

**EVALUATION OF SURFACE TREATMENTS FOR
LOW ALLOY STEELS**

**Part 2. Paint Chromizing, Paint Siliconizing, and
Coating of Titanium-Boron Low Alloy Steel**

SAM TOUR

SAM TOUR & CO., INC.

NOVEMBER 1954

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-406
PROJECT No. 7351

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared by Mr. Sam Tour of Sam Tour & Co., Inc. under Contract No. AF 33(616)-406. The contract was initiated under Task No. 73512 (formerly RDO No. 619-11, "Critical Materials"), and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt J. R. Miller acting as project engineer.

In the carrying out of the work covered by this report, the author gratefully acknowledges the assistance and cooperation of Mr. Wallace Johnson, the inventor of the process, and the direct assistance of the staff of Sam Tour & Co., Inc.

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ABSTRACT

Diffusion coatings produced by chromizing or siliconizing offer considerable promise as heat resistant corrosion protective coatings for use on low to medium carbon, plain carbon or low alloy steels for service at temperatures up to 1200°F. Either of these types of coatings can be applied by the paint process.

The paint used consists of a suspension or slurry containing (a) the desired metal powder (chromium or silicon), (b) a fluoride, (c) glass frits of low and high melting points, (d) a liquid vehicle containing suspension agents and binders, and (e) a volatile thinner.

Substantially no pre-preparation of the steel surface is necessary. The paint is applied by brush, dip or spray. Several coats with intermediate air drying are required. After a preheat, the work is heated or fired in an open furnace. Temperatures of 1900 to 1950°F for 1 to 3 hours are required for chromizing. Temperatures of 1750 to 1850°F for 10 to 30 minutes are required for siliconizing. In either case, as furnace heating proceeds, the binders in the paint burn away and the glass frits melt to form a molten protective, but reactive, blanket enveloping the work and protecting it from oxidation as the chromizing or siliconizing reaction takes place. Upon removal from the furnace and cooling, the glass freezes, shrinks and cracks away, leaving the treated surfaces relatively clean.

The low alloy titanium-boron steels can be paint chromized or paint siliconized. The coatings provide protection against scaling during solution heat treatment at temperatures as high as 2100°F.

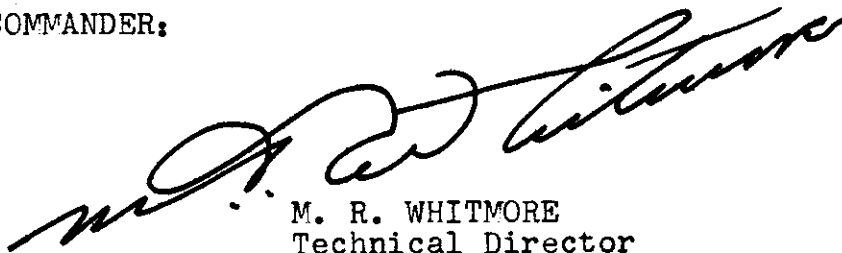
The chromized cases on low carbon steel are continuous, uniform, ductile layers that withstand bending and forming operations and can be welded. The siliconized cases are hard, brittle and zonal in nature, with a thin interfacial zone that is continuous.

Further development work on both the paint chromizing and the paint siliconizing processes is outlined and recommended.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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Section I - Introduction

A survey of the many types of metallic and paint coatings systems used or proposed as heat resisting corrosion protective coatings for plain carbon and low alloy steels indicated that the diffusion types offered the most promise. Inherently, the diffusion types of coating should be less subject to pin hole porosity because the diffusion action is both parallel to and vertical to the surface being coated or treated. This is generally recognized in carburizing and nitriding and should be true in all diffusion processes. By diffusion coating, a surface layer of a low alloy or plain carbon steel can be converted into a high alloy heat resistant and corrosion resistant layer. Since diffusion coating processes are true alloying processes, the coatings so formed should have great adherence. If the elements as added by diffusion form ductile alloys with iron, the coated product should have a certain amount of formability. If brittle compounds or brittle alloys are formed with iron, the reverse would be true.

Among the various metals that might be used to form heat resisting corrosion protective surface layers on plain carbon and low alloy steels, the outstanding ones are aluminum, chromium, and silicon. In the case of aluminum, the brittle iron aluminum compounds must be expected. At temperatures near or above the melting point of aluminum, 1220°F, alloying, the formation of iron aluminum compounds and diffusion begin to take place. At higher temperatures, the diffusion reaction becomes more active. The various processes for the application of aluminum coatings and the nature of the products have been described in some detail in Chapter II of WADC Technical Report 54-209 as prepared under Phase I of Contract AF 33(616)-406.

In the case of chromium, in the absence of carbon or at low carbon levels, the high chromium iron alloys formed by the diffusion process are quite ductile. For diffusion to take place, much higher temperatures are necessary than in the case of aluminum. Conversely, having produced a chromized case, it can be expected to maintain its surface alloy nature for long periods of time at higher temperatures than the aluminum diffusion coatings. In the case of silicon, the high silicon-iron alloys are **hard** and brittle but quite remarkable in their corrosion resistance. The temperatures required for diffusion to take place are higher than for aluminum, although a little lower than for chromium. The various processes for chromizing and siliconizing and the nature of the products have been described in some detail in Chapter IV of WADC Technical Report 54-209 referred to above.

The primary purpose of applying heat resistant corrosion protective coatings to plain carbon or low alloy steels is to make these steels suitable substitutes for high alloy steels of the stainless steel variety. For temperatures up to 800 or 1000°F, where the inherent strength of the plain carbon steels may be adequate, all that is required is that they be protected from oxidation and corrosion attack. For temperatures in the neighborhood of 1000 to 1200°F,

the plain carbon or ordinary low alloy steels have such low creep strength that they cannot compete with the stainless steels.

A report from Cornell Aeronautical Laboratories, WADC Technical Report 52-77 of April 1952 on "Development of Low Alloy Titanium-Boron Steels for High Temperature Service Applications" indicates that these steels offer great promise for service up to 1200°F or slightly above, insofar as creep strength is concerned. To develop the high creep strength properties of these Ti-B steels, it is necessary that they be given a final solution heat treatment by heating to about 2000 to 2100°F for a few minutes and cooling fairly rapidly. Subsequent to such preparatory heat treatment, these steels have high creep strength characteristics at the temperatures indicated. Heating to a temperature in the range of 1400 to 1800°F is destructive of the solution heat treatment condition and results in a loss of creep strength at 1100 to 1200°F. Thus, it is apparent that any coating to be applied to the Ti-B steels must be one that can be applied after solution heat treatment without reheating to above 1250°F or, preferably, one that can be applied prior to the solution heat treatment. In the latter case, the coating should withstand a brief heating to 2000°F. If, simultaneously, the coating would protect the Ti-B steel from scaling during the high temperature solution heat treatment, the coating system would be an ideal one.

Hot dip aluminum coatings on Ti-B steels offer some promise along the above lines. However, the aluminum tends to **diffuse** into the steel quite rapidly at 2000°F. This high rate of diffusion tends to deplete the amount of free aluminum remaining on the outermost surface to act as a corrosion protective coating. The alloyed iron-aluminum compound on the surface provides adequate oxidation protection or heat resistance.

Both chromizing and siliconizing appear most promising as useful and satisfactory coatings for the Ti-B steels if they can be made reasonably free of pin holes and if they can be applied in a practical and economical fashion. Among the various processes which might be used for either chromizing or siliconizing, the paint processes have great advantages over the pack processes. A portion of the work under Phase II of Contract AF 33(616)-406 consisted of research and development work on the paint chromizing and paint siliconizing processes and their possible application to both plain carbon and the Titanium-Boron low alloy steels. This final summary report covers the work done.

Section II - Paint Chromizing

The reactions involved in paint chromizing are the same as those involved in pack chromizing. Chromium as chromium metal or from a chromium rich ferro-chromium reacts with the halogen from a

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halogen-bearing compound to form a gaseous or vapor phase chromium-halogen compound. This vapor phase compound deposits chromium on the surface of iron or steel by a metal replacement reaction and an iron-halogen compound leaves the surface. Atoms of iron are removed from the surface as atoms of chromium take their places. At the temperatures at which the reaction is caused to take place the chromium atoms diffuse into the iron or steel surface to create a chromium rich surface layer. The rate of diffusion is slower than the rate of supply of fresh chromium atoms to the surface. The chromium concentration at the extreme outer face of the surface is of the order of 50% and decreases as the distance into the steel increases from the surface. Since the diffusion process controls the thickness of the high chromium layer produced, it follows that greater case thicknesses will be produced at higher temperatures and for longer periods of time at temperature.

Instead of creating the gaseous or vapor compounds within the confines of a retort or heating chamber, as in pack chromizing, the paint chromizing process produces them within a molten glass or slag blanket or covering on the surface being treated. While the chromizing reaction proceeds, the molten glass blanket protects the surfaces being treated from contact with the air or furnace atmosphere and prevents any scaling from taking place. After the desired chromizing has been obtained in the furnace and the work is withdrawn into the atmosphere to cool, the molten glass blanket freezes and should crack off rather than cling to the surface of the steel.

It is apparent, from the above, that the paint mix to be applied to the surface of the steel must meet a number of very special requirements. (1) It must be of a consistency that permits uniform application by the brush, dip or spray method being used. (2) It must adhere to the surface during drying and heating to the molten stage. (3) It must protect the steel from oxidation during this preliminary heating. (4) As molten, it must be sufficiently viscous to remain in place on vertical surfaces rather than flow downward by gravity. (5) As molten, it must protect the steel from oxidation by furnace gases or air. (6) Within its composition, there must be sufficient finely divided and dispersed chromium metal to react with the halogen compound. (7) Sufficient halogen compound must be present. (8) The halogen compound must be soluble in the molten glass. (9) The chromium-halogen and iron-halogen compounds formed must be soluble in the molten glass. (10) The glass must be sufficiently fluid for this chromium-halogen compound and the replacement iron-halogen compound to travel freely within the molten glass blanket. (11) The molten glass must not attack the steel itself. (12) The glass must have a sufficiently high coefficient of expansion and contraction and must be brittle enough on cooling to crack away from and leave the surface of the steel upon which it was melted.

While most of this formidable list of requirements have been met, with more or less success, by the inventor of the process, there is need for improvement. The paint used consists of a suspension or slurry containing (a) chromium or ferro-chromium powder, (b) a fluoride, (c) a low melting point glass frit, (d) a high

melting point glass frit, (e) a suspension agent, (f) an organic vehicle, and (g) a volatile thinner. The optimum composition, grade and quantity for each of these constituents remain to be determined, although much progress has been made.

The surface of the steel to be paint chromized should be reasonably clean. It can be prepared by degreasing, sand blasting or pickling as for other types of coating, although such treatments are not necessary. If the volatile thinner used in the paint slurry is an organic solvent, a small amount of oil on the surface of the steel is not objectionable. Since the molten glass blanket dissolves iron oxides to some extent, the presence of some rust spots or stains on the surface of the steel is satisfactory. Heavy mill scale should be removed before the application of the chromizing paint slurry.

Owing to the large variations in specific gravity of the individual constituents of the slurry, it is necessary to stir it continuously to maintain dispersion, in spite of the use of a suspending agent in the vehicle and thinner. Consistency of the slurry is maintained by the occasional addition of volatile thinner.

The slurry or paint is applied to the surface by dip, brush or spray methods. For application by dipping, it is necessary to remove the article from the slurry at a controlled constant low speed in order to obtain a uniform coat. The coat should be built up to a thickness of somewhere between $1/16$ and $3/32$ of an inch. This thickness cannot be applied by brush or dip methods in one operation. Several applications are necessary. After each coat is applied it must be allowed to air dry and set for approximately 30 minutes before the next coat is applied. Three to four coats seem necessary to build up the desired thickness. After application of the last coat and a preliminary air dry for approximately 30 minutes, the coat should be force dried by hot air or in an oven at about 200°F for a few hours and it is ready for baking or preheating. A baking or preheating at 700 to 1000°F sets the coating firmly in place and prepares it for introduction into the final high heat furnace for the actual chromizing operation.

Although chromizing begins to take place at 1700°F , diffusion is quite slow at this temperature and it is desirable to use a higher temperature. At 1950°F , the diffusion rate is sufficient to produce a chromized layer containing over 12 to 14% chromium at the interface with the core, of about 0.0015 to 0.002 inch in thirty minutes. To obtain a case of about 0.003 inch in thickness, the time must be extended to approximately 3 hours. During the chromizing treatment, the molten glass blanket remains in place on the surface and protects it from contact with air and, therefore, protects it from scaling. No doubt, the chromizing reaction would proceed more rapidly and deeper cases could be obtained in less time if a higher temperature were used. This would require a change of the glass frit to a higher melting point type. The glass frit mix, satisfactory at 1950°F , becomes too fluid and tends to flow off the surface if held at 2100°F for more than just a few minutes.

After the desired time at temperature, the article being chromized is removed from the furnace and allowed to cool in still air, or cooling can be speeded by use of a fan. Quenching in oil or water is not necessary insofar as chromizing is concerned, but may be employed if desired for other reasons. Faster rates of cooling are more efficient in causing the frozen brittle glass layer to crack and fall away from the surface that has been chromized.

One of the difficulties in the paint chromizing process is the tendency for small particles of chromium metal and small patches of the glass to adhere to the chromized surface. This difficulty was overcome to a large extent by the use of a precoat or first coat of slurry made with no chromium in it and followed by the additional coats containing the chromium. To the extent that some particles still adhered to the surface it was found that they could be removed quite readily by a light sand blasting operation with no apparent effect on the chromized case.

The chromized layer produced by paint chromizing of a low carbon steel is relatively soft and ductile. Micro hardness explorations show hardnesses as low as 152 D.P.H. Bend tests on 1/16 inch thick chromized steel panels show that bending about a 1/8 inch radius produces no fracture or failure of the case. Hammering tests on similar panels showed no failure of the case after considerable deformation. The tests used to determine case failure were immersion in 35% nitric acid solution as well as metallographic examination of cross sections.

Ferroxyl tests for pin hole porosity as well as alternate condensation corrosion tests indicate that some pin hole porosity or iron inclusions are present in the chromized cases. Most of the tests were on panels having cases only 0.001 to 0.002 inch in thickness. It appears that a case thickness of at least 0.003 inch would be desirable.

Section III - Paint Siliconizing

The reactions involved in paint siliconizing are the same as those involved in paint chromizing, as described in Section II, except that silicon or ferrosilicon powder is substituted for chromium or ferro-chromium powder. The replacement reaction, however, proceeds much more rapidly and at a lower temperature. The volume of the silicon deposited seems to be much greater than the volume of the iron removed with the result that the siliconized case produced is under compression. The siliconized layer or case that results consists of three zones which will be more fully described in a later section of this report.

The paint mix for siliconizing must meet all of the same 12 requirements as described for chromizing, with the substitution of silicon for chromium. While most of the requirements have been

met, with more or less success, by the inventor, there is need for improvement. The same paint base is used as for chromizing, except for the substitution of silicon for the chromium.

Since silicon is a powerful reducer for iron oxide, it appears that the process can be used on steel surfaces carrying a small amount of millscale.

There is less difficulty in maintaining suspension of silicon or ferro-silicon powder in the paint slurry than is the case with the slurry for chromizing. The slurry or paint is applied in the same manner, to the same thicknesses, and dried in the same manner as described for chromizing.

The siliconizing reaction begins to take place at 1700°F, proceeds quite rapidly at 1750°F, and very rapidly at higher temperatures. At 1750°F, the action is sufficient to produce a case 0.005 inch thick in 10 to 15 minutes. At 1850°F, a case of 0.010 inch is produced in the same time period. Cases 0.020 inch in thickness have been produced at 1850°F in thirty minutes.

Upon removing the siliconized articles from the furnace, cooling in still air or before a fan provides a sufficient rate of cooling for the slag or glass blanket to spall off. Drastic quenching in oil or water is not desirable, as it tends to cause some of the siliconized case itself to spall.

The siliconized layer produced by paint siliconizing of a low carbon steel is relatively hard and brittle. Micro hardness explorations show hardnesses of 336 to 514 D.P.H. The cases have three characteristic zones. An outer zone made up of coarse columnar crystals, a middle zone containing voids, and a thin inner interfacial zone that is quite continuous and firmly attached to the base steel. This inner zone or interfacial layer is of the order of 0.0005 to 0.001 inch in thickness.

Immersion in 35% nitric acid solution seems to have no effect on siliconized steel. However, the ferroxyl test, as well as the alternate condensation corrosion test, indicate some pin hole porosity or iron inclusions are present. In this case, it does not seem that the overall thickness of the siliconized case is the basic criterion as to whether or not full protection has been obtained.

Section IV - Tests With Plain Low Carbon Steel

Hot rolled and pickled plain carbon, SAE 1010, steel 1/16 inch thick was used for tests with both paint chromizing and paint siliconizing. Panels 1 x 2, 4 x 4, and 4 x 8 inches in size were used according to the purpose of the tests. The 1 x 2 inch panels were used in testing of different slurry mixes and consistencies.

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The 4 x 4 inch panels were used in testing for cleanliness of surface obtainable, for fluidity of the molten glass blanket at the high temperatures, and for some of the oxidation tests in air. The 4 x 8 inch panels were used for tests by the special test methods developed as Part 1 of Phase II of the work and as covered in a separate final summary report.

Table I - Paint Chromizing Plain Low Carbon Steel shows the effect of increasing temperatures on the thickness of chromized cases produced in equal periods of time. Table II - Paint Siliconizing Plain Low Carbon Steel shows the effect of both time and temperature on the thickness of the siliconized cases produced.

The typical microstructure of a chromized case produced on plain low carbon steel by the paint chromizing process is shown in Figure 1 (plate 15666--250X).

Table I - Paint Chromizing Plain Low Carbon Steel

<u>Temperature OF</u>	<u>Time at Temperature Minutes</u>	<u>Thickness of Case Inches</u>
1700	30	0.0006
1750	30	0.00064
1800	30	0.0009
1850	30	0.00096
1900	30	0.0017
1950	30	0.0018

Table II - Paint Siliconizing Plain Low Carbon Steel

<u>Temperature OF</u>	<u>Time at Temperature Minutes</u>	<u>Thickness of Case Inches</u>
1750	5	0.004
1750	10	0.004
1750	15	0.006
1750	30	0.010
1800	30	0.018
1850	5	0.007
1850	10	0.008
1850	20	0.015
1850	30	0.020
1900	15	0.014
1950	15	0.016

Chromized plain carbon steel panels were subjected to oxidation tests at 1350°F in air in an electric furnace. Only slight superficial oxidation developed in the course of 135 hours of exposure. No failures occurred. Metallographic examination showed some changes in the microstructure of the base metal, some diffusion of the chromium into the base metal and a diminution in the sharpness of the line of demarcation between the case and the base metal, as shown by metallographic etching techniques.

The typical microstructure of a siliconized case produced on plain low carbon steel by the paint siliconizing process is shown in Figure 2 (plate 15819, 100X). The three zones of the case, as previously described, are evident. The continuous nature of the innermost or interfacial zone of a siliconized case is shown in Figure 3 (plate 15770, 500X).

Siliconized plain low carbon steel panels were subjected to oxidation tests at 1350°F in air in the same manner as the chromized panels previously described. These tests were continued for a total period of 135 hours at temperature. No failures occurred.

Section V - Tests With Low Carbon Titanium-Boron Steels

Low carbon low alloy titanium-boron steels were supplied by the Materials Laboratory WADC in three types, (a) 3% chromium, 1% molybdenum, (b) 3% chromium, 1% molybdenum, 1% vanadium, and (c) 6% chromium, 1% molybdenum.

Bright uniform chromized cases, impervious to 35% nitric acid, were developed on small panels of each of these three steels by a chromizing treatment of 10 minutes at 1950°F followed by 3 minutes at 2050°F. A number of 4 x 8 inch panels of these steels were chromized and used for tests by the special test methods developed as Part 1 of Phase II of the work and as covered in a separate final summary report.

Table III - Paint Chromizing Titanium-Boron Steel shows the effect of increasing temperatures and time on the thickness of chromized cases produced. It will be seen that the rate of chromizing is substantially the same as for plain low carbon steels. The chromized case plus the molten slag or glass blanket gave complete protection from scaling or oxidation during the high temperature solution heat treatments at 2100°F. No noticeable differences were observed between the three types of titanium-boron steel.

Table IV - Paint Siliconizing Titanium-Boron Steel shows the thickness of siliconized cases obtained in the treatment of the titanium boron steels. Again, no noticeable differences were observed between the three types of titanium-boron steel.

Table III - Paint Chromizing Titanium-Boron Steel

<u>Temperature OF</u>	<u>Time at Temperature Minutes</u>	<u>Additional Treatment</u>	<u>Thickness of Case Inches</u>
1850	30		0.0012
1900	15	3 mins. at 2100°F	0.0012
1950	30		0.0015
1950	60	3 mins. at 2100°F	0.0022
1950	210		0.0031
2100	3		0.0008

Table IV - Paint Siliconizing Titanium-Boron Steel

<u>Temperature OF</u>	<u>Time at Temperature Minutes</u>	<u>Additional Treatment</u>	<u>Thickness of Case Inches</u>
1750	30		0.010
1850	15	3 mins. at 2100°F	0.0125
1850	30		0.0136
1850	30	3 mins. at 2100°F	0.0171
2100	3		0.0084

The typical structure of a chromized case produced on the titanium-boron steel by paint chromizing process is shown in Figure 4 (plate 15670--250X).

Chromized low carbon titanium-boron steel panels were subjected to oxidation tests at 1350°F in air in an electric furnace for 6 hours and 70 hours, respectively, and then examined metallographically. The sharp line of demarcation between the high chromium case and the base metal was found to become less sharp and to move into the base metal. At 1350°F there seems to be a slow diffusion action. After 70 hours at that temperature, the case appeared to have increased in thickness, but was still intact and of sufficiently high chromium content to resist scaling or severe oxidation. The thin superficial oxide layer which formed at the 1350°F temperature during the 70 hour exposure was only 0.00012 inch in thickness. Figure 5 shows the structure of the case X250 after the 70 hour period referred to above.

The typical microstructure of paint siliconized cases on the titanium-boron steels were found to be substantially the same as on the plain low carbon steels and as illustrated in Figures 2 and 3.

Siliconized titanium-boron steel panels were subjected to oxidation tests at 1350°F in air in the same manner as the chromized panels. No failures occurred during the test period of 135 hours.

Simultaneous siliconizing and solution heat treatment of the titanium-boron steels was not found practical. The siliconizing reaction proceeds so rapidly at 2050 or 2100°F that the siliconized case becomes entirely too thick. Case thicknesses of 0.020 inch on both sides of a sheet of metal only 0.062 inch thick are considered too heavy for the brittle type of case resulting from siliconizing. The buildup of siliconized cases of the order of 0.020 inch thick on both surfaces of a panel is accompanied by an increase in overall thickness of about 0.015 inch. It was interesting to note that these thick cases were so stressed and so brittle that spontaneous cracking occurred at room temperature over a considerable period of time. Each crack is accompanied by the sound of a "click" or "tick". Thin panels, heavily siliconized, could be caused to emit these sounds by bending with the pressure of a person's fingers.

Siliconizing for a short period of time at 1750 to 1800°F was found to give a siliconized case on the titanium-boron steels that, after first cooling to remove the glass blanket, was adequate to protect the steels from scaling during subsequent heating to 2050 or 2100°F for solution heat treatment.

Section VI - Discussion and Conclusions

Both chromizing and siliconizing offer great promise as surface treatments for providing heat resistant oxidation and corrosion protective coatings on plain carbon and low alloy steels. Of the various known methods of chromizing and siliconizing, the paint method seems to be the simplest, easiest of application, and should prove to be the most practical and economical.

In all surface treatments, or surface coatings, the basic problem is to overcome the tendency to pin hole porosity of the coating or surface alloy developed. With sufficient additional development work on the paint methods, it is believed that this can be accomplished.

There is some question as to whether the ferroxyl test or corrosion tests carried out directly on paint chromized or siliconized surfaces has proven that the coatings produced did have pin holes. There is a possibility that these tests have indicated only that there are free iron inclusions in or on the coatings. The fact that the coated panels are fully resistant to 35% nitric acid would seem to indicate that the problem is iron inclusions rather than pin holes. Metallographic examinations did not indicate that pin holes extending entirely through the coatings were present. It is unfortunate that it was not possible to extend the work to include a nitric acid pickle or passivating treatment of the panels before giving them the ferroxyl test or exposing them to various corrosion tests. It is significant that the coatings withstand many hours of oxidation tests at 1350°F in air without showing pin point oxidation and scaling.

To produce a chromized coating of adequate thickness by the paint chromizing method, it appears that a treatment of 3 hours at 1900°F or 2 hours at 1950°F may be necessary. Since this treatment does not require a controlled atmosphere furnace or packing in a sealed box or retort, the extended time at the high temperature is not serious from the equipment standpoint. The question of warping or sagging of shapes in the furnace at these temperatures for these periods of time must be considered. The plain carbon and low alloy steels have little strength at such temperatures and tend to creep out of shape. This is one disadvantage of the paint method as compared with the pack method, where the packing compound can provide some support to the parts **being** chromized.

Contrails

The low alloy titanium-boron steels can be paint chromized and, without intermediate cooling, heated to a higher temperature for a few minutes for the necessary solution heat treatment. The problem of how to provide these steels with adequate surface protection against scaling during solution heat treatment and against oxidation and corrosion in service at temperatures up to 1200°F seems to be answered by the paint chromizing method.

The high chromium alloy surfaces produced by chromizing low carbon steel are ductile and adherent. Parts so treated may be bent or formed after treatment. No doubt, they may be spot or resistance welded. Apparently, this is true for all low carbon steels, whether plain or low alloy. For medium carbon or high carbon steels, the rate of chromizing is decreased, the thickness of the high chromium alloy layer is less for a given time and temperature of treatment and the alloy layer is less ductile. Formability is decreased, but joining by welding should not be affected. There is little evidence to support any suspicion that chromized cases on medium carbon steel will spall or peel.

Further work with the paint chromizing process should be directed towards (a) the development of better glass frits, (b) improvement in binders and suspension agents used in the slurry, (c) development of spray methods for application of the paint, (d) investigation of the pin hole versus free iron inclusion problem, (e) elimination of the pin holes or free iron inclusions, (f) determination of the effect of an addition of some silicon powder to the paint mix, (g) study of the effect of adding other metal powders such as copper, nickel and molybdenum to the mix, (h) determination of the best kind and optimum quantity of halogen-bearing compound to use in the mix, and (i) elimination of incrustations left on the surfaces.

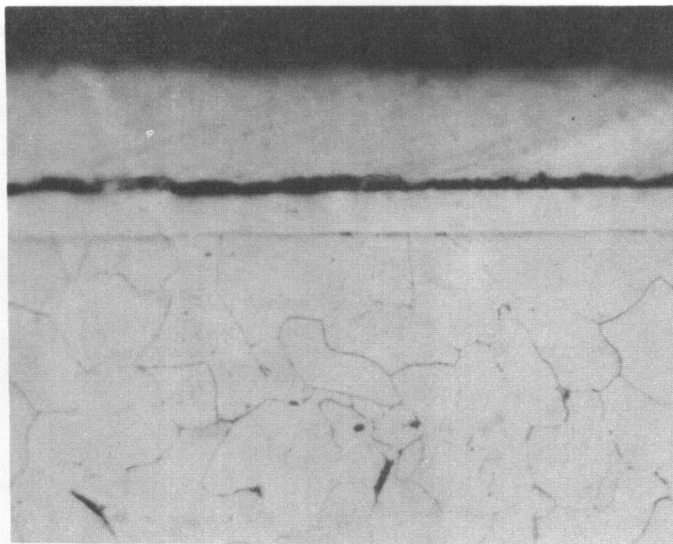
To produce a siliconized coating of an overall thickness of 0.010 inch requires a treatment of 30 minutes at 1750°F, of about 15 minutes at 1800°F and only about 10 minutes at 1850°F. The treatment is in an open furnace with no atmosphere control necessary. Retorts or packing boxes in the furnace are not necessary. The problem of warping or sagging of shapes is much less than in the case of paint chromizing where higher temperatures and longer periods of time are required.

The titanium-boron steels can be paint siliconized and, after cooling and removing of the slag blanket, can be reheated in air to the high temperatures required for their solution heat treatment without scaling. Siliconized titanium-boron steels are resistant to scaling or oxidation during long periods of time in air at temperatures as high as 1350°F.

The high silicon alloy surfaces are hard and brittle. After siliconizing, no forming is possible. Little is known about whether siliconized surfaces can be spot or resistance welded. It is believed that they can be joined by arc welding with stainless steel filler metal.

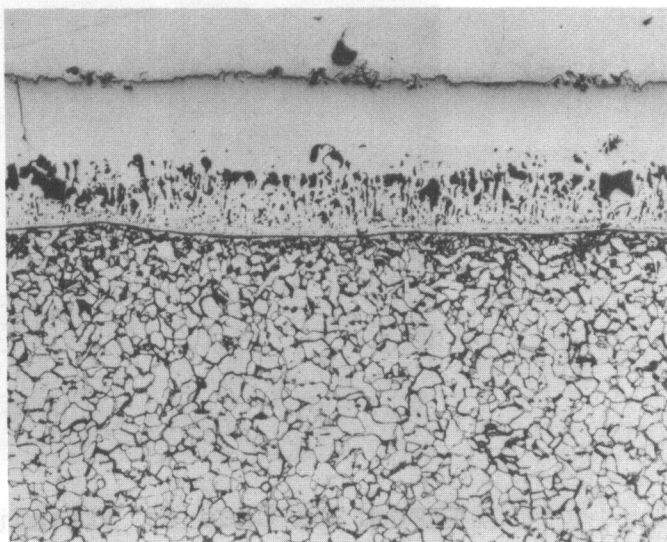
Siliconizing can be applied to low or medium carbon steels and to alloy steels with equal facility.

Further work with the paint siliconizing process should be directed towards (a) the development of better glass frits, (b) improvement in binders and suspension agents used in the slurry, (c) development of spray methods for application of the paint, (d) investigation of the pin hole versus free iron inclusion problem, (e) elimination of the pin holes or free iron inclusions, (f) determination of the effect of an addition of some aluminum powder to the paint mix, (g) study of the effect of adding other metal powders such as chromium, copper, nickel and molybdenum to the mix, (h) determination of the best kind and optimum quantity of halogen-bearing compound to use in the mix, and (i) development of thicker continuous interfacial zone layers with thinner overall siliconized layers.



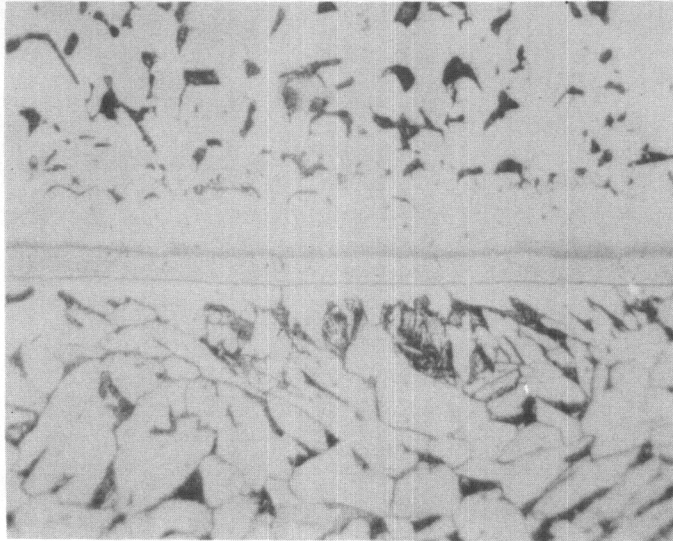
Chromized Case on Plain Low Carbon Steel.

Fig. 1 Plate 15666 Mag. 250X



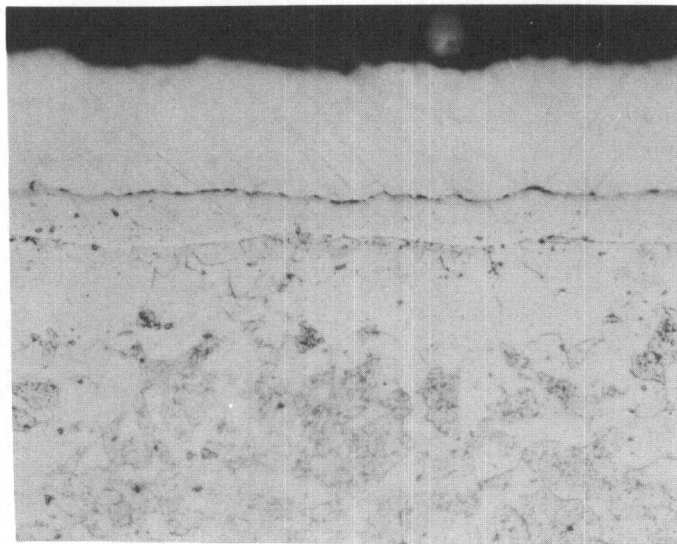
Siliconized Case on Plain Low Carbon Steel.

Fig. 2 Plate 15819 Mag. 100X



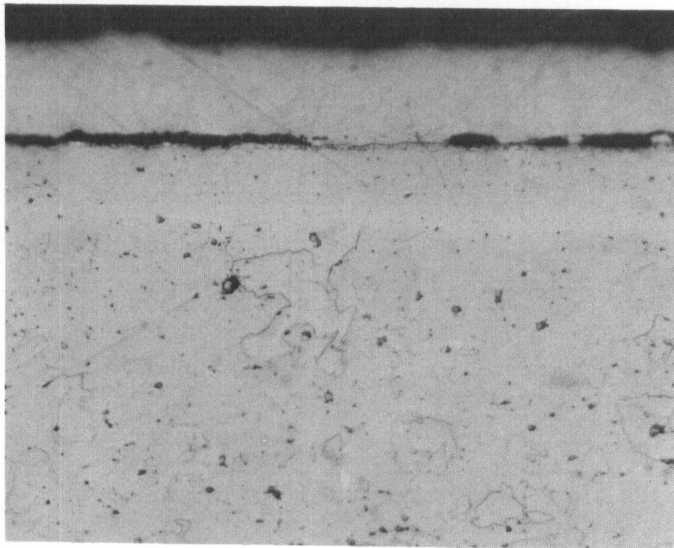
Interfacial Zone of Siliconized Case.

Fig. 3 Plate 15770 Mag. 500X



Chromized Case on Titanium Boron Steel.

Fig. 4 Plate 15670 Mag. 250X



Chromized Case on Titanium Boron Steel
After 70 Hours at 1350°F.

Fig. 5 Plate 15672 Mag. 250X