

Sept. 30, 1952

C. G. GOETZEL

2,612,442

COATED COMPOSITE REFRACTORY BODY

Filed May 19, 1949

2 SHEETS—SHEET 1

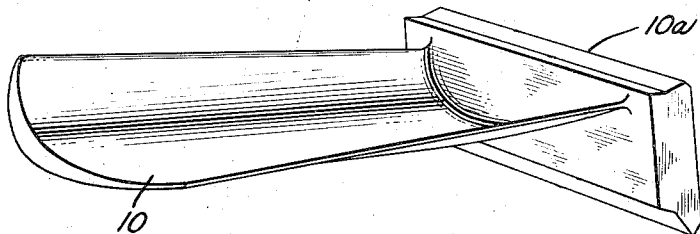


Fig. 1

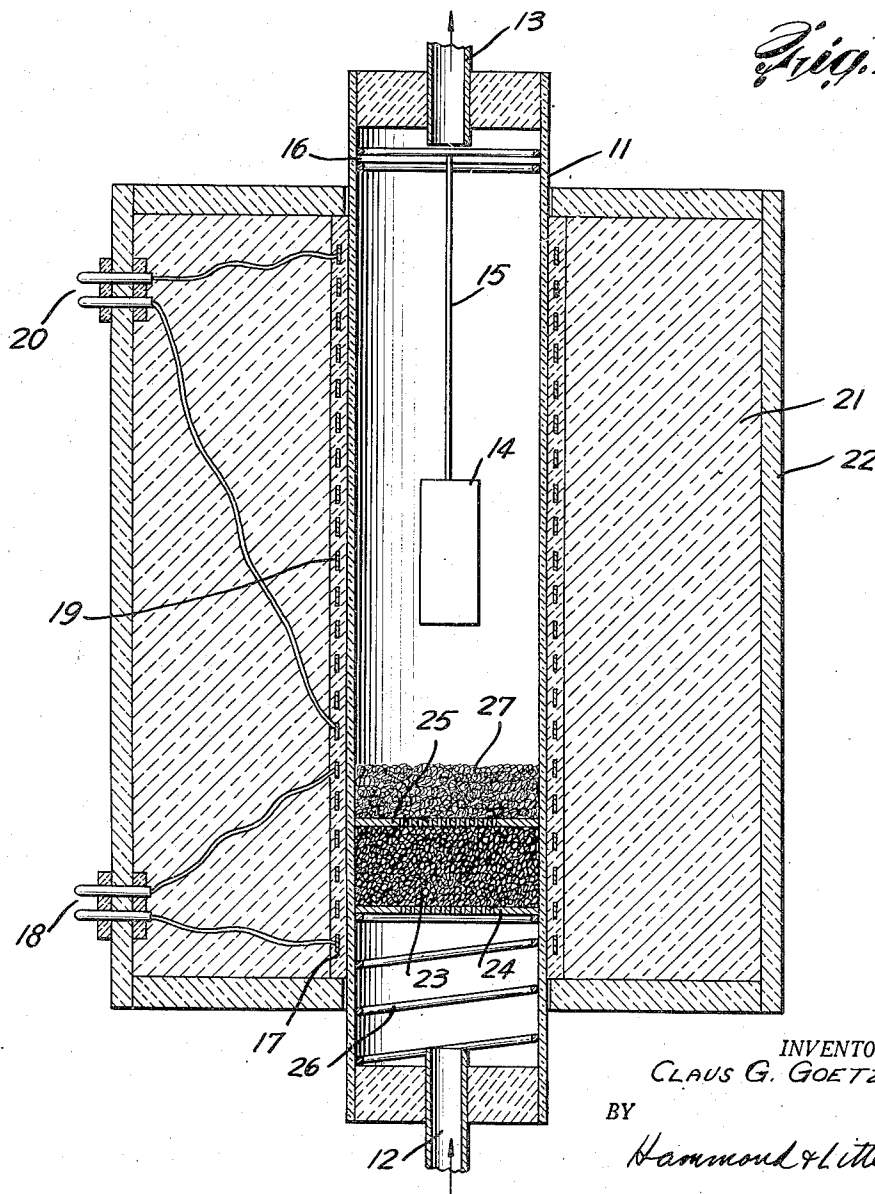


Fig. 2

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2 SHEETS—SHEET 2

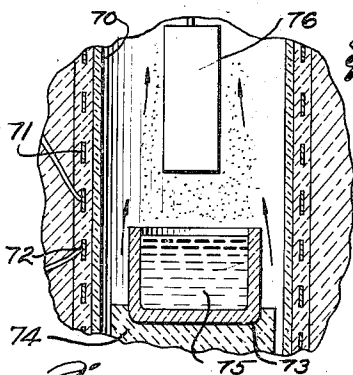


Fig. 4

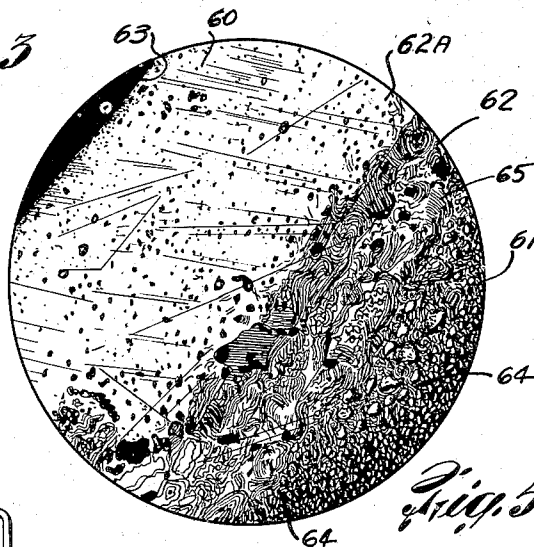


Fig. 5

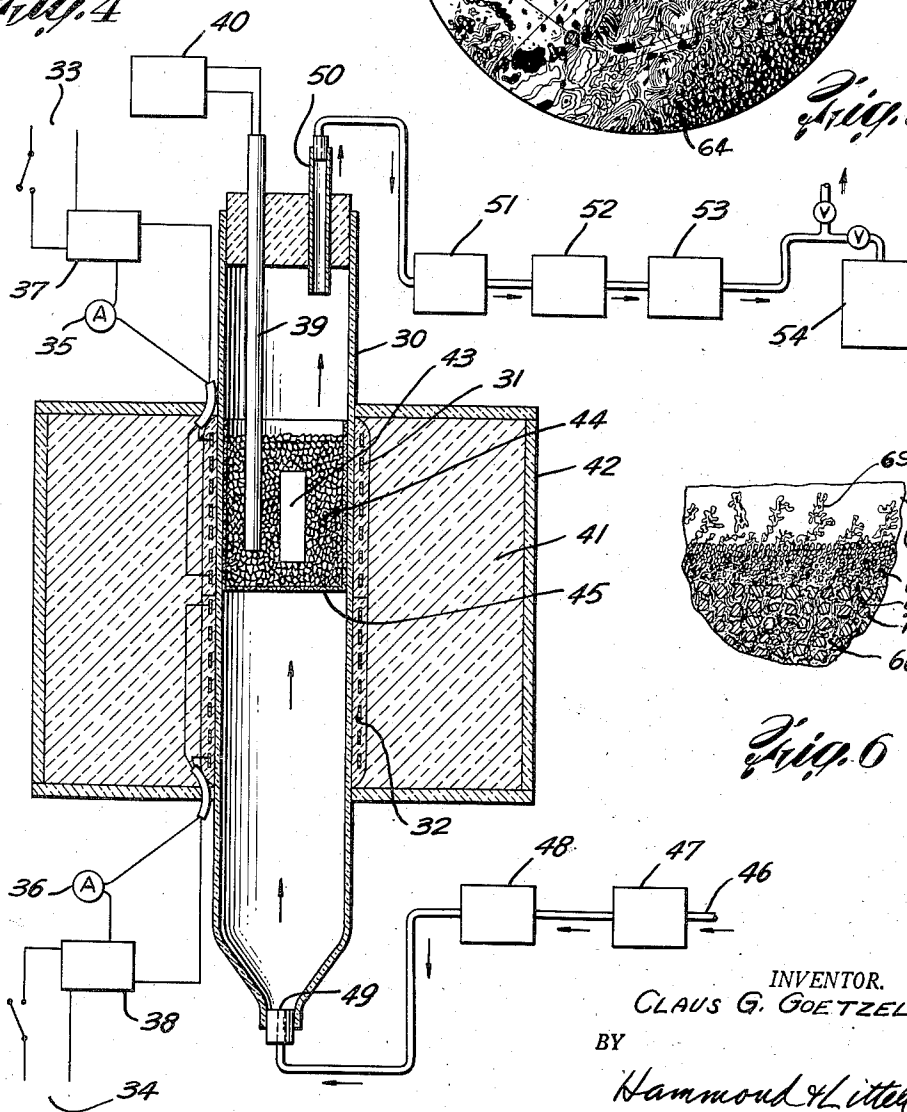


Fig. 6

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COATED COMPOSITE REFRACTORY BODY

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5 Claims. (Cl. 75—22)

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This invention relates to protective surfaces on structural components useful for high temperature and oxidizing or corrosive atmosphere conditions, and particularly to a protective surface for refractory metal components, especially composite body materials.

Components suitable for use as buckets, blades, valves, nozzles, and the like, in gas or steam turbines, jet engines, and devices having similar temperature and atmosphere conditions have been difficult to provide. Such components must have certain desirable physical characteristics so that the component will withstand the stresses involved at the high temperature of operation and will not deteriorate in the oxidizing or corrosive conditions existent. The elements must have high hot tensile strength, hot fatigue strength, and high resistance to creep at elevated temperatures. Materials containing stable compounds such as borides, silicides, and nitrides, of the refractory metals tungsten, molybdenum, titanium, zirconium, chromium, etc., or such stable oxides as those of the metals aluminum, magnesium, zirconium, silicon, or beryllium, or such stable carbides as those of the non-metals silicon or boron, are desirable from a corrosion and oxidation resistance standpoint. The materials just mentioned containing these compounds, however, are generally inferior in their combination of physical properties, such as cohesive strength, resistance to mechanical and thermal shock, and heat conductivity. Compounds based on the combination of carbon with the refractory metals tungsten, molybdenum, titanium, zirconium, tantalum, columbium, etc., possess better sets of physical properties, particularly, resistance to thermal and mechanical shock and cohesive strength. This is especially true when they are alloyed with certain metallic binders such as cobalt or nickel. One of the difficulties is that the aforementioned refractory metal carbides base materials are not stable as far as oxidation and corrosion resistance at high temperatures.

As an example, titanium carbide, zirconium carbide, molybdenum carbide, or tungsten carbide tend toward thermal decomposition into CO_2 , TiO , ZrO , MoO_3 , WO_3 , respectively, at temperatures in the range of 1400–1700° F. Especially in the case of molybdenum carbide and tungsten carbide, the high vapor pressure and volatilization tendency of the molybdenum and tungsten trioxides contribute to a rapid destruction of the cemented carbide materials when they are exposed to oxidizing or corrosive attack above 1500° F. Some improvement is attained

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by alloying the individual carbides, such as titanium carbide with tungsten carbide, but the order of the improvement is insufficient for practical purposes especially under conditions of use as exacting as components for gas turbines and jet engines.

Iron and steel have been surface treated by coating the same by straight electrodeposition or plating, spraying, or by the so-called "impregnation" treatments involving diffusion and metal atom exchange mechanisms between the deposited metal and the base metal. The depositing of the surface metal in the impregnation treatments can be through immersion of the component in a salt bath, immersion in a powder pack containing the surfacing materials, or by exposing the body to a gas stream containing the surfacing metal in the form of a volatile compound, such as a halide, or plurality of halides.

The aforementioned surfacing treatments especially of the "impregnation" type, are most effectively applied to the pure metals which form complete or substantially complete solid solutions in any portion of the binary system because of the high diffusion rates involved. An example is iron, or molybdenum, or tungsten, when chromium is used as a surfacing metal. When several phases or compounds are formed by alloying of the surfacing and the base metal, the diffusion rates are slowed so that the impregnation or diffusion treatment requires higher temperatures, more times, and a higher concentration of the surfacing metal or material in the compound which is in contact with the body to be protected. This is true, for example, when the base metal is nickel or cobalt and the deposited metal is chromium.

The impregnation treatment is still more impeded and in certain uses wholly ineffective if the base metal contains a compound such as a carbide as a major constituent, for example, eutectoid or hyper-eutectoid steel, or cast iron. The reason for this is that the carbide, such as iron carbide, interferes with the metal atom exchange mechanism between the base metal and the deposited surface material. The carbide also interferes with the inward diffusion of the atoms of the deposited metal.

As will be explained hereafter, the barrier of the carbide against diffusion of the deposited metal into the interior of the base material is utilized to advantage in the present invention. If such a barrier did not exist, the high surface temperature involved would cause the diffusion process to continue indefinitely while the ele-

ment is subjected to the high temperature. As a result, the concentration of the surfacing material would progressively become diluted at the surface and would become insufficient to withstand external corrosive attacks. As an example of this effect, a body of molybdenum which has been surface impregnated with chromium through deposition of chromous iodide vapors would withstand the oxidizing atmosphere of still air at 1800° F. for the short time of only 5 to 10 minutes. A similar body of pure tungsten identically treated would withstand exposure to air at such a temperature for only 20 to 30 minutes. A body consisting mostly of a refractory carbide, such as tungsten carbide or titanium carbide cemented with a relatively small portion of cobalt or nickel (for example, 3 to 13%), would practically entirely prevent migration of atoms of chromium or other surfacing elements into the structure and of tungsten or titanium toward the surface free to combine with halogen. Thus, the mechanism of atom exchange would be substantially inhibited by the carbide structure so that the deposited surface metal would merely be in the form of a plate without a strong bonding or merger with the base material. For this reason, differences in the coefficient of expansion of the base material and the deposited metal would tend to cause a spalling off of the deposited surface material during heating or cooling of the body and an immediate break-down of the protection of the base material would follow.

One of the principal objects of the invention is to provide a method for making an article which will have the desired high physical characteristics at high temperature under oxidizing and corrosive conditions of operation.

One of the features of the present invention is to overcome the prior defects by the use of an intermediate metallic phase between the refractory carbide core structure and the deposited and diffusion alloyed surface metal casing, said intermediate phase serving to provide a medium wherein a merger can take place with the outside casing.

Such an arrangement will permit the metal atom or other transfer exchange mechanism between the intermediate phase and the surface casing to take place unhindered for a limited depth before the barrier against further inward diffusion of the deposited surface metal becomes effective. Preferably, the diffusion takes place so that the surface metal will penetrate through the intermediate phase and to a limited extent into the binder in the refractory carbide core structure. It also provides a buffer or cushion-like intermediate metallic layer of great ductility which will absorb the stresses caused by differences in the expansion of the cemented carbide base material and the deposited surface metal or stable oxide compound formed thereof. It is preferable, though not absolutely essential, that the intermediate metallic surfacing layer or phase should be of the same metal or materials as the metal or alloy used as the binder for the carbides. By making the intermediate phase of the same metal as the binder, the intermediate surface casing, shell or layer can thoroughly be united and merged with the binder or cementing network of the carbide material by a self-diffusion process, said self-diffusion process taking place either in the solid or in the liquid state. It is desirable that the intermediate phase metal be one which will not form barrier compounds,

such as carbides, in conjunction with the skeleton or base carbides.

The intermediate phase may be deposited or formed on the component in various manners, such as by painting or spraying. Also, it could be formed thereon in an infiltration step of the skeleton, if such is used, or in a hot pressing operation wherein manipulations can be made so that a layer of the binder metal will completely encase the component. If the intermediate phase is painted or sprayed on the component this must be done prior to the sintering operation as will be explained hereafter. One of the main essentials is that the intermediate phase film should be uniform on all of the surfaces of the component.

Following the placement of the intermediate phase on the component, surfacing "impregnation" of the component is carried out. Surface impregnation with the chemically stable heat oxidation and corrosion resistant element or materials may be theorized to be based on a metal atom exchange between the deposited surface material and the intermediate phase. This emphasizes the necessity for a sufficient quantity or thickness of the intermediate phase material so as to allow for the desirable metal atom exchange process. At the same time, the intermediate phase preferably should not be so thick as to prevent the limited penetration of the surfacing metal into the binder in the base material.

The surface deposited metal may be placed on the intermediate phase in various manners, such as by deposition from the vapor phase, salt bath, or powder pack methods. The vapor phase deposit may be carried out by passing the gas containing either pure metal or metal combined in a compound such as a halide in the vapor phase over the specimen. Pure metal can be used advantageously where the vapor pressure conditions are correct to deposit the surface metal or alloy directly from the metal vapor state. The vapor phase deposit may be accomplished by means of an impregnated pack arrangement wherein the component is placed in a pack of suitable material and the gas passed therethrough, the gas reacting with the material in the pack to form the vapor phase for deposition on the surfaces of the component. Similarly, the gas may be passed over or through the surfacing metal while the metal is in liquid state so as to carry along the metal vapors. The surface metal also may be deposited by means of conventional powder pack and salt bath methods.

It is also desirable to consider the surface material from the view point of stability of either the pure metal or an oxidic compound formed thereof when exposed to the oxidizing atmosphere of the high temperature of the service of the component. As will be explained hereafter, it is more advantageous to employ alloys which are selected so that one constituent forms stable complex oxides. Also, a single metal may be used which forms directly a mechanically stable oxide at high temperatures. For deposition from the vapor phase, the preferred metals are those of high vapor pressure and those which form halogen compounds and which are readily susceptible to thermal decomposition upon deposition on the intermediate phase on the surface of the body to be encased.

These and other objects, advantages and features of the invention will become apparent from the following description and drawings which are merely exemplary.

In the drawings:

Figure 1 is a perspective view of a turbine blade in conjunction with the present invention which can be advantageously applied.

Figure 2 is an elevation in section showing one form of apparatus for depositing the surfacing metal on the intermediate phase of a component.

Figure 3 is a fragmentary view of a modified form of the invention seen in Figure 2 wherein the gas is passed over molten metal.

Figure 4 is a sectional view of another form of apparatus for depositing a surface material on a component.

Figure 5 is based on a photomicrograph (X250) of a specimen made in accordance with the present invention.

Figure 6 is an enlarged diagrammatic representation of a surface section of a component made in accordance with the present invention.

As previously mentioned, the invention is especially adapted for use with a cemented refractory metal carbide composite body.

The cemented refractory metal carbide component can be made in various ways. For example, the metal powders may be mixed, sintered and pressed as is well known in the art. Also, the carbide base metal may be formed into a skeleton having pores therethrough, said skeleton thereafter being infiltrated with the cementing metal or alloy of lower melting point than the skeleton. As previously set forth, the refractory metal base carbide materials may be such as titanium carbide, zirconium carbide, molybdenum carbide, or tungsten carbide, refractory metal meaning a metal or material having a melting point above iron which is about 2800° F. Various combinations of these carbides also may be used as desired.

The binder or cementing metal or alloy may be one that is suitable for the purpose, and selected from the 6th to 8th group and 4th series (3rd period) of the periodic table. As an example, nickel or cobalt or alloys thereof can be used as will be set forth hereafter.

The preferred refractory metal base carbide is titanium carbide for the major phase of the base material because titanium carbide has a unique set of properties for the purpose herein, such as a low specific gravity (4.2) and high hardness (Vickers Diamond Pyramid No. 3200 at room temperature). It also has a limited but significant affinity and solubility toward certain of the binder metals such as cobalt, nickel, chromium or alloys thereof. As an example, if combined with cobalt in a weight ratio of 8 parts titanium carbide, and 2 parts cobalt, a hardness of Rockwell A-92, combined with a transverse rupture strength of 200,000 p. s. i. at room temperature and up to 100,000 p. s. i. at 1800° F. is attained. Similar values are possible with zirconium carbide having nickel or cobalt as the binder metal. Also, titanium carbide is a more stable compound at elevated temperatures than most of the other carbides and does not decompose and liberate carbon which forms alloys with certain of the metals used as a binder and/or the intermediate layer, for example, nickel.

The composite body which is to be surface treated can be made in various manners such as:

- (1) Cold pressing, presintering, and sintering;
- (2) Hot pressing;
- (3) Infiltration of the binder metal into the presintered or sintered carbide skeleton.

Any of these methods are useable for this invention, the choice depending upon prevailing

economic and industrial conditions, or on the ultimate physical properties desirable. These to a certain extent are affected by the particular method of producing the carbide body.

In the infiltration process, the skeleton may be infiltrated with the binder metal in various manners. As an example, the skeleton may be formed in a mold under pressure, either dynamic or static, or a combination thereof, following which the skeleton may be sintered and removed from the mold or the mold may be transferred to the infiltration zone. The infiltration may be carried out by capillary action, under pressure, under vacuum or in various manners. Also various heat treatments may be given the infiltrated skeleton after infiltration.

If ordinary cold pressing, presintering and sintering, methods of producing the cemented carbide body are employed, the intermediate surface phase or casing can be applied in various ways. The pressed or "green" cemented carbide compact can have the metal painted thereon using an organic vehicle such as collodion or lacquers. Also the presintered cemented carbide compact can have the intermediate metal phase painted thereon.

This intermediate metal phase, for example, can be cobalt or nickel corresponding to the binder material of the cemented carbide compact. It also is possible to spray the intermediate phase material on the pressed "green" cemented carbide compact, or to spray it on the presintered cemented carbide compact. When spraying is used, to apply the intermediate phase, the metal or alloy should be in conventional powder form, such as Schori process powder. In order to have improved surface adherence of the sprayed-on articles to the comparatively hard surfaces involved or encountered in the presintered compact, an alloy with a distinct difference between the solidus and liquidus thereof can be used to advantage which can be sprayed on in the mushy state. An example of this would be an alloy of nickel and chromium in the ratio of 80-20.

The intermediate surface layer applied by painting or spraying on to the cemented carbide compact is diffused and/or fused with the binder phase of the cemented carbide body in the subsequent sintering operation.

It is essential that the painting or spraying be accomplished prior to the sintering operation because in the final sintered form, the base material is too hard and dense to receive and retain the powder particles impinged on the surfaces by the spray gun. Also, a double sintering of the carbide would be necessary so as to obtain complete fusion and merger of the intermediate phase with the cementing or binding material. In the second sintering operation, there would be a tendency to destroy the physical characteristic and structure of the carbide material accompanied by excessive and detrimental grain growth.

When hot pressing is used to form the carbide compact, painting and/or spraying of the intermediate metal phase would be disadvantageous because the base metal would be too hard and dense to retain the particles and a disadvantageous second high sintering temperature would be required to obtain a fully dense shrunk film of the painted layer.

Thus, it is preferable to employ electroplating methods when a hot pressed compact is involved for furnishing a uniform and dense sur-

face shell of the intermediate phase such as Co, Ni, Ni-Co, or Ni-Cr alloy. The plated surface film of the intermediate phase is then diffused and merged with the cementing metal during a subsequent heat treatment. The subsequent heat treatment may be slightly below or slightly above the melting point of the binder metal or liquid phase respectively of the cemented carbide material; such as 2350° F. for tungsten carbide, cobalt eutectoid; and 2550° F. to 2650° F. for cobalt containing dissolved titanium carbide, and in any case substantially below normal sintering temperature to avoid the detrimental grain growth and deterioration of physical characteristics and structure of the cemented carbide base material.

The extent of the diffusion heat treatment also depends upon the characteristics of the cemented carbide system. In systems of great solubility, such as WC-Co, where an eutectoid is formed, the treatment must be below the melting temperature of the low melting phase and the time relatively short. Where there is a very limited solubility, such as the system TiC-Co, the temperature can be near the formation temperature of the liquid phase and a longer time employed.

One of the preferred manners of furnishing the intermediate phase in connection with the hot pressing of the compact is a method whereby a uniform shell of the intermediate phase can be furnished by the binder metal proper. This can be accomplished by carrying out the hot pressing operation in such a manner as to squeeze out the binder material during compaction so as to enrich the surface regions of the carbide compact at the expense of the interior regions. As an example, an 80-20 of TiC-Co mixture can be hot pressed at 2900° F. at 2500 p. s. i. in order to obtain a cobalt-enriched surface on the compact. The compact in such an operation is subjected to a minimum of six heat cycles ranging from 2700° F. to 3000° F., and the pressure is applied in the form of an impact blow at the moment the peak temperature is reached. During cooling to 2700° F., the binder metal freezes and thus is fixed in position. By repetition of the heat and press cycles, a progressive build-up of the surface regions with cobalt binder metal will occur.

When an infiltration method is employed to form the cemented carbide body, it is desirable to encompass the refractory skeleton bodies in a ceramic carbide or other suitable material mold with sufficient space left between the surface of the skeleton body and the walls of the mold cavity to allow for the formation of a thin continuous surface film of the liquid infiltrant metal. Such a method of providing the intermediate phase on the skeleton is of particular advantage because no further heat treatment is required to integrally fuse and merge the surface layer of the intermediate metal with the binder metal network of the carbide skeleton. Various thicknesses of the intermediate surface phase can be obtained under controlled conditions depending upon the method of producing the layer.

As mentioned, it is desirable to have the intermediate phase continuous in thickness as well as in adherence and anchorage to the cementing metal network of the carbide structure. The thickness of the intermediate phase layer preferably is in the order of .002" to .020", the exact thickness thereof depending on the type of final surfacing material to be used and also on the

process of applying the material. If, for example, pure chromium is to be used as the surface element, and cobalt as the intermediate phase layer as well as for the binder for the carbide, a surface layer of .002" thickness of chromium can be used with a minimum of .003" thickness of the intermediate cobalt layer. In such an instance, the same thicknesses would apply if the surface layer were of chromium-rich alloy phases with cobalt, for example, cobalt-rich solid solution and intermediary compounds, such as Co₂Cr₃.

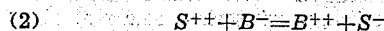
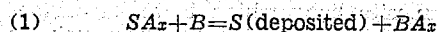
The maximum thickness should be that to guarantee some penetration and roots into the binder network of carbide. This may be in the order of .015" for the aforementioned chromium surface element on the cobalt intermediate phase.

The preferred manner for deposition of the surface metal is by the vapor phase methods involving either pure metal or a compound of metal that thermally decomposes upon deposition, initiating a metal atom exchange process. In the case of pure metals, chromium, silicon, zirconium or aluminum, are the most desirable. Although pure chromium as surfacing casing is desirable for reasons of technical simplicity and economy of the process, the oxide of chromium (Cr₂O₃) formed when exposing the metal to high temperature oxidizing atmospheres lacks some stability from a mechanical standpoint, and tends to mechanically disintegrate and flake and spall off thus constantly exposing fresh metal surfaces to the oxidizing atmosphere. This would eventually result in completely wearing through the chromium metal surface. Hence metals resulting in more stable oxide films such as zirconium, silicon or aluminum are preferred for very high temperature application (above 2000° F.).

If the case formation process employs the previously mentioned mechanism of preferred decomposition of a compound, the halides of chromium, silicon, zirconium, or aluminum, such as chromous chloride, chromous iodide, silicon chloride, zirconium chloride, or aluminum chloride are suitable for the process.

Instead of the pure metals, it may be more advantageous and preferred to employ alloys of chromium with other metals mentioned which tend to form more stable complex oxides. Examples of alloys of chromium with elements to form a more stable oxide, are compounds of chromium with aluminum, with silicon, with zirconium; with aluminum and silicon; with aluminum and zirconium; or with aluminum, silicon and zirconium. In either case, double or triple halides, such as the chlorides, bromides or iodides of chromium plus aluminum; chromium plus silicon; chromium plus zirconium; chromium plus aluminum plus silicon; chromium plus aluminum plus zirconium; or chromium plus aluminum plus silicon plus zirconium; must then be employed.

It can be theorized that the exchange reactions taking place between the base metal and the surfacing metal by means of diffusion are as follows:



where

S (surfacing metal) may be Cr, Si, Al, Zr, alloys,

B (base metal) may be Co, Ni, alloys,

A[±] (halogen) may be Cl, I, Br

It is to be understood, however, that the exact mechanism of diffusion or atomic interchange of the complex system may not be known. In some cases there may be an ion-exchange and in others an atomic migration, or there may be some other phenomena involved.

With the various mentioned elements, the following may be taken as examples of the specific reactions in relation to the above.

- (1) $\text{CrCl}_2 + \text{Co} \rightarrow \text{CoCl}_2$
- (2) $\text{CrI}_2 + \text{Co} \rightarrow \text{Cr} + \text{CoI}_2$
- (3) $\text{CrCl}_2 + \text{Ni} \rightarrow \text{Cr} + \text{NiCl}_2$
- (4) $\text{AlCl}_3 + \text{Co} \rightarrow \text{Al} + \text{CoCl}_2 + \text{Cl}$
- (5) $\text{AlI}_3 + \text{Co} \rightarrow \text{Al} + \text{CoI}_2 + \text{I}$
- (6) $\text{AlBr}_3 + \text{Ni} \rightarrow \text{Al} + \text{NiBr}_2 + \text{Br}$
- (7) $\text{SiCl}_4 + 2\text{Co} \rightarrow \text{Si} + 2\text{CoCl}_2$
- (8) $\text{SiBr}_4 + 2\text{Ni} \rightarrow \text{Si} + 2\text{NiBr}_2$
- (9) $\text{ZrCl}_2 + \text{Co} \rightarrow \text{Zr} + \text{CoCl}_2$
- (10) $\text{ZrI}_2 + \text{Ni} \rightarrow \text{Zr} + \text{NiI}_2$

As previously mentioned, one of the uses for the present invention is in conjunction with a turbine blade for gas turbines, an example of which is seen in Figure 1 of the drawings. In such a component, the blade 10 is joined to a foot portion 10a, the foot portion 10a being insertible into a suitable aperture in the wheel of the turbine or jet engine.

One manner in which vapor phase impregnation or deposition of the surface metal or alloy can be carried out is one where the component is suspended in the metal halide gas stream, one form of apparatus being illustrated in Figure 2. Furnace tube 11 may be of sillimanite or other suitable refractory material. Said tube is arranged with a gas inlet pipe 12 and a gas outlet pipe 13; the component 14 being suspended by means of a wire or rod 15 from the holding elements 16 within tube 11. The component 14 may be a cemented carbide refractory element with the intermediate phase surface material thereon.

The heating elements for the furnace, preferably of molybdenum or tungsten, may be divided into two sections, there being a lower element 17, connected to the terminals 18 for the purpose of maintaining a predetermined temperature in the lower part of the furnace and a second heating element arrangement 19 connected to terminals 20 for maintaining a predetermined temperature in another portion of the furnace. As will be explained hereafter, the temperature in the vapor generation portion can be maintained lower than the temperature where the deposition takes place on the component. The heating elements and tube may be surrounded by an insulating filler material 21 held in a suitable gas tight housing 22.

The granular metal material is located inside of tube 11 and may be held in position by means of perforated plates 24 and 25, plate 24 being suitably positioned by means of a spring or other support 26. A Nichrome mesh work 27 may be placed over the upper perforated plate 25 as a screen to prevent solid particles from being carried over. Dry HCl gas is passed through inlet tube 12 and the gas generating zone at the lower end of the cylinder. The gas generating zone includes the granular metal which if of chromium is kept at a temperature of about 1500° F., chromous chloride vapor being generated as the dry HCl gas passes over the metal. The unstable gas then flows into contact with the component

14 in which zone a temperature is maintained of 1800° F. to 2700° F. depending on the cemented carbide system involved. If desirable, an inert gas such as argon, nitrogen or hydrogen may be used as a carrier for the chromous chloride. It also is possible to reverse the flow and permit the heavy chromous chloride vapors to descend rather than rise.

As previously mentioned, it also is possible to deposit other metals in a similar manner from the vapor phase such as silicon, zirconium, and aluminum.

An apparatus for deposit of the pure metal from the vapor phase is shown fragmentarily in Figure 3, the remainder of the furnace being similar to that illustrated in Figure 2. Refractory tube 70 may have heating elements 71, 72 surrounding the same and a ceramic or other suitable material metal holder 73 can be held in place in said tube by refractory block 74. The metal 75 in the pot 73 is kept in molten state by the heating elements. The hydrogen or other gas passing up through the passage between the pot and the walls will carry metal vapor onto and deposit the same on specimen 76. The temperature in the zone of the pot may be maintained at about 3100° F. and the temperature in the specimen zone at about 2750° F.

Another and preferred manner in which the surface metal can be deposited from the vapor phase is by use of an impregnated ceramic carrier pack arrangement, such as is illustrated in Figure 4. In general, the component is placed in contact with a mixture of a suitable ceramic, such as glazed Alundum or sillimanite grains, and chromium, silicon, aluminum and/or zirconium metal granules. The temperature is maintained between 1650° F. to 2500° F. and a mixture of hydrogen and hydrogen chloride gas passed through the pack which generates a chromous or other chloride vapor which is deposited on the surface of the component.

As a specific example, there may be 7% hydrogen chloride in the gas with a total flow of 500 cm.³/min. at one atmospheric pressure. The pack granules may be 10-20 mesh.

Referring to Figure 4, the refractory furnace tube 30 has a pair of heating elements 31, 32 connected to power sources 33 and 34, respectively. Ammeters or other suitable instruments 35, 36 are provided in conjunction with suitable potentiometers 37, 38 for controlling the power input and thereby the heating by the coils for heating the furnace tube. A suitable thermocouple or temperature measuring apparatus 39 and indicator 40 may be provided for the purpose of indicating the temperature in the pack or controlling the same. Insulating material 41 may be contained in casing 42 surrounding the furnace tube 30. The component which is to have a surface deposited thereon is indicated at 43 packed in the granular pack 44, the impregnated ceramic carrier pack 44 being supported in a suitable Nichrome suspension basket 45. The composition of the pack will be discussed hereafter. Hydrogen and HCl gas may be supplied to pipe 46 in any desired proportions, said gas being passed through a concentrated sulphuric acid absorption receptacle 47 and calcium chloride receptacle 48 to insure that the gas is absolutely dry. The hydrogen and HCl gas is fed through inlet 49 to the furnace tube and the temperature of the furnace tube is suitably adjusted.

The gas passing through the impregnated carrier pack will generate chromous chloride when chromium is used therein and will deposit

it on the surface of the component. Outlet 50 carries the gas from the tube into the water absorption receptacle 51, then through concentrated sulphuric acid absorption receptacle 52 and then the calcium chloride absorption receptacle 53. It is evident, of course, that the connections can be varied as desired and various combinations used. As mentioned before, various metals may be used in the place of chromium or a combination of these metals with chromium can be used in order to provide the desirable surface deposit. Examples of methods of surface impregnation to form binary, ternary, or quaternary alloys are given hereafter. First the pack composition is set forth and then the procedure for carrying out the impregnation. An apparatus such as that shown in Figure 4 is suitable for the purpose.

First will be given examples of a chromium aluminum binary surface impregnation by the pack gas treatment.

A. Cr-Al.—Binary surface alloy—

A1. Pack composition: 50% (by weight) of 50-50 Cr-Al pulverized fused prealloy, —10-20 mesh granules; 50% Al_2O_3 , or sillimanite, —10-20 mesh.

Procedure: Dry hydrogen—flow 1000 cc./min.; HCl —flow 70-100 cc./min. Passed through pack for 6-30 hr., 1740-2280° F. in alternate current, 4 reversals/hr.

A2. Pack composition: 33% of 50-50 Cr-Al prealloy, ground to —325 mesh; 17% CrCl_2 crystals; 50% Al_2O_3 , MgO , ZrO_2 or BeO , —325 mesh.

Procedure: Dry hydrogen—flow 1200 cc./min. Passed through pack for 6-30 hr., 1740-2280° F.

A3. Pack composition: 30% of 50-50 Cr-Al prealloy ground to —325 mesh; 15% CrCl_2 crystals; 5% NH_4Cl ; 50% Al_2O_3 , MgO , ZrO_2 or BeO , —325 mesh.

Procedure: Dry hydrogen—flow 1200 cc./min. Passed through pack for 6-30 hr., 1740-2250° F.

Next a chromium silicon binary alloy may be deposited in accordance with the following procedure:

B. Cr-Si.—Binary surface alloy—

B1. Pack composition: 50% (by weight) of Cr granules (pure, *electrol.*), —10-20 mesh; 50% Al_2O_3 or sillimanite granules, —10-20 mesh.

Procedure: Dry hydrogen—flow 100 cc./min., passed through liquid SiCl_4 at 200-210° F. (boiling pt.). Gas mixture is passed through pack at 2200°-2500° F. for 1 to 16 hours.

B2. Pack composition: 40% (by weight) of 60-40 Cr-Si (compound CrSi) pulverized prealloy (produced by fusing briquetted mixtures of Cr_2O_3 plus SiC), ground to —325 mesh; 10% NH_4Cl ; 50% Al_2O_3 , MgO , ZrO_2 or BeO , —325 mesh.

Procedure: Dry hydrogen, flow 1250 cc./min., passed through pack for 6-30 hr. at 1800-2200° F.

B3. Pack composition: 49% of 60-40 Cr-Si (compound CrSi) prealloy, —325 mesh; 49% Al_2O_3 , MgO , ZrO_2 , or BeO , —325 mesh; 2% iodine. Procedure: Dry hydrogen, flow 1000 cc./min., passed through pack for 6-30 hr. at 1800-2200° F. (as an alternate, dry hydrogen or helium is blended with pure chlorine gas (99%), flow 1000 cc./min. and passed through pack).

A chromium zirconium binary surface alloy can be deposited as follows:

C. Cr-Zr.—Binary surface alloy—

C1. Pack composition: 50% of Cr granules (pure, *electrol.*), —10-20 mesh; 50% Al_2O_3 or sillimanite granules, —10-20 mesh.

Procedure: Dry hydrogen, flow 1000 cc./min., blended with a mixture of 4:1 of Cl and He , flow 750 cc./min.; passed through zirconium metal or zirconium hydride powder kept at 750° F. in closed container. (As an alternate, ZrCl_2 is first produced by passing the 4:1 Cl-He mixture over the Zr powder, then subliming the vaporized ZrCl_2 into a powder and then passing the hydrogen over it). The hydrogen-zirconium-chloride gas mixture is passed through the pack for 2 to 30 hours at 1560-2100° F.

C2. Pack composition: 40% of diffusion-sintered 50-50 ZrCr alloy powder pulverized, ground to —325 mesh; 10% NH_4Cl ; 50% Al_2O_3 , MgO , ZrO_2 or BeO , —325 mesh.

Procedure: Dry hydrogen, flow 1250 cc./min., passed through pack for 6 to 30 hrs. at 1800-2500° F.

As examples of a ternary surface alloy of chromium, aluminum and silicon, the following procedure may be used:

D. Cr-Al-Si.—Ternary surface alloy—

D1. Pack composition: 40% of 40-40-20 Cr-Si-Al pulverized fused prealloy, —10-20 mesh; 10% NH_4Cl ; 50% Al_2O_3 or sillimanite granules, —10-20 mesh.

Procedure: Dry hydrogen, flow 1000 cc./min. HCl , flow 70-100 cc./min., passed through pack for 4-30 hrs. at 1750-2300° F. in alternating current, 4 reversals per hour.

D2. Pack composition: 30% of 20-40-40 Cr-Si-Al pulverized fused prealloy, —325 mesh; 15% CrCl_2 crystals; 5% NH_4Cl ; 50% Al_2O_3 , MgO , ZrO_2 or BeO , —325 mesh.

Procedure: Dry hydrogen, flow 1250 cc./min., passed through pack for 6-30 hrs. at 1800-2500° F.

Another ternary surface alloy of chromium, aluminum and zirconium can be deposited as follows:

E. Cr-Al-Zr.—Ternary surface alloy—

E1. Pack composition: 40% of 50-50 Cr-Al pulverized fused prealloy —10-20 mesh; 10% NH_4Cl ; 50% Al_2O_3 or sillimanite granules, —10-20 mesh.

Procedure: Dry hydrogen, flow 1000 cc./min., blended with 4:1 Cl-He gas mixture, flow 750 cc./min. passed through zirconium metal or zirconium hydride powder kept at 750° F. in closed container, and then passed through the pack for 2 to 30 hours at 1650-2200° F.

E2. Pack composition: 30% of 50-50 Cr-Al pulverized fused prealloy, —325 mesh; 15% ZrCl_2 powder; 5% NH_4Cl ; 50% Al_2O_3 , MgO , ZrO_2 or BeO , —325 mesh.

Procedure:

I. ZrCl_2 produced by passing 4:1 Cl-He gas mixture, flow 500-1000 cc./min. over zirconium metal or hydride powder at 750° F., sublimation of the vaporized ZrCl_2 into a powder.

II. Dry hydrogen, flow 1000 cc./min., passed through the pack for 2 to 30 hours at 1800°-2500° F.

A quaternary surface alloy containing chromium, aluminum, silicon, and zirconium may be deposited according to the following methods:

F. Cr-Al-Si-Zr.—Quaternary surface alloy—

F1. Pack composition: 40% of 40-40-20 Cr-Si-Al pulverized fused prealloy, -10-20 mesh; 10% NH_4Cl ; 50% Al_2O_3 or sillimanite granules, -10-20 mesh.

Procedure: Dry hydrogen, flow 1000 cc./min., blended with 4:1 Cl-He gas mixture, flow 750 cc./min., passed through zirconium metal or zirconium hydride powder kept at 750° F. in closed container, and then passed through the pack for 2 to 30 hours at 1650-2000° F.

F2. Pack composition: 30% of 40-40-20 Cr-Si-Al pulverized fused prealloy, -325 mesh; 15% ZrCl_2 powder; 5% NH_4Cl ; 50% Al_2O_3 , MgO , ZrO_2 or BeO , -325 mesh.

Procedure:

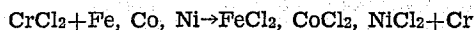
I. ZrCl_2 produced by passing 4:1 Cl-He gas mixture, flow 500-1000 cc./min. over zirconium metal or hydride powder at 750° F. sublimation of the vaporized ZrCl_2 into a powder.

II. Dry hydrogen, flow 1000 cc./min., passed through the pack for 2 to 30 hours at 1800-2500° F.

An illustration of the invention based on an X250 photomicrograph is seen in Figure 5 wherein the chromium deposited surface phase is indicated at 60 and the tungsten carbide body cemented with 20% of a binder of cobalt at 61. The intermediate phases are seen at 62 and 62A of cobalt and cobalt chromium alloy formed by diffusion. The cobalt chromium alloy contains eutectic indicated, for example, at 65, and the outer surface of the specimen is shown at 63. The cobalt chromium alloy also penetrates into the tungsten carbide base such as may be seen, for example, at 64. At least a portion of the cobalt and chromium form an eutectic in the intermediate phase and where penetration takes place into the tungsten carbide base.

A schematic representation is seen in Figure 6 wherein the refractory metal carbide grains are indicated at 70 and the cementing metal or alloy at 66. The intermediate phase of the same material as the binder is shown at 67 and the deposited surface metal or alloy is indicated at 68. In the process, an eutectic of the cobalt chromium metals will be formed and may travel or migrate into the surface layers such as indicated at 69. The eutectic also is indicated at 69A as penetrating into the cemented tungsten carbide base.

As previously mentioned, a salt bath chromizing or other depositing process might be used wherein the component is brought into contact with a stable halogen salt as a constituent of a molten bath such as CrCl_2 , the temperature in such an instance being maintained at about 2000° F.-2500° F. for several hours. In such a process, the free chromium would be made available at the previously deposited and integrally merged intermediate metal surface of the component through the exchange reaction:



Other metals such as silicon, zirconium, or aluminum, or alloys thereof with chromium, may be similarly deposited. It is also possible to deposit these other metals or alloys directly in the vapor form when the conditions bearing on the vapor pressure characteristics are correct for deposition.

A tungsten carbide powder with a powder size of from 1/2 to 7 micron can be mixed with 13% by weight cobalt of -325 mesh and the mixture hot pressed at approximately 2650° F. under a pressure of about 2 tons per square inch in a procedure involving alternating heating and pressing cycles as mentioned hitherto. The resulting body can be observed to possess a surface region enriched in the cobalt binder metal. In addition, an intermediate phase of nickel then can be electroplated thereon with a thickness of about .002-.005" thickness. The specimen then can be placed in an apparatus similar to that seen in Figure 4 of the drawings. The pack which can be used is an equi-volume mixture of 10-16 mesh electrolytic chromium modules and white glazed Alundum grains. The furnace then can have hydrogen chloride and hydrogen gas passed therethrough in the ratio of 8-10% for thirty hours, the furnace being maintained at between 1830° F. and 2010° F., the flow rate being 1000 cc./min.

Also, a tungsten carbide-cobalt body made in the same manner as that just described can be additionally plated with cobalt and then placed in a similar pack and subjected to a 6% HCl/H_2 gas flow for 30 hours at a flow rate of 1000 cc./min. and a temperature of 1830° F. to 2010° F.

Further, a titanium carbide powder with a size of 1/2 to 7 microns can be mixed with 20% cobalt and hot pressed at approximately 2900° F. under a pressure of 2 tons per sq. inch. The specimen then can be additionally nickel plated and placed in an impregnation pack similar to the tungsten carbide cobalt specimen just mentioned, the furnace being maintained at about 2100° F. for the chromizing process.

It is to be understood that composite bodies made in accordance with the present invention can be used for various purposes. The placement of the intermediate casing layer of the composite body and the surface case also can be performed in various manners. The term "metal" means a single metal or an alloy. Also, the precise mechanism of the deposition and bonding is not necessarily that of an atom exchange, but may be some other process, such as a thermal decomposition of the compound liberating metal ions followed by atomic migration, or may be some other phenomena. Details of carrying out the process and the apparatus involved can be varied from those shown without departing from the spirit of the invention, except as defined in the appended claims.

What is claimed is:

1. The method of producing composite bodies adapted to withstand corrosion at a high temperature comprising compacting said composite bodies from a refractory metal carbide powder selected from a group consisting of titanium carbide, molybdenum carbide, tungsten carbide and zirconium carbide powder, cementing the said bodies with a metal selected from a group consisting of iron, nickel and cobalt, applying to the surface of said cemented bodies an intermediate layer of the metals used for the cementing step, covering said intermediate metal layer with a surface coating of a substance selected from a group composed of chromium, zirconium, aluminum, silicon and their halides and thermally merging said intermediate and said surface layers into a bond therebetween and with said cemented body.

2. In a method according to claim 1, the step of using the same metal for the cementing of

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said composite bodies and for the formation of the intermediate layer.

3. In a method according to claim 1, the step of compacting the composite body from a titanium carbide powder, cementing the same with a metal selected from the group consisting of iron, cobalt, nickel, applying to the said cemented body an intermediate cobalt layer and covering the same with a surface layer of a substance selected from a group consisting of chromium, zirconium, aluminum and silicon.

4. In a method according to claim 1, the step of compacting the composite body from a titanium carbide powder, cementing the same with a metal selected from the group consisting of iron, cobalt, nickel, applying to the said cemented body an intermediate nickel layer and covering the same with a surface layer of a substance selected from a group consisting of chromium, zirconium, aluminum and silicon.

5. A composite body which is corrosion resistant at a high temperature consisting of a refractory metal powder selected from the group consisting of titanium carbide, molybdenum, carbide, tungsten carbide and zirconium carbide powders and being cemented by a metal selected from a group consisting of iron, nickel and cobalt, said body being coated with an intermediate layer

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of the metals used for the cementing step and being surface coated with a substance selected from a group composed of chromium, zirconium, aluminum and silicon, the said body being integrally united with the intermediate and the surface layer.

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