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PRODUCTION OF CORROSION-RESISTANT COATINGS ON COPPER INFILTRATED FERROUS SKELETON BODIES

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FIG. 1

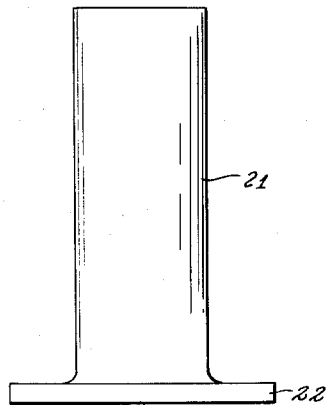


FIG. 2

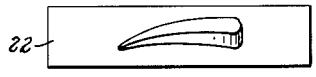
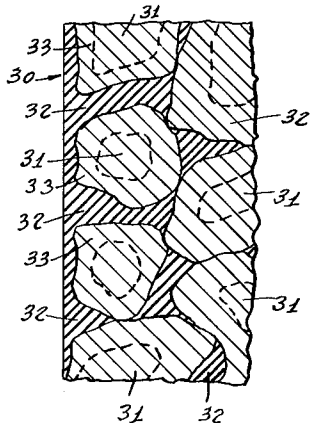


FIG. 3



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PRODUCTION OF CORROSION-RESISTANT COATINGS ON COPPER INFILTRATED FERROUS SKELETON BODIES

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2 Claims. (Cl. 117—50)

This invention relates to methods for producing corrosion-resistant coatings on shaped bodies formed of a copper infiltrated ferrous skeleton and to the resulting articles. More particularly, the invention relates to the production of chromium-containing corrosion-resistant surface layers on shaped articles produced by infiltrating a ferrous skeleton of the desired shape with a copper infiltrant. This application is a continuation-in-part of my application Ser. No. 746,871 filed May 8, 1947, now abandoned.

Goetzel Patent 2,456,779 and Stern Patent 2,566,752 (issued on application Ser. No. 54,396 filed October 14, 1948) disclose and claim the production of high-strength precisely shaped metal articles, such as jet engine compressor blades, out of copper infiltrated porous ferrous skeletons.

In many applications, for instance, when used as jet engine compressor blades, such copper infiltrated ferrous skeleton articles must be provided with a corrosion-resistant coating to prevent corrosion of their exterior within oxygen-containing atmospheres in which they operate.

A great many intensive efforts have been made in the past to provide the exterior of such copper infiltrated ferrous skeleton articles with a corrosion-resistant coating by causing chromium from a gaseous or liquid chromium compound to deposit on the surface of the article heated to an elevated temperature and to form a corrosion-resistant coating enclosure for the article. However, as far as I am aware, all such prior efforts failed and they were all unsuccessful.

The present invention is based on the discovery that a tightly adherent-containing corrosion-resistant chromium surface layer may be formed on the surface of a copper infiltrated ferrous skeleton article such as a jet engine compressor blade if the copper content is removed from a thin surface layer of the article before subjecting it to any of the known actions by which a chromium surface layer is formed on the exterior of the ferrous article.

It is also among the objects of the invention to provide a novel process for forming a corrosion-resistant chromium coating enclosure for the exterior of a copper infiltrated ferrous skeleton article.

The foregoing and other objects of the invention will be best understood from the following description of exemplifications thereof, reference being had to the accompanying drawings wherein,

Figs. 1 and 2 are elevational and top views, respectively, of a copper infiltrated ferrous skeleton article shown in the form of a jet engine compressor blade which has a corrosion-resistant chromium surface coating of the invention; and

Fig. 3 is a greatly enlarged cross-sectional view of a surface portion of the compressor blade in a direction transverse thereto indicating in a general manner the structure of the chromium surface layer portion of the blade.

The features of the present invention are based on discoveries made in connection with efforts to provide a

corrosion-resistant enclosure coating for jet engine compressor blades formed of a copper infiltrated ferrous skeleton having critically accurate dimensions and great strength—which prior to the invention had to be made out of stainless steel by precision forging or casting—and the features of the present invention will be described herein, by way of exemplification, in connection with such blades.

Figs. 1 and 2 show one form of such jet engine compressor blade **21** after the final forming operation. Arrays of such compressor blade **21** are arranged to be secured by their roots **22** to the cylindrical surfaces of axially aligned rotor and stator of a known form of axial jet engine compressor.

Each radially extending compressor blade **21** has a fluid-guiding air-foil shape of a cross-section indicated by the end surface **23** in Fig. 2 with a narrow trailing edge **24** and a thicker front edge **25**. The outer end **23** of each blade is shown twisted relatively to its inner end **27** adjoining the root **22**.

The air-foil shaped blade **21** is formed by powder metallurgy technique out of a porous ferrous skeleton which is infiltrated with a cuprous infiltrant and subjected to a series of treatments whereby it is given the required precise shape and dimensional accuracy as well as the required great strength.

Briefly, such jet engine compressor blades may be produced on a large-scale production basis by the following procedure.

Iron powder of —100 mesh to —325 mesh particle size, containing about 1% lubricant, such as a stearic acid compound, is compacted in a die under a pressure of about 25 t. s. i. (tons per square inch) to form a porous green blade skeleton having a shape generally conforming to the shape of the desired blade. The porous green blade skeleton is then sintered at about 1150° C. in an atmosphere of cracked ammonia for one hour. The sintered ferrous skeleton is then subjected to a sizing or coining operation within another die under pressure of 40 t. s. i. in which the porous ferrous skeleton is given the desired final shape, and wherein its density is increased to the desired degree. The coined ferrous skeleton is then infiltrated with a cuprous alloy at a temperature of about 1160° C. within an atmosphere of cracked ammonia at which the infiltrant remains at molten condition and at which elevated temperature the infiltrated ferrous skeleton is maintained for a period for 2 to 2½ hours, or in general, from 1 to 6 hours. After cooling, the resulting copper infiltrated ferrous skeleton blade exhibits a tensile strength of 80,000 p. s. i. (pounds per square inch) and an elongation of 7%.

The so-produced copper infiltrated ferrous skeleton is then given a solution heat treatment at a temperature of 870° C. in an atmosphere of cracked ammonia for 30 minutes and cooled by oil quenching. The solution heat treatment decreases the tensile strength of the copper infiltrated skeleton to 60,000 p. s. i. and increases its elongation to 14%, in which condition it is then given, by coining in a proper die, the required final shape and dimensional accuracy. After such final coining operation, the copper infiltrated ferrous skeleton blade is subjected to a precipitation hardening treatment in which it is held at 500° C. in air for one hour, after which it may be returned to normal temperature. The resulting blade has a tensile strength of 90,000 p. s. i. and 8% elongation.

The so-formed and treated copper infiltrated ferrous skeleton is then polished and made ready for producing on its exterior a corrosion-resistant chromium surface coating of the present invention which is effective in suppressing and/or preventing corrosion thereof.

It should be noted that the features of the invention—involving the provision of a corrosion-resistant chromium surface layer coating on the exterior of a copper infiltrated ferrous skeleton article—is not limited to jet engine compressor blade made in the manner just described, but they are applicable to any other copper infiltrated ferrous skeleton article produced by known prior art procedures, irrespective of the shape of the article.

As explained above, in the past, it has been found impossible to provide copper infiltrated ferrous skeleton articles with a tightly adhering chromium surface layer enclosure that would suppress and prevent corrosion thereof.

The present invention is based on the discovery that if a copper infiltrated ferrous skeleton article of great density, such as described above, is first treated to remove from its exterior surface layer about 0.0005 to 0.001 inch thick of its copper, and then subjected to any of the known chromium coating treatments, there will be formed on the exterior of the article a continuous tightly adhering corrosion-resistant coating enclosure which will not corrode and will suppress corrosion of underlying body strata in hot oxygen-containing atmospheres.

The copper content of the surface layer of the article may be removed by any known copper removing or copper dissolving treatments. A simple treatment of this nature consists of immersing the copper infiltrated article in solution of chromic acid, for instance, of the type used as chromium plating bath, and leaving it therein for a period sufficient to cause all copper content of a thin surface layer of the article about 0.0005 to 0.001 inch thick, to be dissolved and removed, leaving an exterior ferrous surface layer of the article which is effectively free from copper.

Suitable chromic acid solution are those containing per liter of solution 400 to 250 grams chromic acid (CrO_3) and 4 to 3 grams sulfate (SO_4).

By way of example, the following chromic acid solution is satisfactory for removing the copper content from the surface layer of copper infiltrated ferrous articles;

500 grams chromic acid per liter of solution
50 grams sulphuric acid per liter of solution

Best results are obtained with the solution maintained at 85° to 90° C.

Instead of chromic acid solutions, cyanamide solutions of the type used for dissolving copper, may be employed for removing the copper content from the surface layer of such copper infiltrated ferrous articles.

Any of the known methods for depositing chromium from a gaseous or liquid chromium compound on the surface of a metal body heated to an elevated temperature below its melting point may be used for depositing on and forming a chromium coating enclosure on the surface layer of an article treated in the manner described above in accordance with the principles of the invention.

Among such known chromium coating processes, one that was found particularly suitable for practicing the invention, involves an exchange or displacement reaction of the metal of the treated body with the chromium constituent of a gaseous or vapor phase of a chromium halide, such as chromous chloride gas, at an elevated temperature in the range between about 900° to 1200° C. in accordance with the formula:

$$CrCl_2 + M \rightarrow Cr + MCl_2 \quad (1)$$

wherein M represents the metal of the body which is being coated with chromium.

In such process, the chromium of the chromous chloride gas replaces the metal on the surface of the treated body causing some of the chromium deposited on the surface of the body to alloy therewith, and to diffuse into its interior while the gaseous chloride of the displaced metal escapes, the process being carried on until the deposited chromium forms a continuous chromium coating on the exposed surface of the article.

Instead of chromous chloride, other chromium halides may be used for effectively carrying out the chromium-coating process in accordance with the principles of the invention.

There will now be described, by way of example, the procedure of the invention whereby copper infiltrated ferrous skeleton jet engine compressor blades produced in the manner described above, are provided with a tightly adhering corrosion-resistant coating enclosure on the entire exterior surface, and which procedure over-comes the difficulties which made it impossible to provide heretofore a corrosion-resistant chromium coating on the exterior of copper infiltrated ferrous skeleton articles.

The articles, to wit, jet engine compressor blades produced in the manner described above, are placed within an aqueous solution of chromic acid containing about 400 grams of chromic acid CrO_3, and 4 grams sulfate SO_4 per liter of solution maintained at 90° C. The articles are left in the solution for a period sufficient to cause the dissolution of copper present on the exterior surface layer of the articles to a depth of about 0.0005 inch, leaving on the exterior of the article a porous surface layer about 0.0005 inch thick consisting of essentially the sintered ferrous skeleton particles, and substantially bare of any free copper.

The so-treated articles having a thin surface layer which is substantially free of unalloyed copper—are thoroughly washed to remove therefrom all traces of acid, whereupon they are ready for subjection to the surface chromium coating treatment.

The so-treated articles are thereupon packed within a chromous chloride producing pack mass inside of treatment baskets of suitable heat-resistant metal, such as a chromium nickel iron alloy. The pack material may consist, for instance, of a chromium alloy, such as ferro-chromium mixed with titanium oxide. Good results are obtained with a pack consisting of about 20% titanium oxide by volume, the balance consisting of ferro-chromium containing about 70% chromium and 30% Fe. As an alternative, the pack material may consist of 50% by volume ceramic lumps, such as porcelain pieces, and the balance ferro-chromium.

The treatment baskets containing the articles packed within the chromium alloying pack are then placed in a retort in which they are heated to a temperature in the range between 900° C. and 1250° C., and a stream of hydrogen and hydrogen chloride gas is passed through the retort for producing therein reactions which cause chromium atoms to be deposited on the copper depleted porous thin surface layer of the treated articles and to form on the exposed surface of the article a continuous coating enclosure of chromium with some of the deposited chromium diffusing into the interior of the sintered ferrous particles of the surface layer and becoming alloyed therewith.

In such surface coating treatment, the hydrogen chloride gas passing through the retort interacts with the ferro-chromium to form chromous chloride gas. The chromium of chromous chloride gas replaces iron atoms of the ferrous surface layer of the article, primarily by an exchange reaction. Part of the chromous chloride gas is absorbed by the packing material, such as in the titanium oxide or in the ceramic material of the pack.

This treatment is continued until the chromium deposited on the surface of the article is in equilibrium with the chromium of the pack, in which condition the deposited chromium will form a continuous chromium coating enclosure firmly anchored to the surface layer of the article.

Good results are obtained with a chromium surface alloying treatment carried on as follows.

During the initial part of the treatment purified dry hy-

drogen is caused to flow through the enclosed retort space while the temperature is raised to about 950° C. Thereafter, the flow of pure hydrogen is continued for 4 hours, at the same temperature of about 950° C. Thereafter, the baskets within the retort are subjected to a succession of 5 treatment sequences at about 950° C., each treatment sequence lasting about 6 hours and consisting of (*a*) passing through the retort a mixture of 20 parts of hydrogen and 3 parts of HCl gas for one hour, followed by (*b*) passing pure hydrogen for one hour followed by passing the same mixture of hydrogen and HCl gas as in (*a*) for one hour, followed by passing pure hydrogen as in (*b*) for 3 hours. After a succession of 6 such treatment sequences, the treatment is ended by turning off the heat and permitting the retort with its content to cool while continuing the flow of hydrogen through the retort until its contents are cooled to about room temperature.

On completing this treatment, the articles removed from the retort have on their exterior a continuous dense chromium surface layer which exhibits excellent corrosion-resistance under prolonged salt spray tests, and which also resists attack by 30% HNO_3 cold or hot and which also resists corrosion in oxygen containing atmospheres at raised temperature, such as prevailing in the compressor space of jet engines or gas turbines.

Fig. 3 indicates, in a general way, the characteristics of a particle structure in a cross-sectional area of a surface portion of an article, such as a jet engine compressor blade, produced out of a copper infiltrated ferrous skeleton and provided with a chromium alloyed surface layer in the manner described above.

The exterior surface layer **30** of the body is formed by minute sintered ferrous particles **31**. The spaces or pores **32** between the individual ferrous particles of the surface layer **30** bare of the copper infiltrant which has been removed by the chromic acid treatment. However, these pores **32** between the ferrous particles **31** are filled by the chromium alloy structure formed of chromium into which iron of the iron particles has diffused. In addition, deposited chromium has also diffused into the surface layers of the ferrous particles **31** to form, on the surface on each ferrous particle continuous surface layer **33** the exterior of which contains only chromium. In this way the entire exterior of the article is provided with a continuous, oxygen-impervious, corrosion-resistant surface layer enclosure **34** of pure chromium which resists corrosion and prevents corrosion of the underlying strata of the article while tightly adhering thereto and forming a firmly bound and anchored structure thereof.

As stated above, the invention is not limited to copper infiltrated ferrous skeleton articles produced in the specific manner described above. In general, the invention is applicable to any ferrous material skeleton which is infiltrated with copper and/or a copper alloy. Such article may be produced conveniently in a combined powder metallurgical infiltrating process by compacting and sintering powdery ferrous material and infiltrating the pores of the ferrous skeleton with a copper or copper alloy infiltrant. The skeleton may be produced by compacting powdery ferrous material such as pure iron or iron powder admixed with carbon powder, or iron powder admixed with powdered alloying components or alloyed steel, care being taken that the carbon content should not exceed about 0.20% to 0.25% by weight of the iron content.

The porous ferrous compact so formed, and having a density of about 70% to 90%, may be presintered at about 700 to 1100° C. so as to increase its strength, and and to promote diffusion between the iron and carbon and other alloying components, if present, and to reduce its porosity to a predetermined extent. The porous sintered skeleton so formed is thereafter infiltrated with a melt of copper or copper alloy, the latter containing among other components, manganese, in an amount of about 1 to 5%.

Furthermore, the invention is not limited to the specific chromium coating procedure described above. Thus, a suitable chromizing pack or chromizing material may consist of an intimate mixture of about 40% by weight powdery alundum cement and about 60% chromium is formed, and methyl alcohol added until the mixture attains the desired consistency. The articles to be coated are placed in a container, for instance a retort, the net cement-like mixture of chromizing material is packed into the container around the article, and the whole is vibrated or shaken so as to secure the desired close contact between the packing mix and the areas of the article to be coated. The retort and its contents are heated thereafter in hydrogen, cracked ammonia or any other suitable protective atmosphere at about 950° C. for a time period sufficient to cause the deposition of chromium. With a pack of the composition stated, a sixteen hour treatment will give a uniform and dense chromium case.

To speed up the reaction and accordingly reduce the time of heat treatment, a small percentage of hydrochloric acid can be added to the wetting agent (alcohol). The article so treated also had a bright silvery appearance when removed from the pack.

By providing the sintered and infiltrated articles with a porous surface layer, the deposited chromium will fill the pores of the surface layer and form thereon a continuous corrosion-resistant chromium surface layer, with some of the deposited chromium being diffused into and forming a firm bond with the underlying surface layers of the article.

If copper infiltrated ferrous skeleton articles are treated in the manner described above and then subjected to a chromium surface coating action in a chromizing pack at about 1100° C., the deposited chromium and the ferrous particles of the surface layer will mutually diffuse into each other thereby providing an intermediate chromium-alloyed layer which united alloy anchors the outer continuous chromium layer to the bare material.

The formation of corrosion-resistant case was also observed when powdery chromium and ferro-chromium, in equal amounts, for instance, were mixed with the chromium-plating pack. Depending on whether methyl alcohol, alone or admixed with a small percentage of hydrochloric acid, were used as wetting agents for the pack, the time period of heating at about 1100° C. was 16 hours or considerably less, up to 5 to 8 hours only. Of course, this time period also depends on the desired thickness of the coating, the desired depth of its penetration into surface layers of the shape, and on the temperature applied; the temperature depends largely on the extent to which an alloy is to be formed. The composition of the pack is also a factor determining the time period of heat treatment.

In another run, ferro-columbium and titanium hydride, either alone or in mixture were admixed in minor amount with the chromizing pack of the composition previously stated. Upon heating to about 900° C. for only 5 hours, a deep and corrosion-resistant surface case was obtained. It appears that ferro-columbium and/or titanium hydride promote the reaction resulting in the desired deposit or coating.

The features and principles underlying the invention described above in connection with specific exemplifications, will suggest to those skilled in the art many other modifications thereof. It is acordingly desired that the appended claims be construed broadly and that they shall not be limited to the specific details shown and described in connection with exemplifications thereof.

I claim:

1. In the method of producing a corrosion-resistant exterior on a shaped metal body, such as a compressor blade, formed out of ferrous metal particles sintered into a shaped porous skeleton and infiltrated with a cuprous metal infiltrant filling the pores of the skeleton and thereafter heat-treated to give it great strength, the procedure comprising selectively removing from an exposed

surface layer of said body to a depth of about 0.0005 to about 0.001 inch in thickness substantially all free copper present on the outwardly facing areas of and in the pores between the ferrous metal particles of said surface layer and thereafter subjecting said surface layer to a chromium depositing treatment in which chromium from a chromium compound is deposited on the ferrous metal particles of said layer and caused to form with the ferrous metal of said exterior surface layer a substantially continuous, dense, oxidation and corrosion-resistant enclosure tightly anchored to the exterior of said body and suppressing corrosion of underlying copper infiltrated strata of said body.

2. In the method of producing a corrosion-resistant exterior on a shaped metal body, such as a compressor blade, formed out of ferrous metal particles sintered into a shaped porous skeleton and infiltrated with a cuprous metal infiltrant filling the pores of the skeleton and thereafter heat-treated to give it great strength, the procedure comprising selectively removing from an exposed surface layer of said body to a depth of about 0.0005 to about 0.001 inch in thickness substantially all free copper present on the outwardly facing areas of and in the pores between the ferrous metal particles of said surface layer and thereafter subjecting said surface layer to a chromium depositing treatment in which chromium from a gaseous chromium compound is deposited on the ferrous metal particles of said layer and caused to form with the ferrous metal particles of said exterior surface layer a substantially continuous, dense, oxidation and corrosion-resistant enclosure tightly anchored to the exterior of said body and suppressing corrosion of underlying copper infiltrated strata of said body.

References Cited in the file of this patent

UNITED STATES PATENTS

2,216,928	Wilson	Oct. 8, 1940
2,304,259	Karrer	Dec. 8, 1942
2,323,162	Talmage	June 29, 1943
2,344,138	Drummond	Mar. 14, 1944
2,387,335	Leonard	Oct. 23, 1945
2,401,483	Hensel	June 4, 1946
2,412,698	Van De Horst	Dec. 17, 1946
2,456,779	Goetzel	Dec. 21, 1948
2,566,752	Stern	Sept. 4, 1951
2,612,442	Goetzel	Sept. 30, 1952
2,622,043	Roush	Dec. 16, 1952
2,633,628	Bartlett	Apr. 7, 1953