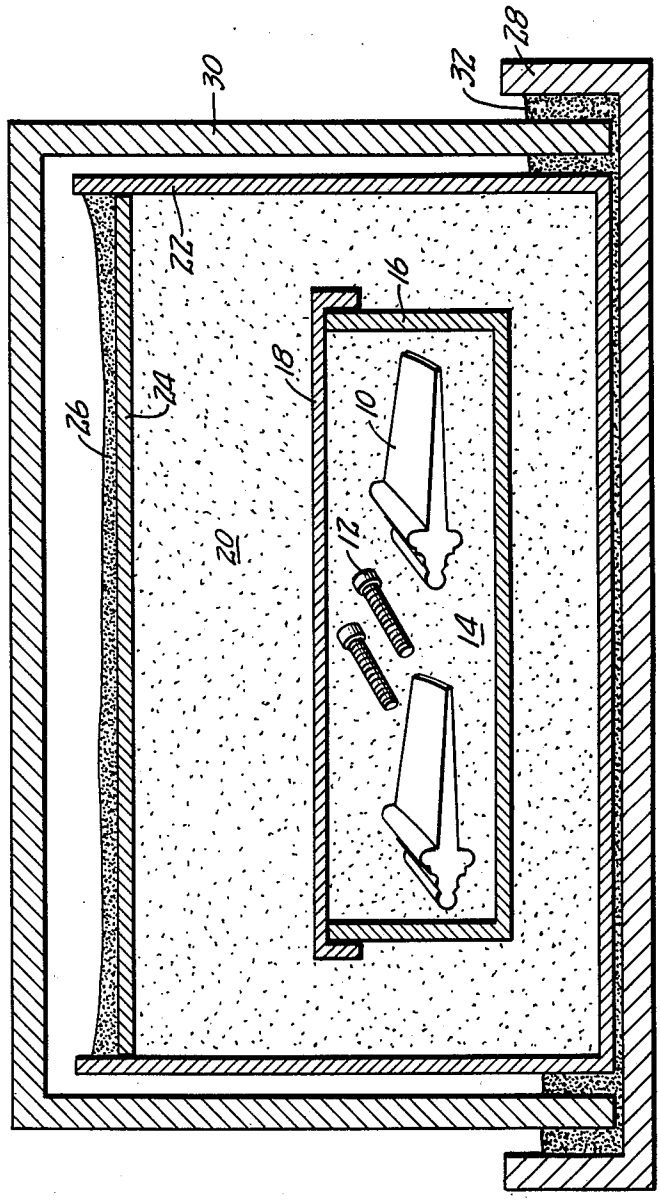
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DIFFUSION COATING OF NON-FERROUS METALS

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DIFFUSION COATING OF NON-FERROUS METALS

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This invention relates to the surface treatment diffusion coating of metal articles composed essentially of non-ferrous metals and their alloys to improve the oxidation resistance and other properties of such parts when they are exposed in use to oxidizing conditions and high temperatures and, more particularly, to the diffusion coating of materials such as silicon into the surface of metal articles formed of such non-ferrous metals as molybdenum, colombium, tungsten, rhenium, vanadium, titanium, tantalum, and the like, and alloys thereof, by an indirect pack impregnation treatment involving a source of volatile halide as a transferal medium and at temperatures generally below the re-crystallization temperature of the metal being coated. This application is a continuation-in-part of our copending application, S.N. 667,210, filed June 21, 1957, and now abandoned.

The rapid development of, among other things, jet and rocket engines in recent years has created an increasing demand for metal parts having improved mechanical and chemical and refractory properties at high temperatures and under severely oxidizing conditions. Among the metals which have found increasing acceptance for such purposes are molybdenum and its alloys and such metals as titanium, tungsten, zirconium, and beryllium, as well as other non-ferrous metals and alloys mentioned above such as tungsten, vanadium, rhenium, tantalum, colombium, etc. Such metals may be particularly useful for high temperature applications because they are capable of retaining a high proportion of strength and toughness for prolonged exposure to very high temperatures and, with proper working, to the repeated and drastic heatings and coolings through extended temperature ranges. Thus, for example, molybdenum and its alloys may be heat treated and mechanically worked to yield a metal article having a crystal structure such that the metal not only has exceptional strength and toughness, but also retains its properties up to temperatures even above 2000° F. for extended periods of time, and still higher temperatures for short periods of time.

Although such metals and alloys may retain their strength and other mechanical characteristics at high temperatures, they may be subject, although to different degrees, to a disadvantage that, when heated in air or other oxidizing atmosphere at such elevated temperatures, they have a strong tendency to oxidize, at least in the absence of a protective and oxidation resistant coating or casing thereon. Also, as is well known, some or all of the foregoing non-ferrous metals have a recrystallization temperature or characteristic temperature range such that, if the metal article composed thereof is held at or within such temperature range (for example, approximately 2500° F. for molybdenum), an irreversible recrystallization or change of the crystal structure occurs with concommitant irreversible alteration of the mechanical properties and/or dimensional stability of the metal part. This is to be distinguished from the common ferrous metals, the internal crystal structure of which can be both repeatedly and reversibly altered or controlled by heat treatment.

For some applications such characteristic may be desirable, as when molybdenum articles are held at temperatures of approximately 2500° F. or higher for an

extended period of time and allowed to re-crystallize into a brittle form which can then be mechanically worked as desired (commonly referred to as molybdenum in "a hot-cold worked condition," meaning the "cold working" of metal at below its re-crystallization temperature, although while quite hot, as well understood); and, in other applications, the dimensional changes or mechanical property changes occurring with such metals when heated to the characteristic point where they develop a different crystal form cannot be tolerated. In any case, the characteristic irreversible recrystallization changes, whether desired or not in the particular application, form basic metallurgical considerations distinguishing such metals from the ferrous metals in particular with regard to surface treatment thereof to enhance the oxidation resistance at high temperatures.

It is, accordingly, to the various, but frequently inconsistent, advantages and disadvantages and characteristics of these non-ferrous metals to which this invention principally relates.

For example, the highly refractory characteristics of molybdenum silicide or tungsten silicide or titanium silicide may be known, as are molybdenum or tantalum or other non-ferrous metal articles having on the surface thereof an oxidation resistant coating of silicide. If it is attempted, however, to form such silicide coating by, for example, a so-called "cementation" process whereby a source of silicon is mechanically or electrically applied over the surface of the article and then heated for diffusion of the silicon from the coating into the surface of the article or if, on the other hand, a silicide coating is attempted to be formed by decomposition of such gaseous materials as silicon tetrachloride by heat in an atmosphere of which the metal article is suspended, it may be found that the temperature range necessary for the production of the desired coating of the silicide in such an environment to a thickness or degree optimum for the desired oxidation resistance does in fact exceed the aforementioned re-crystallization point of the metal article itself with, of course, the aforementioned disadvantages stemming therefrom.

Also, if the metal article is suspended in a gaseous atmosphere, the point of support may provide a true "Achilles' heel" and/or other difficulties of accurate high tolerance control of the uniformity and/or thickness of the coating produced. Similarly, if it is attempted to produce a diffusion coating of another oxidation resistant material, such as, chromium, on such non-ferrous metals, either the temperature difficulty may be experienced, with regard to the temperature range of crystallographic change, or difficulty may be experienced in producing a coating or case of the desired thickness or depth into the surface of the metal article for optimum or desired oxidation resistance at high temperatures and/or of optimum ductility for maintaining a uniform and impenetratible coating of the metal article despite heat expansion movements, thermal shock, and flexing thereof in use.

According to this invention, however, there is provided for the "siliconizing" or diffusion coating of material such as silicon in the surface of non-ferrous metal articles of the character described by the use of an indirect pack impregnation where the metal article to be treated is embedded in a refractory pack of a source of the material to be coated and including a decomposable or volatile source of halogen material as a carrier medium for the material to be coated for diffusion coating at temperatures less than the aforementioned recrystallization temperatures of the metal articles and yet producing on or in the surface of the articles a desirably oxidation-resistant outer layer or casing or coating of the desired depth or thickness. Also this invention includes the controlling and predeter-

mining of various constituents of the diffusion coating pack so that the material to be coated forms a volatile or decomposable halide which is volatile or decomposable within the desired coating forming temperatures and so that, considering that thermodynamic and free energy considerations may indicate the direction and extent to which any diffusion of any material in the pack proceeds, the various pack constituents and the composition of the article being treated and the operating temperatures selected are all correlated with each other so that a diffusion of the metal to be coated occurs into the surface of the metal article preferentially to a diffusion of material from the surface of the metal article into the pack and/or on to the retort or container in which the diffusion coating operation is being carried out.

It is an object of the present invention to provide coated or cased metal parts or articles of the non-ferrous metals of the character described wherein the basic metal of the article retains, after treatment, the toughness and strength characteristics of the untreated basis metal, and the case or coating provides a superior oxidation-resistant protective layer or zone enveloping the core.

It is another object of the invention to provide metal parts or articles essentially composed of non-ferrous metals having unfavorable properties after recrystallization temperature and being capable of being rendered into a hot-cold worked condition and to provide coating or casing thereon having superior oxidation-resistant properties and erosion resistant properties at high temperatures.

A further object of the invention is to provide parts or articles essentially composed of metals of the character described and having a protective layer of silicide on the surface thereof, which parts are capable of withstanding substantial stresses for substantial periods of time in drastic oxidizing atmospheres and at high temperatures in excess of 1800° F. and which retain these properties after repeated heating and cooling cycles.

It is still another object of this invention to provide a siliconizing treatment for non-ferrous metals of the character described whereby the desired depth and effectiveness of the silicide coating or zone achieved at temperatures below the recrystallization temperature of the nonferrous metal base, but averting the embrittling effect of excessively high treating temperatures.

A still further object of this invention is to provide an indirect pack impregnation process for the diffusion coating of material such as silicon and the like into the surface layer of articles composed essentially of non-ferrous metals of the character described, which process includes the use of a pack of refractory material in which the article to be coated is embedded, a diffusible source of silicon or other coating material, and a source of halogen compound as a carrier element to form with the coating material a halide which is volatile or decomposable within the operating temperature range of a diffusion coating process.

It is still a further object of this invention to provide a method of forming a silicide coating on the surface of metal articles composed of non-ferrous metals of the character described such that the thickness of the silicide coating can be readily varied as desired and within the coating operation temperature ranges.

A still further object of this invention is to provide a diffusion coating pack, particularly for use with non-ferrous refractory metals of the character described having an internal recrystallization temperature range, which includes, in addition to refractory material in which the metal is embedded, a source of the material to be coated so selected that, when co-related to the metal article to be coated and the desired coating operation temperature below the recrystallization temperature of the article, the governing thermodynamic considerations provide for diffusion of the material to be coated toward and into the surface of the nonferrous metal article, and with the pack also including a source of halogen such that, at the desired coating operating temperatures, the material to be coated will form with the halogen a halide which is both volatile and decomposable within the coating operation temperature ranges.

Other objects of the invention will be in part obvious and in part pointed out hereafter.

As indicated above, the present invention is particularly applicable in forming silicide coatings on articles composed of the various nonferrous base metals of the character described and including, as above noted, molybdenum articles and high molybdenum alloys. Among the particular materials with which satisfactory results have been achieved according to this invention may be, for the purposes of illustration, included, molybdenum alloys with from 0.1% to 5% of an alloying metal such as titanium, tungsten, zirconium, or beryllium, or various mixtures of these elements. Typically molybdenum alloys to which the present method is applicable are as follows: (*a*) titanium 0.22%, zirconium 0.08%, molybdenum 99.7%; (*b*) titanium 0.45%, molybdenum 99.55%; (*c*) titanium 2.09%, molybdenum 97.91; (*d*) tungsten 5%, molybdenum 95%; (*e*) beryllium 0.2%, carbon 0.05%, molybdenum 99.75%.

In addition to the foregoing, as noted above, satisfactory results have also been achieved according to this invention in the siliconizing of articles composed from metals which are primarily colombium, tungsten, rhenium, vanadium, tantalum, etc., as well as alloys thereof. Such application of this invention to the particular nonferrous metals provides for producing an effective protective coating of silicide on the surface of the metal article and without heating the metal article to a temperature such that recrystallization and embrittlement occur therein, by treating the metal article in a siliconizing pack of a type described in detail hereafter.

In carrying out the method of this invention, the appropriate base metal or alloy is shaped to the configuration desired in the finished article by whatever means may be desired or appropriate and is then embedded in a powdered siliconizing pack in a sealed retort. In general, satisfactory results have been obtained according to this invention with such a pack containing an inert refractory filler, elemental silicon, and a small quantity of the substance that volatilizes at the temperature of the pack to produce elemental halogen for combining with the silicon as a carrier therefor through the pack to produce a halide which is decomposable at the temperatures of the pack, all of the pack materials being in finely divided condition. The retort containing such siliconizing pack and non-ferrous metal articles embedded therein is heated at a temperature of from about 1650° F. to 2300° F. for a suitable period of time, say one to twelve hours or more, to form the desired silicide coating on the base metal.

The thickness of the diffused coating formed is a function of both time and temperature. Thus, if a fairly thin silicide coating is desired, e.g., a coating of 0.0002" thick, heating the pack at a temperature of 1650° F. to 1700° F. for a few hours may be sufficient. On the other hand, if a silicide coating having a depth or thickness of 0.002" to 0.003" is desired to be produced, a temperature of the order of 2000° F. to 2100° F. may be preferred, at which temperature a treatment time of the order of four to ten hours yields a silicide coating of the desired depth. For thicker coatings, longer heating periods and/or higher temperatures should be used, bearing in mind that the temperature should not be so high as to cause embrittlement or recrystallization of the metal article being treated therein.

As indicated above, the pack of the present invention is largely composed of a finely divided material which is refractory and chemically inert under the processing conditions and at the processing temperatures. A preferred filler is finely divided alumina although various other re-

fractory materials that are chemically inert at the reaction temperature, e.g., clays, may satisfactorily be used. The elemental silicon in the pack, which is also in finely divided form, may vary in a proportion of from about 1% to 30% by weight, although the preferred silicon content is of the order of 10% or 11% of the pack.

Various halogen-generating substances may be used in the pack. For example, elemental iodine may be used in conjunction with an inert gas such as argon, or with the compounds such as urea which decomposes at the temperatures of treatment to produce a gas. Decomposable halides such as ammonium chloride, fluoride, bromide, and iodide can also be used. The preferred halogen-generating substance is ammonium iodide. As described, the elemental halogen formed in the pack acts as a carrier to transfer the elemental silicon to the surface of the base metal article where it diffuses into the metal to form the desired silicide coating. When an ammonium halide is used, it is preferably present in the pack to the extent of at least about 0.05% by weight. The upper limit of the halide concentration is not particularly significant, since excessive halide does not appear to produce any harmful effects. However, there is no particular advantage to be gained by using any more than say 1% of ammonium halide.

As illustrative, siliconized molybdenum-base articles which remain oxidation-resistant in air for periods of many hours at temperatures of the order of 1800° F.–2000° F. can be satisfactorily prepared using a pack in which elemental silicon and ammonium halide are the active ingredients; and, also, such treated metals exhibit advantageous thermal-shock-resistant properties, as do the coatings thereon, in use. It has been found however, that the useful life of the siliconized base metals to which this invention relates can be substantially extended and the effectiveness and efficiency of the diffusion coating process substantially enhanced by incorporating in the pack a minor proportion of elemental chromium (or a source thereof) to produce, by co-diffusion of silicon and chromium into the base metal article, a protective coating containing a combination of base metal silicide and chromium silicide or alloys thereof. Preferably the proportion of chromium present in such a pack should be rather carefully maintained between about 1% to 6%, and, desirably, no more than about 10% by weight at the most.

Thus, considering primarily the application of this invention to molybdenum, if the chromium content of the pack is substantially above a very minor proportion such as the 6% to 10% range noted above, a diffusion coating is produced which begins to take on more of the characteristics of a so-called "chromized" coating (rather than a siliconized coating) such as has heretofore been produced by a diffusion coating of chromium. It should be understood, of course, that, for many uses and applications, a diffusion coating of chromium into the surface of a molybdenum or other non-ferrous base article produces advantages which are both useful and desired, but such a coating of chromium and its advantages and characteristics are to be distinguished quite radically from the ultimate characteristics of a similar base article carrying a silicized coating thereon. Accordingly, if it is desired to utilize the advantages according to this invention of obtaining a better silicized coating or enhancing the silicide coating operation by the addition to the pack of a minor portion of chromium, the silicon-chromium ratio in the pack is satisfactorily maintained between about 4–1 and 2–3.

As further illustrative of the utilization of a pack containing both chromium and silicon, it may be noted that a molybdenum article was provided with a siliconized coating according to this invention from a pack including the above noted minor proportion of chromium. The silicide casing was then removed from the article by etching away the molybdenum core with nitric acid. Analysis of this surface case portion showed about 0.2%–0.8% Cr, 39.05% Si, and 59.47% Mo, indicating generally the composition ranges of the outer casings satisfactorily produced by this invention.

As further illustrative of the present invention, one embodiment of a method according to this invention and the article produced thereby will now be described. In the following description reference will be made to the accompanying drawing, which illustrates diagrammatically the interior of a retort suitable for carrying out a siliconizing treatment according to the present invention with the articles to be treated and the siliconizing pack in place therein.

Referring to the drawing, the articles to be treated in accordance with the present invention (for example, molybdenum turbine blades **10** and bolts **12**) are embedded in a pack **14**. In this illustration, the blades **10** and bolts **12** are formed of an alloy of 0.22% titanium, 0.08% zirconium, and 99.7% molybdenum. The pack **14** comprises 3% by weight elemental chromium, 11% by weight elemental silicon, 0.25% by weight ammonium iodide, and 85.75% by weight alumina, all being highly divided to have an average particle size of the order of 300 mesh. The pack containing the articles to be treated is enclosed within an inner retort **16**, formed essentially of molybdenum and having a molybdenum cover **18** therein. Inner retort **16** and its cover **18** are positioned in an outer pack **20**, which may have the same composition as the pack **14**, and which is contained in an outer retort **22** made of stainless steel and having a stainless steel cover **24**. When the inner and outer retorts are assembled, a layer of fusible silicate **26** which fuses at a temperature of the order of 1400° F., is placed on the cover **24**. Upon subsequent heating of the retort, this fusible silicate melts to form a seal, and as the retort is cooled after treatment, the silicate solidifies, thereby preventing air from entering the pack during the cooling period.

The retort assembly as described above is placed on a stainless steel tray **28**, and the stainless steel cover **30** is placed over the whole assembly. A further quantity of fusible silicate **32** is placed around the lower perimeter of cover **30** to form a second seal when the retort is heated.

The tray **28**, and associated outer and inner retorts **16** and **22**, are placed in a furnace and heated to a temperature of 2100° F. for a period of about 12 hours. As the pack is heated up the ammonium iodide decomposes to form ammonia and elemental iodine and, at a somewhat higher temperature, the ammonia decomposes to form nitrogen and hydrogen. A portion of the generated gases flow out through the seals **26** and **32**, which are by this time molten, thereby sweeping out any atmospheric oxygen present in the pack. The hydrogen formed by decomposition of the ammonia provides a reducing atmosphere and reacts with any oxide coating that may be present on the articles being treated. As the temperature of the pack continues to rise, the iodine reacts with the silicon and chromium of the pack to form volatile iodides which carry silicon and chromium to the surfaces of the articles being treated for deposition thereon and diffusion thereinto upon decomposition of the iodide. The deposit of silicon and chromium co-diffuse into the metal surface to form a layer essentially composed of molybdenum and chromium silicides.

At the end of the heating period, the retort and pack are cooled. The seals **26** and **32** solidify in the early stages of the cooling process to form a gas-impervious seal so that no atmospheric air is drawn into the inner retort to come into contact with the treated articles during the cooling period and until after the process is finished. When the retort is cooled substantially to atmospheric pressure, it is disassembled and the treated articles removed therefrom. The materials of the pack can be used over again, provided, of course, that those of

the elements of the pack consumed in the reaction are subsequently replaced.

Molybdenum articles treated in accordance with the foregoing procedure exhibit exceptional oxidation resistance at high temperatures. In one series of tests, articles treated in the manner described above were treated in an oxyacetylene flame to approximately 2600° F., held at this temperature for 15 or 20 seconds, and then quenched in oxygen to room temperature. This heating and quenching procedure was repeated twenty times, after which the articles were maintained in a flowing stream of atmospheric air at 2200° F. for eighteen hours. No failure occurred at any point on the surface of the articles during this test.

As indicated above, a useful degree of oxidation resistance can be achieved by utilizing a siliconizing pack wherein the aforementioned chromium is omitted and the silicon and halogen-generating substances constitute the only active ingredients. A satisfactory pack for use in such an embodiment of the present invention may satisfactorily have substantially the following composition: silicon 11% by weight, ammonium iodide 0.25% by weight, alumina 88.75% by weight. In other respects, the procedure may be the same as that described in detail above.

From the foregoing description, it will be apparent that the present invention provides a protective coating on various non-ferrous metals of the character described and a method of applying such coating capable of satisfying the several objectives set forth at the beginning of the present specification. The treating temperature with such a process is low enough so that the diffusion coating may be applied to the non-ferrous metals having a recrystallization point at a temperature where undesirable recrystallization in the microstructure occurs. Considering a molybdenum article treated in accordance with the foregoing, the toughness and strength of the molybdenum up to a temperature of about 2200° F. to 2300° F. or even higher is adequately retained. On the other hand, the treatment is sufficiently effective to provide a surface layer capable of withstanding oxidation in air at a temperature as high as 3000° F. for at least 15 minutes, or 2200° F. for periods of hundreds of hours, and at a temperature of 1800° F. for much longer periods of time measured in months, or perhaps years. By treating articles in an indirect pack impregnation method in accordance with the present invention, the entire external surface of the article is treated; there are no untreated spots as would be the case if the article were supported by a clamp or other holding device in a treating atmosphere.

A further interesting and useful property that has been observed in respect to articles treated according to the present invention is that the surface layer of base metal silicide and chromium silicide appears to have a self-healing characteristic. Thus, it has been noted, that even when pinholes or other minute imperfections are formed in the surface of the article, oxidation failure of the non-ferrous metal base at such point does not occur, as might be expected, possibly due to the fact that lateral diffusion of the surface layer forms a new protective film at such points. Also, a certain amount of bending ductility, especially at elevated temperatures, is possible without destroying the protective effect of the case.

Also, although some of the foregoing detailed explanation has been particularly directed to the treatment of molybdenum articles, it is to be understood that substantially the same techniques provide satisfactory results in the diffusion coating according to this invention of articles composed essentially of the other non-ferrous metals mentioned and/or alloys thereof. For example, a siliconizing pack (with or without the addition of chromium) in the proportions as set forth above produces satisfactory results in the siliconizing or diffusion coating of silicon into the surface of articles of the other non-ferrous metals mentioned and at desirably low temperatures.

In this latter connection, of course, in a great many, if not most, of the coating operations to which this invention relates, the final controlling factor in the choice of coating constituents and temperatures and technique may well be the crystallographic or microstructure changes of the base metal article as induced by the thermal conditions to which it is subjected during such a coating operation. With this in view, then, and recognizing the thermodynamic indications with the particular substances involved that, in order to produce the desired diffusion coating of the desired substance on to the desired metal, the reaction conditions must be such that the material to be coated, e.g., silicon, is induced to diffuse toward the articles to be coated instead of, for example, having the material of the articles to be coated diffused outwardly therefrom toward either the pack or the retort or having the material to be coated diffusing preferentially to the retort rather than to the articles to be coated. Although the precise constituents of any given pack for coating any given article may vary (including the material from which retort **16** and its cover **18** are fabricated), the particular temperature conditions and pack constituents are readily determined from the foregoing description and from data well known in the chemical and metallurgical arts. Similarly, instead of elemental silicon, such thermodynamic and other considerations may indicate that a silicon compound which has the inherent characteristic of decomposing to provide either elemental silicon or a silicon ion combinable with a halogen ion at the temperatures of operation may be useful. Similarly, the particular halogen-generating material utilized will be selected such that, if the halide is not already volatile and combined with the material to be coated, such combination will occur at one temperature stage during the coating operation to form a volatile halide, which will, in turn, decompose at the surface of the article at a later set of thermal conditions during the operation. Similarly, the choice of the particular material from which inner retort **16** and its cover **18** is made will, as will be understood from the foregoing, be selected so that its chemical and free energy and thermodynamic characteristics are co-related with both the material of the articles to be coated, the desired coating temperature range, and the chemical characteristics of the source of materials to be coated and the halogen-generating carrier.

It is of course to be understood that the foregoing description is illustrative only and that numerous changes may be made in the conditions, proportions, and ingredients specifically disclosed without departing from the spirit of the invention as defined in the appended claims.

What is claimed is:

1. In a method of producing a high temperature oxidation resistant and thermal shock resistant diffusion silicon coating surface layer on an article formed of metal selected from the group consisting of molybdenum, colombium, tungsten, rhenium, vanadium, tantalum, and mixtures and alloys thereof and which has the inherent characteristic of undergoing an irreversible crystallographic change when heated above a characteristic temperature, the steps which comprise enclosing said article in a pack of powdered material containing a source of silicon and a small amount of a volatilizable halogen generating substance as essential active ingredients and an inert filler, and heating said article in said pack to a temperature higher than that causing volatilization of said halogen substance but less than the temperature at which said irreversible crystallographic change occurs effecting said diffusion coating of silicon into the surface of said metal article.

2. A method as received in claim 1 in which said pack also contains a source of chromium for diffusion along with said silicon into the surface of said article during said heating step.

3. A method as recited in claim 1 in which said metal

article is heated in said pack to a temperature of about 1600° to 2300° F.

4. A method as recited in claim 2 in which the ratio of silicon to chromium in said pack is within the range of about 4:1 to 2:3.

5. A method as recited in claim 4 in which said pack contains 1 to 30% by weight of silicon, 0.05 to 1% by weight of an ammonium halide, 1 to 6% by weight of chromium, and the remainder powdered inert refractory material.

6. An article of manufacture having good mechanical strength and high temperature oxidation resistance and thermal shock resistance, which comprises a core of metal selected from the group consisting of molybdenum, colombium, tungsten, rhenium, vanadium, tantalum, and mixtures and alloys thereof, and which undergoes an irreversible crystallographic change when heated above a characteristic temperature, said article having an outer diffusion coated silicon surface layer on said core, and said metal core as coated having a crystal structure which has not undergone said crystallographic change.

7. An article as recited in claim 6 in which said diffusion coated surface layer consists essentially of a silicide of said metal of said core and chromium, with said silicide content being substantially greater than said chromium content.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

June 5, 1962

Patent No. 3,037,883

Richard L. Wachtell et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 42, before "achieved" insert -- are --; column 5, line 9, strike out "the"; line 10, after "urea" insert a comma; same column 5, line 16, for "base" read -- basis --; column 8, line 71, for "received" read -- recited --.

Signed and sealed this 27th day of November 1962.

(SEAL)
Attest:
ESTON G. JOHNSON
~~ERNEST W. SWIDER~~
Attesting Officer

DAVID L. LADD
Commissioner of Patents