-aluminum alloy can be achieved by control of the chemical composition of the aluminum coating. For example, the addition of silicon or of beryllium to the aluminum coating metal appears to be beneficial in this respect. However, the use of each of these elements is accompanied by certain undesirable effects.

As we have mentioned, attempts have been made to produce aluminum coated steel sheets by cladding, that is, by uniting a sheet of aluminum to one of steel by subjecting them to rolling pressure followed in most cases by annealing. None of these has so far produced a fully commercial article. The mechanical bond created by rolling alone will not withstand deformation, and when the mechanically bonded product is annealed to bring about metallurgical bonding by alloying, the previously mentioned brittle alloy of iron and aluminum is formed.

It is also possible to electroplate aluminum upon a steel base. The coatings so far produced in this way, however, have shown such porosity that it has been necessary to heat them to fusion temperature to close up the pin holes.

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

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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 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 bimetallic article having a ferrous base united with a coating of aluminum which will adhere to the base when the article is deformed. It is another object to provide a process for producing such a bimetallic article. Other objects will appear in the course of the following description of our invention.

It is obvious that a ductile or deformable aluminum coated ferrous article must have a steel base low in carbon content, and it is such a steel base which we contemplate for the article of our invention. A representative analysis of such a low carbon steel is as follows:

	Percent
Carbon	.06
Manganese	.32
Phosphorus	.009
Sulfur	.051
Silicon	.001

Our invention is not limited to steels of this particular composition, however. The coating metal we contemplate is aluminum of better than 99% purity, a representative analysis being as follows:

	Percent
Aluminum	99.8+
Iron	.12
Silicon	.07
Titanium	.01
Chromium	.02

Our invention is not, however, limited to such high purity aluminum, but includes aluminum of commercial purity, and also aluminum alloys the properties of which render them suitable for coating purposes.

We have found that the brittle iron-aluminum alloy, previously mentioned, which forms when a steel article is coated by immersing it in molten aluminum, or by the annealing of a clad article, can be greatly reduced in thickness if the steel base is first carburized to provide it with a thin case or surface layer of high carbon content. We have found that for given conditions of coating, the thickness of this layer is not critical once it exceeds a certain value, and that the steel base carburized to or beyond this certain value behaves when heated with aluminum as though it were a homogeneous plain carbon steel base having a carbon content equivalent to that of its case. Our invention, therefore, comprises an article having a low carbon steel base with a thin surface layer of carburized metal to which the aluminum coating is tightly bonded. Under certain conditions articles of our invention also exhibit to microscopic examination a layer of iron-aluminum alloy between the aluminum coating and the steel base and extending into the carburized layer of the latter. Our invention also comprises a method of producing such an article having as its essential step the carburizing of the low carbon steel base to produce thereon a thin surface layer of carburized metal above mentioned. We prefer to coat our ferrous base so prepared by dipping it into molten aluminum, but it is also possible to coat the base, when it is a sheet or strip, by cladding it with thin aluminum strip or foil and heat treating the clad article. It is also possible to carry out our process by electroplating aluminum on a low carbon steel base provided with a thin case, as has been mentioned, followed by a heat treating step to fuse the coating sufficiently to close up pin holes.

We shall hereinafter describe our process as applied to the hot dipping of steel wire. The first step is to carburize the surface of the wire, and as the process of carburizing is well-known in the art, we do not consider it necessary to dwell upon it here. We have successfully used natural gas as a carburizing medium and have carburized our steel base metal by passing it through a natural gas atmosphere held at a temperature in the range from 1550° F. to 1700° F. The length of time for carburizing varied from a few seconds to 4 minutes. Both the temperature and the length of time can be varied over a considerable range as long as a case of the required depth is attained, as will be discussed fully later on. The natural gas which we employed is composed of more than 90% methane. Under certain conditions it deposited excess carbon on the surface of the wire, which we found it necessary to remove. Wire which required cleaning after carburizing was cooled down approximately to room temperature, mechanically scrubbed, and pickled in hydrochloric acid. The carburized wire with clean surface was then introduced into an atmosphere of dry hydrogen maintained at a temperature of about 1300° F. and held there for a time sufficient to reduce any oxygen compounds on the wire surface. The preheated wire was then transferred without exposing it to air into a bath of molten aluminum held at a temperature of about 1300° F. where it received its aluminum coating.

As we have previously indicated, the depth of carburized case provided on the base metal is a factor highly significant in determining the thickness of the iron-aluminum alloy layer which forms during hot dipping. This relation is graphically shown in the attached figures, to which reference is now made.

Fig. 1 is a photomicrograph at a magnification of 500 diameters of a section through the surface of a piece of uncarburized low carbon rimmed steel after it was immersed for 9 seconds in a molten aluminum at 1300° F. Fig. 2 is a photomicrograph also at a magnification of 500 diameters of the same steel as of Fig. 1 after it was immersed for 64 seconds in molten aluminum at 1300° F. Figs. 3 and 4 represent articles of our invention. Fig. 3 is a photomicrograph of a piece of the same steel as that of Fig. 1 which was carburized to provide a case depth of about .0018" and then immersed for 9 seconds in molten aluminum at 1300° F. Fig. 4 is the same steel as that of Fig. 3 after it was immersed for 64 seconds in molten aluminum at 1300° F.

Fig. 5 is a graph of the effect of immersion time in molten aluminum plotted against the depth of iron-aluminum alloy formed for a number of steels having different thicknesses of carburized surfaces, as hereinafter set out.

Fig. 6 is a graph of the slope of the iron-aluminum alloy growth rate plotted against the carbon content for a number of specimens of steel base having different carbon contents.

In Figs. 1-4 steel base 1 is provided with an aluminum coating 2. It will be observed in Fig. 1 that the uncarburized steel immersed for 9 seconds in molten aluminum at 1300° F. exhibits an unmistakable iron-aluminum alloy layer 3 at the interface between steel base 1 and aluminum coating 2. It will be observed in Fig. 2 that the iron-aluminum alloy layer 4 is of much greater depth when the steel is immersed in molten aluminum for 64 seconds.

Fig. 3 illustrates graphically the great improvement afforded by our invention. Here the iron-aluminum alloy layer 5 is much thinner than the corresponding layer 3 of Fig. 1. The dark area 6 is the carburized case which, as has been mentioned, is about .0018" deep measured from the original steel-aluminum interface. Fig. 4 is perhaps even more striking. Here the iron-aluminum alloy layer 7 is actually of less depth than the corresponding layer 3 of Fig. 1 although the time of immersion was about seven times as long for the specimen of Fig. 4 as it was for that of Fig. 1. Again, the dark area 6 is the carburized case of the same depth as in Fig. 3.

Figs. 3 and 4 show that longer times of immersion in molten aluminum allow the iron-aluminum alloy to penetrate deeper into the carburized case. The depth of case, measured before immersion, must exceed that reached by the alloy layer if the protective effect of the case is to be maintained, but it is not necessary to provide a case depth greatly in excess of that of the alloy layer which will form during the time of immersion contemplated.

With reference to Fig. 5, it will be convenient first to consider curve 9, which was obtained from a piece of low carbon rimmed steel of the composition previously mentioned which was not carburized. Samples of this steel were immersed in molten aluminum at 1300° F. for different periods of time and the thickness of the iron-aluminum alloy layer formed on each sample was measured. Curve 9 is a plot of these quantities and indicates that the thickness of the iron-aluminum alloy layer is directly proportional to the square root of the time of immersion of the steel in aluminum. It is convenient next to consider curves 10, 11 and 12. Curve 10 was obtained from a series of samples carburized to a depth of .0018"; curve 11 from samples carburized to a depth of .0029", and curve 12 from samples carburized to a depth of .0047". The steel base in all these cases was otherwise identical to that of the samples of curve 9. It will be observed that curves 10, 11 and 12 practically coincide, which indicates that a case depth of .0018" is more than sufficient for immersion times up to 144 seconds, and that increase of case depth beyond this figure has no beneficial effect on the thickness of the iron-aluminum alloy layer formed. The fact that curves 10, 11 and 12 are straight lines indicates that when low carbon steels are carburized to provide a case of depth sufficiently greater than that of the alloy layer formed, they behave as though they were homogeneous steels of carbon content equal to that of their case. Curve 13 was obtained from samples of the steel otherwise identical to that of curve 9 but carburized to a depth of .0010", and curve 14 was obtained from like samples carburized to a depth of .0006". It will be noticed that these steels behave like those of curves 10, 11 and 12 for relatively short immersion times, but then bend rather sharply upward as immersion time is increased.

It was noted in the discussion of the curves of Fig. 5 that curve 9, which was plotted for uncarburized low carbon steel, is a straight line. We have found that a homogeneous steel base of any carbon content will give a plot which is also a straight line but having a slope with respect to the abscissa which decreases with increase in the carbon content of the steel. Fig. 6 illustrates how this slope varies with carbon content. Curve 15 was plotted from samples preheated at 1650° F. and dipped into molten aluminum at 1300° F. Curve 16 was plotted from samples preheated at 1300° F. and dipped into molten aluminum at 1300° F. The two curves 15 and 16 coincide for all practical purposes, which indicates that it makes no difference as far as alloy penetration is concerned whether the steel base is in the austenitic or the ferritic state when it is immersed in aluminum. The two curves 15 and 16 show a knee or break at a carbon content of about .20 to .25% and their slope beyond this carbon content is constant at a relatively low value. Thus, as far as rate of alloy penetration is concerned, the critical carbon content of the base or of the carburized case on a low carbon base is seen to be between .20 and .25%.

It is clear from a consideration of the curves of Fig. 5 that a case depth of about .0006" is sufficient for low carbon steel dipped in molten aluminum at 1300° F. for times up to about 25-30 seconds. A case depth somewhere around .0018" is safe for immersion times up through 144 seconds. The critical case depth depends upon the temperature of the aluminum bath and the time of immersion, and these may be varied over a considerable range as commercial considerations dictate. For every set of coating conditions the critical case depth can

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be determined and if the steel base is carburized to this thickness or beyond, the thickness of the iron-aluminum alloy which forms during coating will vary linearly with time of immersion. In other words, the iron-aluminum alloy will form at the same rate as though the steel base were a homogeneous carbon steel of a carbon content equal to that of its case.

In commercial operation the process will preferably be carried on continuously and be adjusted so that the steel base is continuously carburized to or beyond the critical depth for the temperature at which the molten aluminum is held and the time the steel base remains immersed therein. This is quite easy to check experimentally, even though the critical depth of carburized case may not be known for the processing conditions. It is only necessary to immerse in the molten aluminum a homogeneous specimen of carbon steel base of the same gauge as that to be processed but of a carbon content equal to or somewhat greater than that of the carburized case and hold it there for the length of time established for processing. The thickness of iron-aluminum alloy layer formed thereon may then be measured microscopically and compared with that formed on the steel base to be processed. If they are substantially the same, the steel being processed is sufficiently carburized. If the thickness of alloy layer on the steel being processed is greater than that on the high carbon sample, the steel has not been carburized to a sufficient depth. We prefer to carburize to a carbon content beyond the knee of Fig. 6 but as the improvement for carbon contents exceeding about .25% is rather small, the exact value of carbon content reached beyond this figure is not too important.

We claim:

1. A bimetallic article comprising a low carbon steel base, a thin carburized surface layer on said base of a depth microscopically identifiable at a magnification of 500 diameters, and a coating of aluminum tightly bonded to the carburized surface layer.

2. A bimetallic article as in claim 1 having a thin layer of iron-aluminum alloy at the interface between steel base and aluminum coating extending into the carburized surface layer.

3. A bimetallic article comprising a low carbon steel base, a thin carburized surface layer on said base of a depth microscopically identifiable at a magnification of 500 diameters, a thin layer of iron-aluminum alloy on said carburized surface layer, and a coating of aluminum on said iron-aluminum alloy layer.

4. A bimetallic article as in claim 3 in which the thin layer of iron-aluminum alloy extends into the carburized surface layer.

5. A bimetallic article as in claim 3 in which the carburized surface layer has a carbon content in excess of about .20% by weight of the low carbon steel base.

6. The method of producing a ductile bimetallic article having a low carbon steel base and an aluminum coating comprising carburizing the surface of the low carbon steel base to a depth microscopically identifiable at a magnification of 500 diameters and then applying thereto an aluminum coating, the bimetallic article being heated as an incident to the coating thereof to a temperature at which iron and aluminum form a brittle alloy.

7. The method of producing a ductile bimetallic ar-

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ticle having a low carbon steel base and an aluminum coating comprising carburizing the surface of the low carbon steel base to a depth microscopically identifiable at a magnification of 500 diameters and passing the base without exposing it to air through molten aluminum.

8. The method of claim 7 in which the low carbon steel base surface is carburized to a depth exceeding that of the iron-aluminum alloy layer formed when the carburized base is passed through molten aluminum.

9. The method of producing a ductile bimetallic article having a low carbon steel base and an aluminum coating comprising carburizing the surface of the low carbon steel base to a depth microscopically identifiable at a magnification of 500 diameters, treating the carburized surface with a medium to remove oxygen therefrom and passing the base without exposing it to air through molten aluminum.

10. The method of producing a ductile bimetallic article having a low carbon steel base and an aluminum coating, comprising carburizing the surface of the low carbon steel base to a depth microscopically identifiable at a magnification of 500 diameters, preheating the carburized surface in a reducing gas, and passing the heated base without exposing it to air through molten aluminum.

11. The method of claim 10 in which the temperature of preheating is about that of the molten aluminum.

12. The method of producing a ductile bimetallic article having a low carbon steel base and an aluminum coating, comprising heating the low carbon steel base in a medium to carburize it to a depth microscopically identifiable at a magnification of 500 diameters and remove oxygen therefrom, and passing the heated base without exposing it to air through molten aluminum.

13. The method of producing a ductile bimetallic article having a low carbon steel base and an aluminum coating, comprising carburizing the surface of the low carbon steel base to a depth microscopically identifiable at a magnification of 500 diameters, removing therefrom excess carbon deposited thereon during carburizing, preheating the carburized surface at a temperature about that of molten aluminum in a reducing gas for a time sufficient to remove oxygen therefrom, and passing the preheated base without exposing it to air through molten aluminum.

14. The method of producing a ductile bimetallic article having a low carbon steel base and an aluminum coating, comprising heating the low carbon steel base in a carburizing medium so as to carburize its surface to a depth microscopically identifiable at a magnification of 500 diameters, cooling the carburized steel base, removing from the carburized steel base excess carbon deposited thereon during carburizing, heating the clean carburized surface of the steel base in a reducing gas for a time sufficient to remove oxygen therefrom, and passing the heated steel base without exposing it to air through molten aluminum.

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