Jan. 15, 1935. B. J. SAYLES 1,988,217

CALORIZED STEEL ARTICLE

Filed June 15, 1934 2 Sheets-Sheet 1

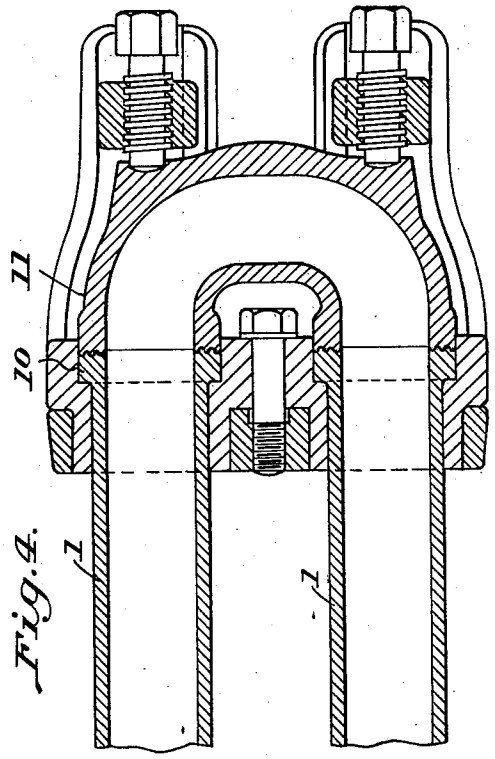



Fig. 4.

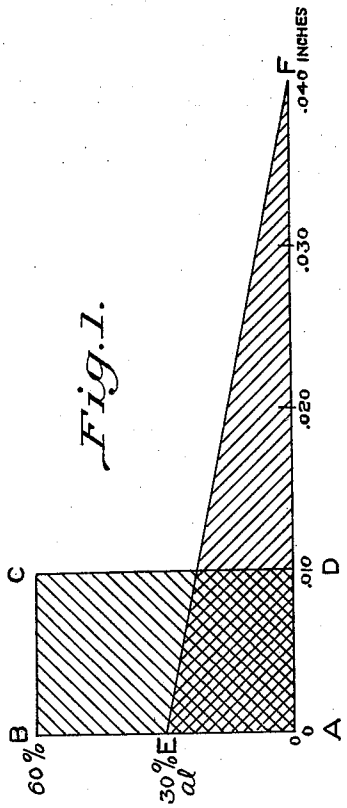



Fig. 1.

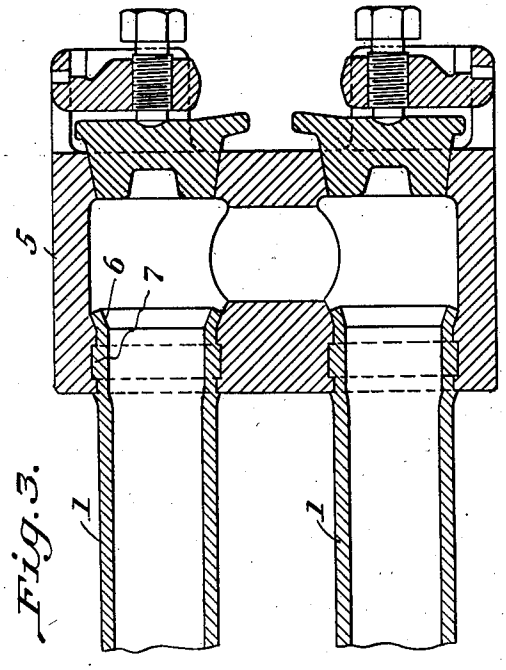



Fig. 3.

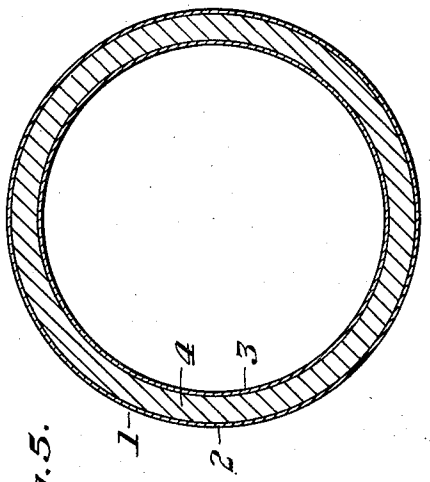



Fig. 5.

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CALORIZED STEEL ARTICLE

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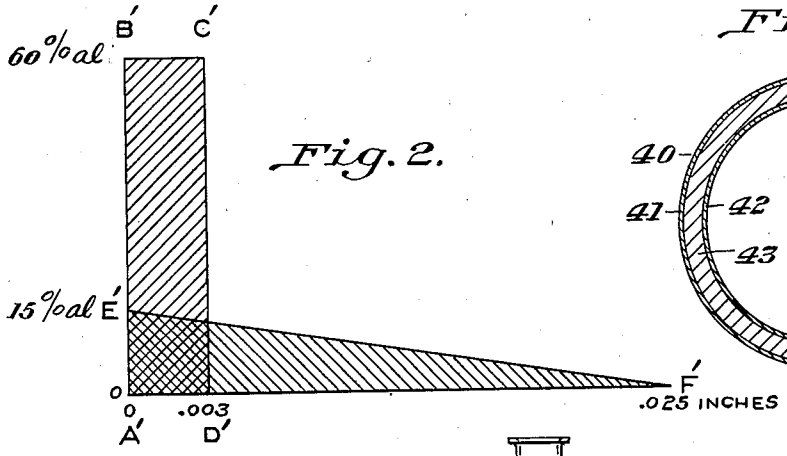



Fig. 2.

Fig. 8.

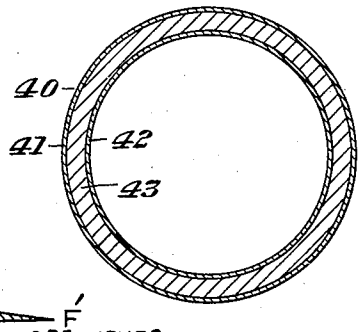



Fig. 7.

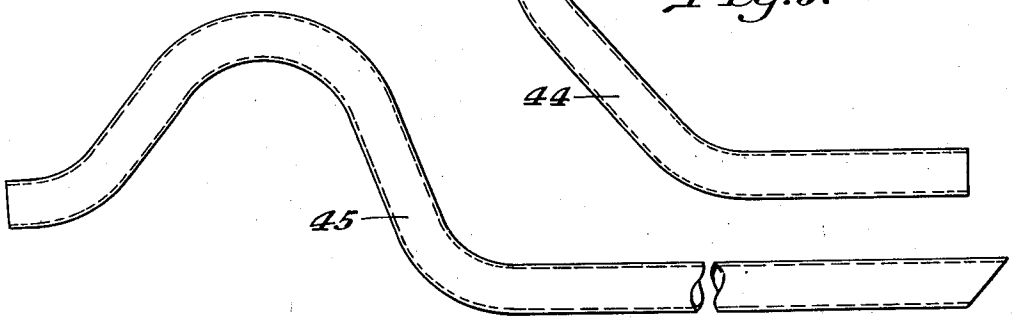



Fig. 6.




Fig. 9.

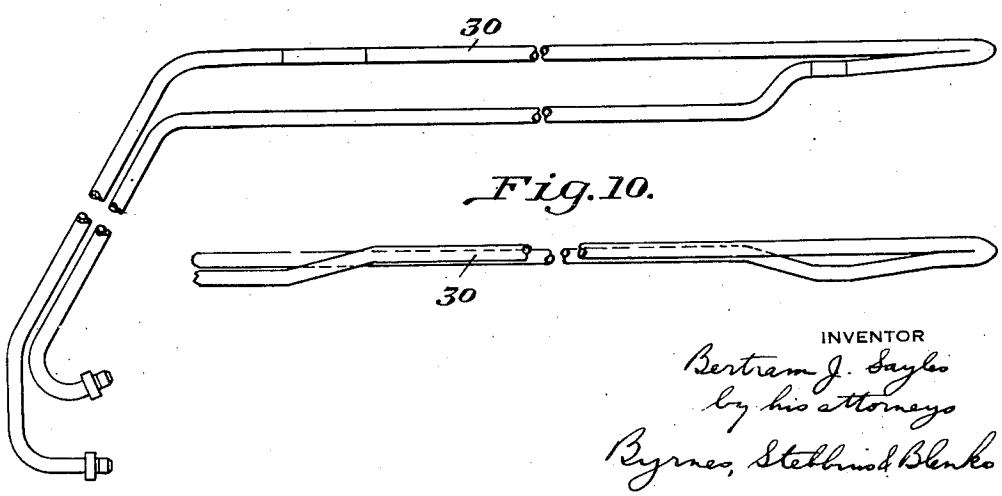



Fig. 10.




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# UNITED STATES PATENT OFFICE

1,988,217

## CALORIZED STEEL ARTICLE

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Application June 15, 1934, Serial No. 730,737

17 Claims. (Cl. 148—31)

The present invention relates to calorized steel articles, and more especially to articles intended for use at temperatures normally not in excess of about 1500° Fahrenheit, and which may be subject to deformation or abrasion. Examples of such articles are oil still tubes, superheater tubes, recuperator or air heater tubes, heat exchanger and condenser tubes, automobile exhaust piping, and various other articles which require a resistance to oxidation and corrosion, and which require a tightly adherent ductile surface.

For example, oil still tubes are operated at wall temperatures of about 1000 to 1300° Fahrenheit and are subjected to high pressures at these temperatures. The outside of the tubes is exposed to the oxidizing action of the heating gases and the inside of the tubes is subjected to the corrosive action of sulphurous compounds in the oil. Carbon is deposited on the inside of the tubes, requiring frequent cleaning of the tubes by tube cleaners to cut out the tightly adherent carbon deposits. In installing the tubes in the oil still the ends of the tubes are expanded to fit the end fittings, so that the tubes and any protecting coatings on the tubes must be sufficiently ductile to withstand such expansion.

Superheater tubes for steam boilers are subjected to somewhat similar conditions, in that they are exposed to the oxidizing and corrosive effect of the furnace gases. In fabricating superheater tubes they are generally bent, which requires that any protecting coating must be of sufficient ductility to allow the tubes to be bent without cracking or spalling off. The interior of the tubes is also subject to oxidation due to the dissociation of the steam.

In the case of the exhaust piping for an automobile, the steel is subjected to both oxidation at high temperatures and to acid corrosive attack. The pipe between the exhaust manifold and muffler becomes heated so that its outside is subjected to destructive oxidation. The inside of the pipe is also subjected to the corrosive attack of the highly heated exhaust gases. The tail pipe beyond the muffler is subjected to acid corrosive attack by the condensate from the exhaust gases. The automobile piping is usually bent cold, which requires that the piping and any protective coating thereon should be able to withstand such cold bending.

As can be seen from these specific examples, the steel must have a high surface stability, that is to say, it must be highly resistant to change or deterioration such as produced in ordinary steel for example by oxidizing, corroding, or the like, agents. Such surface can be imparted by the well-known calorizing process. The aluminum coating as heretofore applied by the ordinary calorizing processes has not been ductile and tends to exfoliate or crack off when the surface is subjected to deformation or abrasion. The calorizing coating usually contains about 50% or more aluminum concentration. While it has a high surface stability in resisting oxidation and corrosion, this high aluminum surface alloyage is extremely brittle and cannot be deformed without rupture and spalling from the steel beneath. It is not tightly adherent to the steel, since there is a fairly sharp line of demarcation between the high concentration of aluminum on the surface and the body of the steel.

These characteristics have precluded the successful application of calorizing to articles which are subject to deformation or abrasion.

I have discovered that the usual calorizing coating may be modified so as to impart to it a considerable ductility and great adherence to the body of the steel, and at the same time retain a sufficiently high resistance to oxidation and corrosion for the purposes intended. Briefly stated, I have found that by a proper heat treatment following the usual calorizing operation, the brittle high aluminum concentration at the surface may be diffused into the body of the steel without destroying its high surface stability but imparting to it the necessary ductility and adherence to the underlying metal required in articles which are subject to deformation or abrasion.

In the drawings, which illustrate certain preferred embodiments of my invention,—

Figures 1 and 2 are diagrams illustrating the diffusion of the aluminum into the steel in accordance with my invention;

Figure 3 is a view, partly in section, of two oil still tubes embodying my invention and a standard return bend fitting into which they are expanded;

Figure 4 is a similar view showing the tubes as expanded to fit another type of return bend fitting;

Figure 5 is a section through one of the tubes showing the aluminized surfaces;

Figure 6 is an elevation of the piece of automobile exhaust piping between the manifold and muffler on one of the standard makes of automobile;

Figure 7 is a similar view of a tail pipe;

Figure 8 is a section through the piping showing the aluminized surface; and

Figures 9 and 10 are an elevation and a partial plan view, respectively, of a superheater tube embodying my invention illustrating the bending or deformation to which it is subjected in fabrication.

In carrying out my invention, the article, such as an oil still tube, automobile exhaust piping, superheater tube, or the like, which may be made of the usual plain low carbon steel, is first subjected to a surface aluminizing treatment, preferably by the so-called calorizing treatment, in which a thin surface alloyage of the aluminum with the steel is formed. This is preferably carried out by the usual powder calorizing process in which the tubes are placed in a retort with the usual calorizing batch containing about 89% aluminum oxide, 10% aluminum powder and 1% of an energizer such as ammonium chloride, and heated at 1600 to 1800° Fahrenheit, preferably at about 1700° Fahrenheit, to cause a surface alloyage of the aluminum with the steel. Powder calorizing is described in the Van Aller Patent 1,155,974 and the Gilson Patent 1,091,057. Such calorizing treatment results in a surface alloyage of the aluminum with the steel, forming a relatively thin surface alloyage layer about .005 to .010 inches thick and containing an aluminum concentration of from 50 to 75%.

The thickness of this aluminum alloyage may vary somewhat, depending upon the time, temperature and percentage of aluminum in the batch, but is always a relatively thin surface layer of high aluminum concentration.

After the calorizing has been carried out, there is a fairly distinct line of demarcation between the aluminized surface layer and the underlying steel, along which there is a tendency for the surface layer to spall off from the steel if the article is subjected to deformation. The surface alloyage having such high aluminum concentration possesses practically no ductility but is exceedingly brittle and hard.

The articles are next subjected to a prolonged heat treatment in a closed retort at a temperature of about 1650 to 2000° Fahrenheit, preferably at about 1800° Fahrenheit. The heat treatment is sufficiently prolonged so that the high aluminum concentration of the thin surface alloyage is reduced to the point where the alloyage becomes sufficiently ductile to permit the required deformation of the article and where the aluminum is diffused into the steel with a relatively deep penetration, resulting in a tightly adherent aluminized surface. The line of demarcation is entirely obliterated and the aluminum concentration tapers off gradually from the surface into the body of the steel, leaving no plane of weakness or exfoliation. The time for such heat treatment depends upon the temperature employed and the initial amount of aluminum applied to the surface by the calorizing treatment. In general, the time may vary from about 24 hours at 1800° Fahrenheit for the diffusion of a light calorized coating, up to 48 hours at 1800° Fahrenheit for a heavier calorized coating.

In Figures 1 and 2 there is illustrated diagrammatically approximately what is believed to take place. In Figure 1 the cross-hatched rectangle A B C D represents a fairly heavy calorizing as imparted by the initial powder calorizing treatment and is illustrated as a surface alloyage of about 60% aluminum with a thickness of about .01 inches. There is a fairly sharp line of demarcation between the aluminized surface and the parent metal as indicated by the line C D. A heat treatment for about 48 hours at 1800° Fahrenheit results in a redistribution of the aluminum approximately as indicated by the cross-hatched triangle A E F. The percentage of aluminum at the surface is reduced, as diagrammatically indicated, to about 30%, the percentage aluminum concentration tapering off into the body of the parent steel roughly in proportion to the distance of penetration. As illustrated, the total penetration is about 0.04 inches, which is relatively deep compared to the penetration secured by the ordinary commercial calorizing methods. In Figure 2 I have illustrated the operation in producing a somewhat lower surface aluminum concentration. In this case the rectangle A' B' C' D' represents the initial surface aluminization corresponding to a rather light powder calorizing treatment and illustrated as about .003 inches thickness and having the usual aluminum concentration of about 60%. The heat treatment for about 24 hours at 1800° Fahrenheit results in causing a relatively deep penetration of .025 inches of aluminum into the body of the steel, as illustrated by the cross-hatched triangle A' E' F'.

Figures 1 and 2 illustrate diagrammatically typical instances. The exact percentage of aluminum concentration at the surface and character of penetration may be varied to suit the individual requirements, as I will now explain.

Iron-aluminum alloyages such as those universally produced by the usual calorizing processes and containing over about 35% aluminum are very brittle and hard and cannot be used on articles which require deformation or are subject to abrasion. However, if the aluminum concentration be reduced below about 35%, the character of the alloyage undergoes a marked change in that the surface alloyage becomes ductile and can be bent with the article without cracking. An aluminum concentration of about 35% appears to be about the upper limit below which a surface alloyage possesses some ductility. The lower limit of aluminum concentration is determined by the required resistance of the surface to oxidation or corrosion. If the oxidation and corrosive conditions are not extremely severe, a surface of fair resistance may be made with the aluminized surface diffused down to a surface concentration of about 5%. However, 9% appears to be about the lower limit of aluminum concentration for very effective resistance to oxidation and corrosive attack.

In general, the greater the aluminum concentration, the higher the surface stability, and balanced against this, in general, the lower the aluminum concentration, the greater the ductility. In the making of any specific article, the aluminum concentration is maintained as high as possible while securing the requisite ductility. For example, in making oil still tubes, which are subjected to fairly severe oxidation and corrosive attack and in which extreme deformation is not required in expanding the tubes in the end fittings, a surface aluminum concentration of about 30% is preferred. In the making of automobile exhaust piping, in

which the oxidizing and corrosive conditions are not as severe but in which the conditions of deformation and vibration are more severe, an aluminum concentration of about 10 to 15% is preferred.

I will now describe certain typical embodiments of my invention with reference to the manufacture of oil still tubes and superheater tubes, and of automobile exhaust piping, particularly as such description will set forth certain other advantageous effects of the heat treatment upon the physical properties of the steel.

*Oil still tubes*

In making oil still tubes, they are first given a fairly heavy initial surface alloyage by the usual calorizing treatment, forming a surface alloyage layer of about .005 to .010 inches thick having the usual aluminum concentration of from about 50 to 75%. The tubes are then subjected to a prolonged heat treatment, preferably about 48 hours, at about 1800° Fahrenheit. This results in a deeply diffused alloyage having about 25 to 30% aluminum concentration at the surface and tapering off to a depth of about .04 inches into the steel. I have found that an aluminum alloyage containing at its surface from about 9 to 35% aluminum concentration has the requisite resistance to oxidation against the heating gases on the outside of the tubes and against the corrosive sulphurous compounds to which the inside of the tubes is subjected. Therefore, the heat treatment should be so regulated that the alloyage at the surface should not be over about 35% aluminum concentration or below about 9% aluminum concentration. The higher the temperature and the longer the time of heat treatment, the greater is the diffusion of the aluminum into the steel with consequent deeper penetration and decreased aluminum concentration at the surface. I prefer to regulate the heat treatment so as to leave a percentage aluminum concentration at the surface of about 20 or 25% to 30 or 35%, usually about 25 to 30%, since this gives excellent resistance to oxidation and corrosion combined with sufficient ductility to withstand deformation in expanding the ends of the tubes into their end fittings.

The heat treatment has another advantageous function in increasing the resistance of the steel against high temperature creep under tension. The prolonged heat treatment results in a grain growth of the crystalline structure of the steel, which has been found to considerably increase the resistance of the steel to slow deformation or creep at the high temperatures of the oil still under the pressures maintained in the tubes.

The tubing most generally employed for oil still tubes at the present time is seamless tubing made of low carbon (about .08 to .18%) steel. I have found that a tubing having increased strength at high temperatures and which can still be successfully treated in accordance with my process, can be made from a steel containing a small amount of molybdenum, about .25 to 2.50%, preferably about .50 to 1%. The carbon is preferably low, about .08 to .18%. I have found that the molybdenum used in such percentages does not interfere with the distribution and penetration of the aluminum into the steel. Additional strength at high temperatures may be secured by using a small percentage of chromium, about .25 to 2.50%, preferably about 1 to 1.50%, in conjunction with the molybdenum.

In Figure 5 there is illustrated a cross-section of an oil still tube treated in accordance with my process, in which the tube is indicated generally by reference numeral 1. The aluminum alloyage on the outside of the tubes is indicated at 2, and the aluminum alloyage on the inside at 3. The steel between them is indicated at 4.

In Figure 3 there is illustrated the ends of two oil still tubes 1 having their ends expanded into a standard end return bend fitting indicated generally by reference numeral 5. In applying the fitting to the ends of the tubes 1, the ends of the tubes are put into the fitting and expanded by a tube expander in the usual way. As shown in the drawings, the extreme end of a tube 1 is stretched or flared at 6. Also, near the end of the tube it is expanded as indicated at 7 to lock into a recess in the internal bore of the fitting. The expanding of the tubes into this type of fitting is carried out cold, and I have found that the surface alloyage as produced by my process is sufficiently ductile and adherent to the underlying steel so that such cold expansion can take place without cracking or spalling off of the aluminized surface. The crystalline grain growth imparted by the heat treatment employed, while it somewhat increases the stiffness of the metal cold as well as increasing its resistance to high temperature creep, does not reduce the cold ductility enough to prevent expansion of the ends of the tubes cold with the usual tube expander.

In Figure 4 I have illustrated the ends of the oil still tubes 1 as held in another standard type of return bend end fitting. In this type of fitting the end of the tube 1 is upset hot to form a flange 10 which is received in a recess in the internal bore of the fitting indicated generally by reference numeral 11. This requires a considerable deformation of the end metal of the tube, but I have found that the surface alloyage as produced in accordance with my process has sufficient ductility to resist cracking off or spalling during the upsetting operation and to resist cracking except minute surface cracks which do not extend through the surface alloyage.

The oil still tubes processed in accordance with my treatment meet the severe conditions required in the following respects:

1. The surface alloyage, because of its reduced aluminum concentration at the surface below about 35%, and because of the relatively deep penetration with a tapering off of the aluminum concentration into the body of the parent metal, does not crack or spall off when the ends of the tubes are expanded cold into the end fittings, or when the ends of the tubes are upset hot for reception into the end fittings. An oil still tube having the aluminized surface imparted by the usual calorizing treatment cannot stand such deformation because the high concentration surface alloyage is so brittle as to crack and spall off, such spalling occurring along the plane of relatively sharp demarcation between the high concentration alloyage and the steel beneath.

2. The alloyage having the surface concentration of from about 9 to 35% aluminum, still contains sufficient aluminum to effectively resist the oxidation at high temperatures to which

the outsides of the tubes are subjected with the hot gases of combustion employed to heat the still.

3. The aluminum concentration at the interior surface (of from about 9 to 35%) is sufficient to effectively withstand the corrosive action of the sulphurous compounds frequently occurring in petroleum. The corrosive attack of the petroleum is not as severe as the oxidation to which the outsides of the tubes are subjected, so that the interior aluminum alloyage steel resists such corrosive attack even if its richer surface portion is removed in the tube cleaning operations.

4. The surface alloyage on the interior of the tubes, while not brittle and strongly adherent to the parent metal, possesses relatively great hardness and resistance to abrasion, which is an important feature since the tubes must be frequently cleaned by passing through them tube cleaners having cutting blades for removing the tightly adherent carbon deposits. While the high aluminum concentration surface alloyage imparted by the usual commercial calorizing process is extremely hard, it is, nevertheless, very brittle and tends to spall off when subjected to the action of the tube cleaner, so that such tubes cannot successfully withstand cleaning with the tube cleaners. When the still tubes are made of the ordinary low carbon steel without the aluminized surface protection, the steel surface is so soft that in time it is cut away and abraded by the tube cleaners.

As a specific example of such advantage, I may cite a test in which a number of tubes treated in accordance with my process were compared with a number of tubes of the same low carbon steel untreated. A standard tube cleaner was passed through each tube for 150 passes at a speed of five feet per minute, which represents approximately the amount of tube cleaning required for four years' service of an oil still. Such tube cleaning resulted in no measurable abrasion of the surface formed by my process, but after such tube cleaning the surface showed a high polish. The plain steel tubes under the same conditions lost 1/32nd of an inch due to abrasion by the tube cleaner, and the surface also showed bad scoring and scratching.

5. The heat treatment employed in my process for reducing the high surface aluminum concentration and for deeply diffusing the aluminum into the parent metal, considerably increases the resistance of the steel against the slow deformation or creep at the high temperatures employed in the oil stills. Microscopic examination of the metal before and after my heat treatment indicates a considerable grain growth in the crystalline structure of the steel, which is believed to be the cause of such increased resistance to high temperature creep.

Metals at high temperatures do not possess a true elastic limit. If a specimen is heated and immediately pulled in the manner employed for conducting room temperature tests on steel, an apparent elastic limit is recorded. However, if the steel in a heated condition is subjected to loads for an extended period of time, it is found that there is a constant creep or flow of the metal which possesses the general characteristics of a plastic material. This is the condition encountered due to continued tension on the tube walls which are subjected to the still pressure at the high still temperatures. A comparative test on a mild steel tubing untreated, and the same tubing treated in accordance with my process, showed that a load of 1400 pounds per square inch gave a creep value of 1% after 10,000 hours at 1100° Fahrenheit for the untreated steel, whereas it required 2050 pounds per square inch to give 1% creep value after 10,000 hours at 1100° Fahrenheit with the tubing steel after treatment by my process. This shows a 46% increase in the high temperature strength of the steel. A lighter tubing can therefore be employed if treated in accordance with my process, with consequent increase in inside diameter and increased capacity of the still, as well as greater heat conductivity through the thinner wall.

Incidentally, it may be remarked that the tubing subjected to the usual calorizing process does not have such increased resistance to high temperature creep as is imparted by the prolonged heat treatment employed in my process for the redistribution and diffusion of the coating as applied by the usual calorizing processes.

*Superheater tubes*

Superheater tubes are employed in steam boilers for highly superheating the steam. The superheater tubes may be subjected to wall temperatures of about 1300 to 1400° Fahrenheit and to high steam pressures. The outsides of the tubes are subjected to the oxidizing and corrosive attack of the furnace gases, while the insides of the tubes are subjected to oxidation due to the dissociation of the steam.

In Figure 9 is illustrated a typical superheater tube 30 showing the bending to which the tubing is subjected. While the bending is fairly severe, it is generally carried out hot, so that aluminum concentrations substantially the same as those employed in oil still tubes may be used. Superheater tubes are manufactured with substantially the same process conditions as described in connection with the oil still tubes, which do not need to be here repeated. As in the case of oil still tubes, the prolonged heat treatment results in an increase in the creep resistance of the superheater tubes against steam pressures at high temperatures. The molybdenum and molybdenum-chromium alloy steels described in connection with the oil still tubes may be advantageously employed for superheater tubes.

The development of superheaters at the higher temperature ranges has been retarded for lack of a moderately priced tube which will effectively withstand the conditions of service from a standpoint of oxidation, corrosion and creep imposed by such installations.

The molybdenum and chrome-molybdenum steels possess the requisite high temperature strength, but do not have sufficient resistance to oxidation and corrosion, which properties are imparted by the surface aluminizing. On the other hand, surface aluminizing as applied by the usual calorizing processes is not suitable because it will not withstand the deformation in the fabrication of the tubes. My superheater tubes can be made at a relatively low cost and at the same time possess all of the requisite properties required in superheater use.

*Automobile exhaust piping*

Automobile exhaust piping is subject to both high temperature oxidation and corrosive attack. The pipe between the engine and muffler

may become heated by exhaust gases up to 1200 to 1300° Fahrenheit, particularly when it is lagged to protect floor boards, and is therefore subject to high temperature oxidation. The inside of the tube is also subjected to the corrosive attack of the hot gases. The tail pipe beyond the muffler is subjected to the corrosive attack of the condensed gases, particularly in automobiles which are frequently started and stopped. Plain steel tubing, which is usually employed, is frequently perforated before the car has run 10,000 miles. Automobile exhaust piping is bent cold and is therefore subjected to severe conditions of deformation. In making automobile exhaust piping I prefer to employ a surface aluminum concentration somewhat lower than that required from oil still tubes and superheater tubes, since the oxidizing and corrosive conditions are not as severe, and because the lower aluminum concentration better meets the more severe deformation.

In making automobile exhaust piping, ordinary low carbon (.08 to .18%) mild steel tubes of about 14 gauge is preferably employed. The lengths of unbent tubing are first subjected to a rather light surface aluminizing treatment, preferably by the usual powder calorizing method, which results in a rather thin surface alloyage, preferably about .003 to .005 inches thick. The tubing is then subjected to a prolonged heat treatment in a closed retort, preferably for about 24 hours, at about 1800° Fahrenheit. This results in reducing the concentration of aluminum at the surface and a diffusion or penetration of the aluminum relatively deeply into the body of the steel, resulting in a highly ductile, tightly adherent, aluminized surface of sufficient concentration to resist the oxidizing and corrosive conditions encountered. Preferably, the heat treatment is carried out to produce a concentration at the surface of between 10 and 20% aluminum, since this combines good ductility with excellent resistance to the oxidation and acid corrosion encountered in use, although as in the case of the oil still tubes, the surface concentration may vary from 9 to 35%. Good resistance, however, can be secured even if the surface concentration is reduced to as low as about 5%.

The heat treatment required to produce the reduction in the surface aluminum concentration and to cause the penetration of the aluminum into the metal, when carried out as above described, results in coarsening the granular structure of the steel which tends to make the piping more brittle and less adaptable for the cold bending operations. Therefore, after the heat treatment described above, the tubing is subjected to a relatively long soaking period in the order of about 12 hours at the lower critical point, which, for mild steel tubing of .08 to .18% carbon content, is about 1650° Fahrenheit. The tubing should then be cooled rather rapidly in air to inhibit any tendency to a reversion of the structure to a coarse grain size. I have found that such treatment restores the ductility of the tubing so that it can be readily given the necessary bending in fabricating the automobile exhaust piping system.

The tubing treated in accordance with the above described process is a considerable improvement over the plain tubing now employed. My tubing has the requisite ductility for cold bending. The reduction in the aluminum concentration at the surface results in imparting to the aluminized surface sufficient ductility so that the tubing can be bent without surface cracking, and the diffusion of the aluminum into the steel with the tapered off concentration overcomes any tendency for the coating to become exfoliated along a cleavage plane, as would be the case with the usual calorized coating. I have found that while the surface concentration of aluminum is reduced greatly below that of the standard calorized surface, in order to get the requisite ductility, the aluminum concentration is still sufficient to effectively resist oxidation and corrosive gaseous attack at high temperatures, as well as the low temperature attack of acid condensate, to which the parts of the exhaust system are subjected in an automobile.

In Figure 5 of the drawings is illustrated a cross-section of the piping, which is indicated generally by reference numeral 40. In this figure, reference numeral 41 indicates the outer aluminized surface and 42 the inner aluminized surface, which are separated by the body or core 43 of the non-aluminized steel. The usual exhaust tubing is of 18 gauge thickness. I prefer to use somewhat heavier gauge, preferably about 14 gauge, so as to leave the core of soft mild steel forming a substantial percentage of the cross-sectional area.

In Figure 3 there is illustrated the piece of tubing 44 which extends from the engine exhaust manifold to the muffler, the form illustrated being that of one of the commercial automobiles. As shown here, this tubing is subjected to rather sharp bending requiring considerable ductility. This piece of tubing also may be lagged with asbestos, which subjects it to a high temperature under the oxidizing and corrosive gas attack conditions. In Figure 4 there is illustrated the tail pipe 45 of an automobile, illustrating the amount of bending to which such piping must be subjected.

While the present process has been developed primarily for the treatment of the pieces of tubing constituting the tail pipe and the connection between the exhaust manifold and the muffler, the process can be applied to other parts of the automobile exhaust piping system including the muffler and the exhaust manifold, since these parts are also subject to the high temperature oxidation and corrosive gas attack, and I therefore use the words "automobile exhaust piping" as a term of general description and not of limitation, and as applying to any of the parts of the exhaust system.

While I have above described the preferred process of treating the automobile exhaust material, there are other specific methods which may be employed according to my process. One of these methods is to conduct the calorizing and subsequent heat treating operation at a temperature below the lower critical point of the steel, so that grain growth with the impairment of ductility does not take place. For mild steel tubing (.08 to .18% carbon) commonly employed, the lower critical point is about 1650° Fahrenheit, so that in this specific method the calorizing and heat treatment should both be conducted at, say, about 1600° Fahrenheit. This method does away with the necessity of soaking at the lower critical point to restore the grain structure. The calorizing and heat treating at the temperature of about 1600° Fahrenheit result in a rather light aluminum deposit and light diffusion, but the surface alloyage thus pro-

duced is usually adequate for the service conditions encountered.

Another method is to completely bend and fabricate the material before calorizing it. In this case the powder calorizing is performed by the "pack" method, in which the work is packed in a sealed container with the usual calorizing batch and subjected to a prolonged heat treatment. The alloying of the aluminum with the surface of the steel and subsequent diffusion takes place in a single operation. The surface alloyage is usually light, since only that aluminum in contact with the surface of the steel is available for reaction. The pack method may be practiced on automobile exhaust material in one of two ways:

(*a*) The process may be carried out below the lower critical point of the steel for a relatively long period, say, 24 to 48 hours, in which case there is no grain growth of the steel and no need of subsequent grain refinement.

(*b*) The time may be substantially shortened, say, 8 to 16 hours, by raising the temperature to about 1800° Fahrenheit, in which event it is necessary to follow with soaking at the lower critical point to refine the grain.

*Other products*

The invention may be embodied in other specific articles which are intended for use at temperatures normally not in excess of about 1500° Fahrenheit. The specific articles described above, namely, oil still tubes, superheater tubes and automobile exhaust piping, are not subjected to temperatures in excess of about 1500° Fahrenheit. For temperatures below about 1500° Fahrenheit, the diffusion and distribution of the aluminum secured by my heat treatment remains stable and the surface is permanently protected against oxidation or corrosion. On the other hand, if the articles were to be subjected in use to temperatures much in excess of about 1500° Fahrenheit, such higher temperatures would tend to dissipate the aluminum and reduce the surface concentration to a point where it would no longer effectively resist oxidation and corrosion.

The invention is particularly applicable to articles which are subject to deformation in fabrication or in use, or subjected to abrasion or mechanical vibration. Examples of such articles are recuperator or air heater tubes, carbon black burner pipes, coke still bottoms, and bolting materials, particularly for use under heated oxidizing and corrosive conditions. These articles are preferably given a fairly heavy initial calorizing treatment followed by the heat treatment described in connection with the manufacture of oil still tubes, since this gives high resistance to oxidation and corrosion, combined with sufficient ductility and adherence of the coating to meet the conditions encountered.

Heat exchanger and condenser shells, and heat exchanger and condenser tubes, are other examples of articles embodying my invention. Since the heat and corrosive conditions are not as severe, and since the steel is usually subjected to rather severe deformation in fabrication, I prefer to employ a lower aluminum surface concentration as secured, for example, by the process described in connection with the manufacture of automobile exhaust piping.

This application is a continuation-in-part of my copending applications Serial Nos. 684,922 and 684,923, both filed August 12, 1933.

While I have described certain specific embodiments of my invention, it is to be understood that the invention is not so limited, but may be otherwise embodied and practiced within the scope of the following claims.

I claim:

1. A steel article for use at temperatures normally not in excess of about 1500° Fahrenheit, having an aluminized surface with a surface concentration of about 5 to 35% aluminum tapering off gradually into the body of the steel and characterized by its ductility and adherence and its high surface stability.

2. A steel article subject to deformation or abrasion and intended for use at a temperature normally not in excess of about 1500° Fahrenheit, having an aluminized surface with a surface concentration of about 5 to 35% aluminum tapering off gradually into the body of the steel and characterized by its ductility and adherence and by its resistance to oxidation or corrosion.

3. A steel article subject to deformation or abrasion and intended for use at a temperature normally not in excess of about 1500° Fahrenheit, having an aluminized surface with a surface concentration of about 9 to 35% aluminum tapering off gradually with relatively deep diffusion of the aluminum alloyage into the body of the steel and characterized by its ductility and adherence and by its resistance to oxidation or corrosion.

4. A steel oil still tube having an aluminized surface with a surface concentration of about 9 to 35% aluminum tapering off with relatively deep penetration into the steel and characterized by sufficient ductility and adherence of such aluminized surfaces to permit expansion of the tube into the usual end fittings and by resistance to oxidation at the outside of the tube and resistance to corrosion and tube cleaner abrasion at the inside of the tube.

5. A steel oil still tube having an aluminized surface with a surface concentration of about 20 to 35% aluminum tapering off with relatively deep penetration into the steel and characterized by sufficient ductility and adherence of such aluminized surface to permit expansion of the tube into the usual end fittings and by resistance to oxidation at the outside of the tube and resistance to corrosion and tube cleaner abrasion at the inside of the tube.

6. A steel oil still tube having aluminized surfaces heat treated to produce a surface concentration of about 9 to 35% aluminum with relatively deep diffusion of the aluminum alloyage into the body of the steel and characterized by the ductility and adherence of such aluminized surfaces and their resistance to oxidation on the outside of the tube and their resistance to corrosion and tube cleaner abrasion on the inside of the tube, and further characterized by an increased resistance of the steel to creep under tension at high temperatures.

7. A steel oil still tube formed of an alloy steel containing from about .25 to 2.5% molybdenum and having aluminized surfaces with a surface concentration of about 9 to 35% aluminum with relatively deep penetration into the steel and characterized by sufficient ductility and adherence of such aluminized surfaces to permit expansion of the tube ends into the usual fittings and by resistance of such surfaces to oxidation

on the outside of the tube and by resistance to corrosion and tube cleaner abrasion on the inside of the tube, as well as being characterized by high tensile strength at high temperatures.

8. An oil still tube formed of an alloy steel containing .25 to 2.5% molybdenum and from .25 to 2.5% chromium and having aluminized surfaces with a surface concentration of about 9 to 35% aluminum with relatively deep penetration into the steel and characterized by sufficient ductility and adherence of such aluminized surfaces to permit expansion of the tube ends into the usual fittings and by resistance of such surfaces to oxidation on the outside of the tube and by resistance to corrosion and tube cleaner abrasion on the inside of the tube, as well as being characterized by high tensile strength at high temperatures.

9. Steel automobile exhaust piping having an aluminized surface with a surface concentration of about 5 to 35% aluminum tapering off gradually into the body of the steel and characterized by its ductility and adherence and by resistance to oxidation and corrosion to which automobile exhaust piping is subjected.

10. Steel automobile exhaust piping having an aluminized surface with a surface concentration of about 10 to 20% aluminum tapering off gradually into the body of the steel and characterized by its ductility and adherence and by resistance to oxidation and corrosion to which automobile exhaust piping is subjected.

11. An automobile exhaust system containing mild steel tubing having an aluminized surface with a surface concentration of about 5 to 35% aluminum tapering off gradually into the body of the steel and characterized by sufficient ductility and adherence of such aluminized surface to permit bending of the tube in fabricating the exhaust system and by its resistance to oxidation and corrosion encountered in such system.

12. An automobile exhaust system containing mild steel tubing having an aluminized surface with a surface concentration of about 10 to 20% aluminum tapering off gradually into the body of the steel and characterized by sufficient ductility and adherence of such aluminized surface to permit bending of the tube in fabricating the exhaust system and by its resistance to oxidation and corrosion encountered in such system.

13. A superheater tube having an aluminized surface with a surface concentration of about 9 to 35% aluminum tapering off with relatively deep penetration into the steel and characterized by sufficient ductility and adherence of such aluminized surface to permit the deformation encountered in fabricating the tube and by its resistance to oxidation and corrosion.

14. A superheater tube having an aluminized surface with a surface concentration of about 20 to 35% aluminum tapering off with relatively deep penetration into the steel and characterized by sufficient ductility and adherence of such aluminized surface to permit the deformation encountered in fabricating the tube and by its resistance to oxidation and corrosion.

15. A superheater tube having aluminized surfaces heat treated to produce a surface concentration of about 9 to 35% aluminum with relatively deep diffusion of the aluminum alloyage into the body of the steel and characterized by the ductility and adherence of such aluminized surfaces and their resistance to oxidation and corrosion, and further characterized by an increased resistance of the steel to creep under tension at high temperatures.

16. A superheater tube formed of an alloy steel containing from about .25 to 2.5% molybdenum and having aluminized surfaces with a surface concentration of about 9 to 35% aluminum with relatively deep penetration into the steel and characterized by sufficient ductility and adherence of such aluminized surfaces to permit the deformation encountered in fabricating the tube and by the resistance of such surfaces to oxidation and corrosion, as well as being characterized by high tensile strength at high temperatures.

17. A superheater tube formed of an alloy steel containing from about .25 to 2.5% molybdenum and from about .25 to 2.5% chromium, and having aluminized surfaces with a surface concentration of about 9 to 35% aluminum with relatively deep penetration into the steel and characterized by sufficient ductility and adherence of such aluminized surfaces to permit the deformation encountered in fabricating the tube and by the resistance of such surfaces to oxidation and corrosion, as well as being characterized by high tensile strength at high temperatures.

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