

Jan. 27, 1970

N. S. BORNSTEIN ET AL

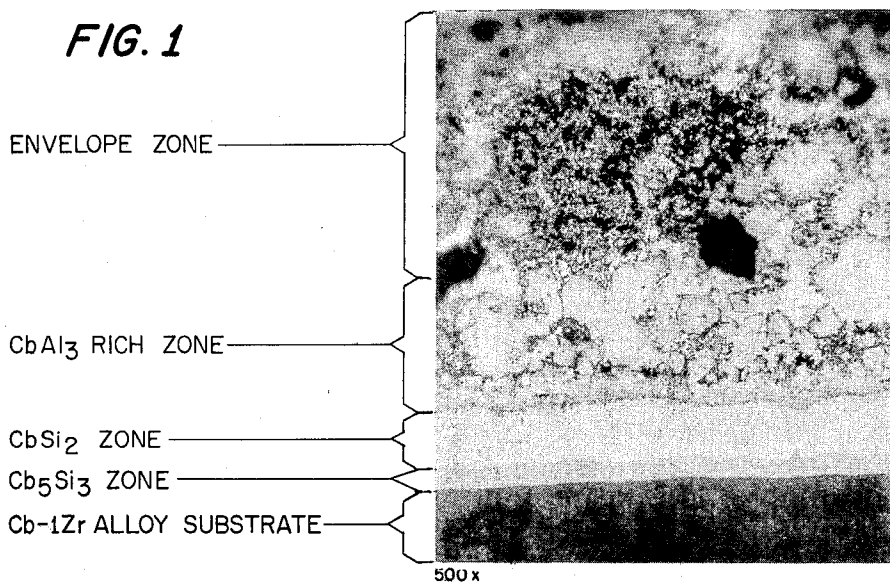
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REFRACTORY METAL ARTICLES PROTECTED FROM ATMOSPHERIC
CONTAMINATION AT ELEVATED TEMPERATURES
BY SURFACE COATINGS

Filed March 16, 1966

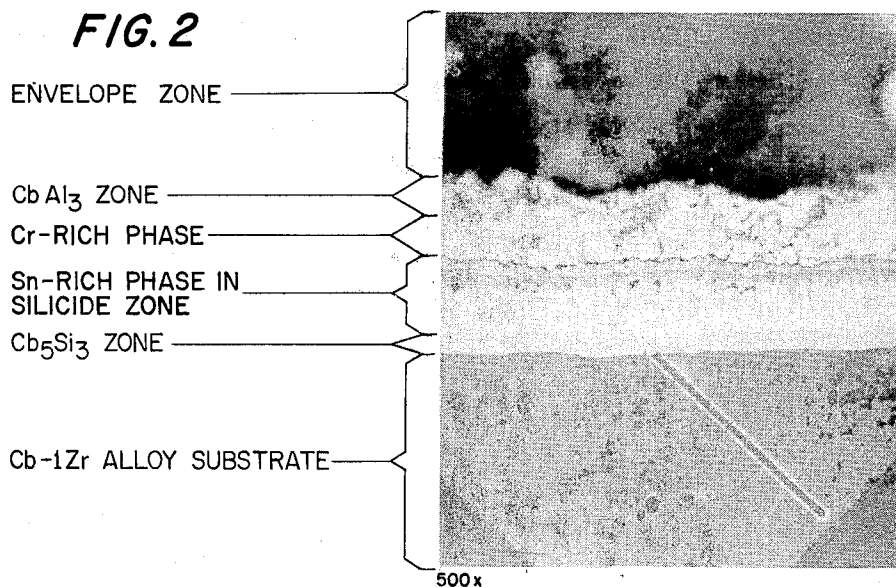
2 Sheets-Sheet 1

FIG. 1



PHOTOMICROGRAPH OF COATED Cb-1Zr ALLOY SUBSTRATE, IN AS HEATED CONDITION

FIG. 2



PHOTOMICROGRAPH OF COATED Cb-1Zr ALLOY SUBSTRATE AFTER EXPOSURE TO AIR AT 2000°F FOR 100 HOURS

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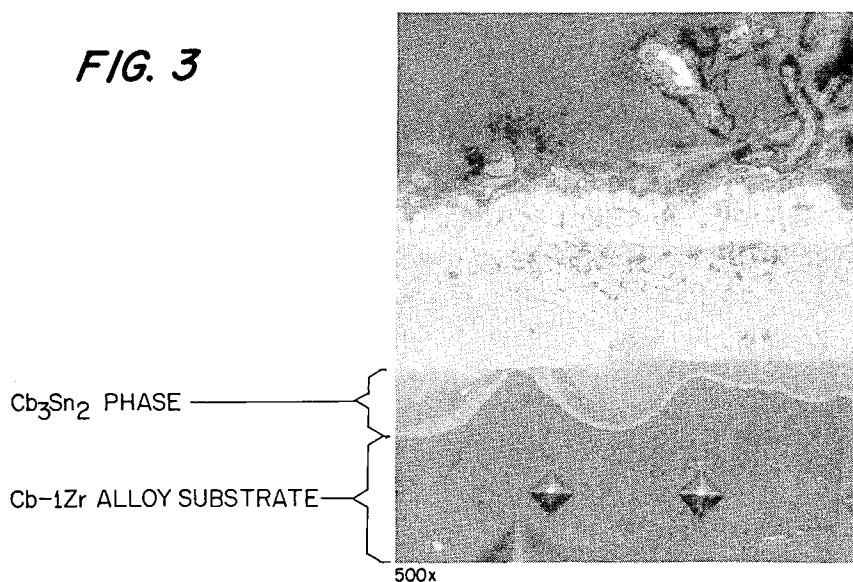
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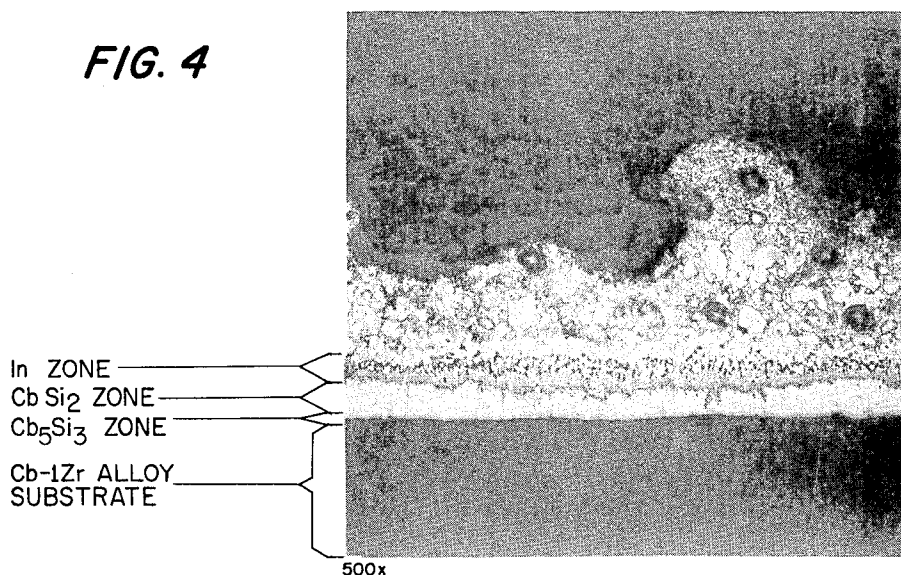
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FIG. 3



PHOTOMICROGRAPH OF COATED Cb-1Zr ALLOY SUBSTRATE AFTER
EXPOSURE TO AIR AT 2000°F FOR 900 HOURS

FIG. 4



PHOTOMICROGRAPH OF In-CONTAINING COATING ON Cb-1Zr ALLOY
SUBSTRATE, IN AS HEATED CONDITION

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REFRACTORY METAL ARTICLES PROTECTED FROM ATMOSPHERIC CONTAMINATION AT ELEVATED TEMPERATURES BY SURFACE COATINGS

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Filed Mar. 16, 1966, Ser. No. 541,472
Int. Cl. B23p 3/00, 3/10

U.S. Cl. 29—194

22 Claims

ABSTRACT OF THE DISCLOSURE

Corrosion resistant, refractory metal-base articles are provided having an interior coating zone adjacent the substrate comprising a silicide, boride, or beryllide of the refractory base metal of the substrate, and preferably also containing indium; and an exterior coating zone comprising Cb, Al, and Sn, with Cr, Ti, and a halide activator as optional ingredients. Preferably, the exterior coating zone contains a surface region comprising Sn, Cr, Al, and Ti, and a subsurface region comprising Cb, Al, and Sn, with Cr, Zn, Ti, and a halide activator as optional constituents. A typical example is a Cb-1Zr alloy sheet having a silicide interior coating zone, and an exterior coating zone having a subsurface region consisting essentially of 53% Sn, 24% Cb, 10% Al, 7% Ti, 3% Cr, 1.5% Zn, and 1.5% LiF, and a surface region consisting essentially of 45% Sn, 30% Cr, 16% Al, and 9% Ti.

This invention relates to coatings for the refractory metals and their alloys that will protect such metals from atmospheric contamination at high temperatures.

More particularly this invention relates to multi-zone coatings for the refractory metals that will protect such metals from atmospheric contamination for long periods of time in intermediate temperature environments, where mechanical and thermal stress requirements are moderate.

The coatings of this invention are designed to protect refractory metal substrates at temperatures of from about room temperature up to about 2000° F. Although these coatings are primarily designed for use in the protection of geometrically complex engineering structures and assemblies made from the refractory metals and their alloys, they are also particularly useful in coating laboratory test specimens of refractory metals.

This invention also relates to a process for creating the protective metal coatings of this invention on refractory metal substrates.

As used in this specification and claims, the term "refractory metals" refers to those non-precious refractory metals having a melting point equal to or higher than the melting point of chromium (Cr) or 3407° F. (1875° C). So defined, the "refractory metals" of this application in ascending order of their melting points are thus: chromium (Cr), vanadium (V), hafnium (Hf), columbium (Cb), molybdenum (Mo), tantalum (Ta), and tungsten (W). The term "refractory metals" as used herein also refers to alloys having refractory-metal bases, as well as to the refractory metals themselves. The invention in its most important aspects relates to protective coatings for Cb-base and Ta-base substrates.

Although silicon (Si) and boron (B) are borderline elements between metals and nonmetals and are sometimes termed "metalloids," for convenience of terminology and precise reference Si and B are referred to herein as "metals." Although Si and B, depending upon the functions they perform in the compounds they enter into, are capable of exhibiting both metallic and nonmetallic

properties, within the scope of this invention their properties more closely resemble those of metals than those of nonmetals. Thus, there is ample justification for referring to these elements as "metals" in this specification and the appended claims.

For many years it has been generally known that the high-temperature strength properties of metals are closely related to their melting points. In general, metals having high melting points thus are capable of forming alloys having high strength at high temperatures. In recent years, the need for new structural materials for service at temperatures in excess of those that can be withstood by conventional structural materials has stimulated interest in those metals having the highest melting points, or the refractory metals and their alloys.

As alloy base materials for high-temperature service, a number of these metals have shown much promise in various high-temperature applications. Perhaps one of the most versatile and promising of these metals is Cb and considerable work has been done to develop it as a structural alloy base for uses in high-temperature environments.

Among the technically more important physical qualities of Cb as an alloy base are its high melting temperature (4474° F.) and its low neutron-capture-cross-section. Further, Cb is inherently a soft, ductile, readily fabricable metal and, although it becomes too weak for practical structural uses at temperatures much above 1200° F., it is capable of being strengthened for use at much higher temperatures by alloying it with various other metals, particularly with other refractory metals. Disadvantageously, Cb is a highly reactive metal at elevated temperatures and will dissolve relatively large quantities of nitrogen and oxygen on exposure to atmospheres containing even small amounts of these elements at moderately elevated temperatures.

Because of the relative importance of Cb, much of the description that follows is based on the use of the coatings of this invention on Cb or Cb-alloy substrates. It will be understood, however, that the scope of the invention is not limited to coatings for Cb-base substrates, but includes coatings for the refractory metals generally. The coatings of this invention are also of primary importance in the coating of Ta or Ta-alloy substrates. To some extent, the nature of the substrate, particularly as governed by the primary or preponderant element present, determines the precise form of the coatings of this invention that is most effective for that particular substrate.

It is well known that no metal is completely resistant to surface contamination from exposure to air at elevated temperatures. Most metals that can be used at high temperatures without surface protection form a thin adherent protective oxide coating during initial exposure. This oxide coating insulates the base metal from further oxidation as long as it remains intact. The pure metals and alloys that exhibit this attribute of self-protection are, however, generally limited in their use to temperatures below about 1800° F.

The refractory metals and their alloys are about the only metals that retain sufficient strength at temperatures above about 1800° F. to make them useful at these temperatures. In recent years the refractory metals have been subjected to extensive study, investigation, and development. Various of the refractory metals that are in sufficiently abundant supply for possible commercial development have been evaluated for numerous high-temperature uses. Unfortunately, none of the refractory metals has sufficient resistance to oxidation or contamination in air at high temperatures to be used without protection.

The refractory metals do not form their own adherent and protective coatings within the temperature ranges

of primary interest for their uses. Many of the most promising of these metals, such as Cb, Ta, and Mo are subject to extremely rapid or even catastrophic oxidation if unprotected in air at temperatures above 1000° F. Such oxidation vitiates and destroys the high-temperature strength of these metals. Accordingly, many efforts have been directed toward forming effective coatings for the refractory metals which inhibit or prevent their oxidation and contamination at high temperatures.

In the past, most of these efforts have been directed to the production of coatings suitable for oxidation protection of the refractory metals at extreme temperatures and short exposure times, such as those which would be encountered by composite structures on atmospheric re-entry. Very little effort has been devoted to the production of protective coatings that will provide long-time protection for refractory metal substrates at intermediate temperature environments from room temperature up to about 2000° F., where mechanical and thermal stress requirements are only moderate. Coatings of this character are of particular utility in providing protection for test specimens being used for laboratory testing and development of refractory metal structures.

In the past, the absence of a protective coating suitable for long-time, intermediate temperature protection has required that such laboratory specimens be tested in inert cover gas test environments. The provision of such testing environments not only requires greatly increased testing expenditures, but also decreases the reliability of the specimens, and hence the value of the test results.

It is obvious that coatings which provide long-time, intermediate temperature protection also would be useful for many applications where refractory metal substrates are to be subjected to such conditions. An example of such a requirement would be in oxidation protective coatings for structural parts of advanced nuclear power plants.

The requirement that refractory metals be tested under an inert atmosphere, due to their oxidation-prone character, is discussed above. However, even when a controlled protective atmosphere is used, unacceptable contamination can result. In certain uses of the refractory metals, the presence of even very small amounts of oxygen in the base metal can have serious deleterious results, even though the strength of the metal member remains substantially unimpaired. This is particularly true when a structural member is used for containment of liquid metals. For example, Cb-alloys, because of their relative strength, availability, and fabricability are outstanding candidates as structural materials for liquid metal containment. Other refractory metals have also displayed favorable compatibility with alkali liquid metals, such as lithium (Li).

Pure Cb shows no susceptibility to solution attack by purified Li at temperatures up to 2200° F. However, when the oxygen in solution in Cb reaches a concentration of as little as a few hundred parts per million, Cb may be rendered sensitive to intergranular Li attack. Under these conditions Li will penetrate grain boundaries of Cb-base alloys and actually seep through the metal. The attack occurs at all temperatures above 1000° F. and is quite rapid, reaching completion in a few minutes.

While this susceptibility to Li attack in Cb may be reduced by alloying the Cb with zirconium (Zr) and heat treating, the Cb will remain susceptible to Li attack if oxygen atoms are present in amounts in excess of twice the Zr atoms present. Accordingly, when Cb or other refractory alloy substrates are desired to be used as structural materials for containment of liquid alkali metals, it is of the utmost importance that the refractory metals, and particularly Cb, be protected from oxidation at all stages of their manufacture. Thus, where these uses are contemplated, it is particularly important that the oxidation resistant coatings of this invention be used,

even though manufacture is to be carried out largely or completely under inert environments.

While combination tin (Sn)-aluminum (Al) coatings, and silicide coatings each have been used in the past to protect Cb, Cb-base alloys, and other refractory metals and their alloys from oxidation, both of these types of coatings have exhibited undesirable shortcomings. Thus, while the Sn-Al coatings have generally provided good oxidation protection for the coated refractory metal substrates at low to intermediate temperatures (1000–1200° F.), these coatings are relatively ineffective at high temperatures. Silicide coatings have been widely used to protect Cb and its alloys (and other refractory metals and their alloys) at high temperatures (2000° F. and higher). These coatings, however, have not provided effective “low” temperature oxidation protection, because of the occurrence known as the silicide “pest phenomenon,” and also because of their failure to provide consistent coating performance.

The silicide “pest phenomenon” may be defined as the characteristic of silicide coatings rendering them prone to consumption by rapid oxidation at low temperatures generally on the order of from about 1100° F. to 1800° F. depending on the particular alloy being coated.

Various other coatings have also previously been provided for Cb- and other refractory metal-base substrates. However, none of these coatings have provided satisfactory oxidation protection to the substrates for long periods of time at intermediate temperatures.

In view of the foregoing, it is a primary object of this invention to provide new and improved protective coatings for refractory metal substrates at intermediate temperatures, whereby such substrates can be subjected to exposure to air at elevated temperatures up to about 2000° F. for long periods of time without danger of oxidation or contamination.

It is a further object of this invention to provide new and improved coatings for refractory metal substrates. These coatings provide excellent protection against oxidation and contamination of such substrates during their subjection to intermediate temperatures, from about room temperature up to about 2000° F., for long periods of time. These coatings are of particular value for refractory metal substrates which are subjected to only moderate mechanical and thermal stresses.

It is another object of this invention to provide new and improved protective coatings for refractory metal substrates that combine the advantages of the high-temperature oxidation resistance provided by silicide coatings, with the advantages of the low-to-intermediate-temperature oxidation protection afforded by Sn-Al coatings.

Another object of this invention is to provide a suitable protective coating for refractory metal test samples, to protect such specimens from oxidation during long-time testing in other than inert atmospheres.

A further object of this invention is to provide new and improved multi-zone coatings for refractory metal substrates that will protect the substrates from oxidation for long periods of time at intermediate temperatures up to about 2000° F.

Another object of this invention is to provide a multi-zone coating for refractory metal substrates which comprises an outer coating zone containing Cb, Al, and Sn, and a refractory metal silicide, boride, or beryllide barrier inner coating zone, which is interposed between the substrate and the outer coating zone.

A further object of this invention is to provide a coating for refractory metal substrates that comprises in a preferred form an Al and Sn containing outer coating zone and a refractory metal silicide inner coating zone interposed between the refractory metal substrate and the outer coating zone, the silicide barrier zone containing indium (In) which exists in a liquid phase at the intermediate range temperatures to which the coated refrac-

tory metals of this invention are designed to be subjected.

A still further object of this invention is to provide improved coatings for refractory metal substrates that will protect the substrates from oxidation and contamination at intermediate temperatures for long periods of time, the coating having a self-healing Sn containing surface zone which prevents contamination or oxidation of the substrate by cracking of the coatings or the formation of defects in the coatings in other ways.

Yet another object of a preferred form of this invention is to provide improved coatings for refractory metal substrates that will protect them from contamination during long exposure to air at intermediate temperatures up to about 2000° F. with a coating having a self-healing metallic subsurface zone backed up by a self-healing metallic surface zone to prevent contamination or oxidation of substrates by cracking or other defects in the coatings.

Additional objects and advantages will be set forth in part in the description that follows, and in part will be obvious from the description, or may be learned by the practice of the invention, the objects and advantages being realized and attained by means of the compositions, particularly pointed out in the appended claims.

To achieve the foregoing objects and in accordance with its purpose, this invention includes as broadly described, a coated metal article having a substrate selected from the group consisting of the refractory metals and alloys thereof and a coating having:

(1) An exterior or surface zone comprising Cb, Al, and Sn; and

(2) An interior coating zone or diffusion barrier layer, interposed between the refractory metal substrate and the surface or exterior coating layer or zone of the coating, described above, comprising a silicide of the refractory metal of the substrate.

In addition to the Cb, Al, and Sn, the exterior coating zone of the coating can contain, as optional ingredients, chromium (Cr), titanium (Ti), and zinc (Zn).

This invention, in its broadest aspects, comprehends the substitution of B or Be for the Si in the interior coating zone or diffusion barrier zone of the coating, so that the barrier zone comprises a refractory metal boride or a refractory metal beryllide, rather than the refractory metal silicide which is used in the above described embodiment.

In a preferred embodiment of this invention the coating also contains In, which exists in a liquid phase at above about 312° F., and hence promotes self-healing of the coating of this invention at most temperatures to which the articles coated in accordance with this invention are subjected.

In accordance with the invention the outer or exterior coating zone consists essentially of from 48 to 58% by weight of Sn, from 20 to 28% by weight of Cb, from 8 to 12% by weight of Al, up to 10% by weight of Ti, up to 5% by weight of Cr, up to 1.5% by weight of Zn, and up to 2% by weight of an alkali metal halide or an alkaline earth metal halide. Preferably Ti is present in an amount of from 5 to 10% by weight of the exterior coating zone, Cr is present in an amount of from 1 to 5% by weight of the exterior coating zone, and the halide activator is present in an amount of from 1 to 2% by weight of the exterior coating zone.

In a preferred form of the invention an overcoating or envelope is applied to the exterior coating zone described above. This overcoating or third coating layer or zone comprises Sn, Al, Cr, and Ti, and when it is used, forms the outside surface region of the exterior zone of the coating. This surface region consists essentially of from 40 to 50% by weight of Sn, from 27 to 33% by weight of Cr, from 14 to 18% by weight of Al, and from 7 to 11% by weight of Ti. When this envelope or surface region is used, the exterior coating zone described above

becomes a subsurface region of the exterior coating zone.

It is highly desirable and greatly preferred to prepare the coatings of this invention in accordance with the last embodiment described above in which two Al-Sn containing layers or regions are applied to form the exterior coating zone on the substrate which has been previously modified with an interior coating zone containing Si, B, or Be.

This invention further embraces a process for protecting the surface of a refractory metal article from gaseous contamination during long-time exposure to intermediate temperatures up to 2000° F. Generally, this process comprises the steps of:

(1) Forming a refractory metal silicide, boride, or beryllide coating on the refractory metal substrate;

(2) Applying over the refractory metal silicide, or the like coating zone, a second coating zone of a coating composition consisting of essentially Sn, Al, Cb, and the halide activator, and as optional ingredients, Cr, Ti, and Zn; and

(3) Applying over the second coating composition, a third coating composition consisting essentially of Sn, Al, Cr, and Ti.

Following the application of each coating composition to the refractory metal-base article, the composite is fired to a pre-determined temperature to produce a uniform and adherent coating on the substrate which is substantially impervious to gaseous contaminants, such as oxygen, at the intermediate elevated temperatures to which the products of this invention are intended to be subjected.

Each of the coating zones of this invention is preferably applied to the substrate, or previously coated substrate, by a cold spray slurry process. In this process the coating composition is dispersed in a vaporizable diluent in an amount sufficient to give the composition a sprayable consistency and then sprayed onto the surface of the substrate. Generally, a binding or sticking agent is included in the suspension of the coating composition. The binding or sticking agent causes particles of the coating composition to adhere both to each other and to the substrate or the other coating composition previously applied to the substrate, as the case may be.

While, as pointed out above, a cold spray slurry process is the preferred method of applying all of the coating compositions of this invention, any other suitable methods can, of course, be used. Thus, the silicide first coating zone can also be produced by a pack-cementation, or a fluidized bed process, as will be apparent to those skilled in the art.

More particularly, the preferred method of applying the refractory metal silicide inner coating zone to the refractory metal substrate is by a transient liquid phase spray slurry process utilizing a mixture of magnesium (Mg) and Si, a mixture of calcium, (Ca) and Si, or a combination of Mg, Ca, and Si. Mg-Si mixtures are preferred and the silicide coating step will be described in terms of this preferred embodiment.

The Mg-Si mixture, containing from 37 to 55% by weight of Mg, and from 45 to 63% by weight of Si, is dispersed in a lacquer vehicle, and sprayed onto the refractory metal substrate. The aggregate amount of Mg and Si sprayed onto the surface is about 20 to 25 mg./cm.². The substrate with this coating in place is then fired for from 4 to 16 hours at a temperature of from 1850 to 2200° F. Most of the Mg is removed from the coating by evaporation during this heat treatment, leaving only the Si which forms an intermetallic composition with the substrate that is oxidation resistant and provides a refractory metal silicide contamination barrier. This adherent silicide zone is believed to consist of a Cb₅Si₃ inner region and a CbSi₂ outer region.

Of course, the lacquer used to disperse the Mg-Si mixture on the refractory metal substrate is also removed by evaporation prior to or during the heat treatment.

The removal of the Mg during the formation of the refractory metal silicide first coating zone, by heat treatment, is important because removal of Mg and other

volatile constituents allows the use of the coated article in environments where evaporation of such constituents could prove highly troublesome. For example, evaporation of such constituents from hot surfaces and condensation on cold surfaces could cause electrical short circuits, change emissivity characteristics of coated articles, destroy bearing surfaces, or the like.

When a Mg-Si mixture is used for producing the first coating zone of this invention (i.e., the refractory metal silicide zone) the optimum composition of the coating, exclusive of the lacquer carrier, is about 42% by weight of Mg and about 58% by weight of Si. Heat treatment of this coating after it has been applied to the refractory metal substrate is preferably at about 2200° F. for about 16 hours.

Under certain circumstances, Ca, Li, or barium can be substituted for the Mg used in the above described process for producing the silicide first coating zone of this invention. Where Ca is used, care must be exercised to avoid a reaction between the Ca and any water vapor which may be present. If such a reaction occurs, there may be a subsequent reaction with the lacquer vehicle to form a gel.

If B or Be is substituted for Si in the first coating composition of this invention, a boride or beryllide first coating zone is produced in the same manner as described above for the silicide coating zone. Coatings thus produced would have the composition MB_2 , or MBe_{13} and M_2Be_{17} , where M represents the refractory metal base of the substrate. A silicide first coating zone is generally preferred to a boride or beryllide zone.

The silicide coating zone should be from about 0.5 to 2 mils in thickness. A thickness of at least about 0.5 mil is necessary to ensure that the silicide zone provides effective oxidation and contamination resistance, and effectively functions as a diffusion barrier between the substrate and the second and third coating zones. If, however, the silicide coating zone has a thickness greater than about 2 mils, spalling is likely to result, with the resulting formation of "rabbit ears." "Rabbit ears" occur when a coating extends over an edge or corner of a substrate and peels off and elongates, resulting in a formation that resembles "rabbit ears."

There is no critical limit on the amount of Si, B, or Be applied to the substrate in the first coating composition, so long as it is in an amount sufficient to form an intermediate refractory metal silicide, boride, or beryllide coating zone of the desired thickness, but is not present in such large quantities as to produce a first coating zone of so great a thickness that spalling is likely to ensue.

The Al and Cb in the second coating composition of this invention react to form an oxidation resistant columbium aluminide intermetallic composition ($CbAl_3$). The first coating zone, formed of refractory metal silicides, inhibits the formation of refractory metal aluminides by the interaction of the Cb or other refractory metal of the substrate with the Al applied in the second coating composition. Therefore, it is necessary that the second coating composition itself contain sufficient Cb for the formation of oxidation resistant Cb-trialuminide. This purpose requires that from 20 to 28% Cb be present in the second coating composition.

The Al in the second coating composition forms the intermetallic columbium aluminide composition ($CbAl_3$) with the Cb present in that composition to provide the primary oxidation and contamination barrier afforded by the second coating zone for protection of the refractory metal substrate. This Cb-trialuminide ($CbAl_3$) provides important oxidation resistance at intermediate temperatures up to about 1800° F. Al is present in the second coating in amounts of from 8 to 12% by weight to fulfill this important function.

Sn is also a primary component of the second coating composition, and it performs a variety of functions in the coating. Al has a limited solubility in Sn, and since Sn

liquefies at a relatively low temperature, it is believed to perform the useful function in the second coating composition of carrying amounts of dissolved Al throughout the coating to bring such Al into contact with unreacted or partially reacted Cb to form the oxidation resistant Cb-trialuminide component of the coating.

This function of the Sn in the coating is believed to be important both in the initial formation of the Cb-trialuminide and in service when diffusion of Cb from the substrate through the silicide barrier layer, after the coating has been subjected to oxidation to the extent that such diffusion begins to occur, might result in formation of subaluminides which do not have the oxidation resistant capacity of the desired Cb-trialuminide ($CbAl_3$). The Sn is believed to transport Al throughout the coating to provide Al for reaction during service with excess Cb which may, under these conditions, diffuse into the second coating zone through the silicide barrier.

The Sn thus gives the coating self-healing properties, since its diffusion in a liquid phase with dissolved Al throughout the coating provides Al for the production of new Cb-trialuminides at any sites in the coating where oxidation resistance may have been reduced by formation of subaluminides less oxidation resistant than $CbAl_3$.

To fulfill these varied and important functions, Sn is present in the second coating composition in amounts, by weight, of from 48 to 58%.

The minor amounts of Ti and Cr which are optionally present in the second coating zone produce greatly improved coating performance. The presence of Ti and Cr in the coatings effectively ameliorates to some extent the "low" temperature aluminide pest phenomenon characteristics which are usually exhibited by Cb-trialuminide coatings (powdering at temperature of about 1300° F.). For these reasons second coating compositions containing Ti and Cr are greatly preferred.

Although applicants do not wish to be bound by any particular theory as to the reasons for the improvement resulting from the addition of Ti and Cr to the coatings, it is believed that Ti replaces some Cb atoms and that Cr replaces some Al atoms in the Cb-trialuminide lattice structure. These substitutions substantially improve coating performance over that normally obtained with unmodified Cb-trialuminide coatings. Additionally, it is believed that Ti and Cr are both soluble to some extent in Cb-trialuminides. The final coating also probably contains minor amounts of Ti-aluminides and Cr-aluminides, since both Ti and Cr form refractory aluminides. For one or more of these reasons, significant improvements in coating performance result from the inclusion of minor amounts of Ti and Cr in the second coating zone.

Both Ti and Cr also have some solubility in liquid Sn, and thus the liquid Sn acts to supply flaws in the coating with the reactive metals used—Al, Ti, and Cr. Until these reactive materials are entirely oxidized or consumed by reaction with the substrate or with oxygen, this self-healing mechanism of the coatings of this invention continues.

The self-healing properties of the coating imparted by liquid Sn (containing dissolved Al, Ti, and Cr) can be used to correct defects such as cracks which may be present in the coating after its initial formation. If such cracks or other defects are present, initial thermal cycling of the coating in use will generally effect healing of these defects, through the self-healing properties imparted by liquid Sn.

Sn in liquid phase is believed to transport Al through the coating by convection and gross carrying as well as through solution of Al in Sn. Because the liquid phase Sn carries Al and other particles to desired reaction sites, it promotes formation of a uniform coating within a minimum exposure time, and at the minimum temperature needed for reaction. Minimum exposure time is made possible because presence of liquid Sn obviates the need of waiting for the intermetallic compounds of

the coating to form by interdiffusion of solids (i.e., Cb, Al, and the like). The use of minimum temperatures is possible because Sn moves Al through the coating rapidly and it is not necessary to heat the coating to the melting point of Al, but only to that of Sn.

Another component of the second coating composition is an activating agent comprising an alkali metal halide or alkaline earth metal halide. The halide activating agent serves to flux the metal powders used in the production of the second coating, particularly the Al, and promotes coalescence, wetting, fusion, and reaction of the metal powders to create the desired intermetallic composition.

The activating halide also serves to reduce oxide films on the metal powder particles, particularly on Al as the coated substrate is heated up, thereby promoting the desired intermetallic reaction.

The remaining optional metal component of the second coating composition, namely, Zn—like Ti and Cr, discussed above—is believed to achieve various functions that improve coating performance, such as increasing long-term oxidation resistance, promoting self-healing properties, and deoxidizing.

After the second coating composition has been applied to the substrate, preferably by a cold spray slurry process, it is heat treated at from 1900 to 2000° F. for from 1 to 16 hours, and preferably for from 1.5 to 4 hours. This heat treatment produces an adherent second coating zone formed from the second coating composition on the previously silicide-modified substrate. The second coating composition is preferably applied to the article being coated in an amount of about 30 to 35 mg./cm.² of surface area, although this amount is not critical.

Following this heat treatment, the third coating composition comprising Sn, Cr, Al, and Ti is preferably applied to the composition. The Sn and Al in this third coating composition provide excess amounts of these elements in the coating which modify the Cb-aluminides formed in the second coating layer.

The Ti and Cr in the third coating composition also modify the Cb-aluminides of the second coating zone, and provide improved coating performance, for the reasons discussed above.

It will be noted that substantially greater amounts of Cr are incorporated in the third coating composition, when it is used, than may be optionally present in the second coating composition. The incorporation of these greater amounts of Cr in the third coating step is possible because Cb is not present in the third coating composition. If such large amounts of Cr are added in the second coating step, it is believed a competing reaction occurs between Cr and Cb in the second coating for production of Cr-aluminides rather than the desired Cb-aluminides. For this reason, much lesser amounts of Cr are used in the second coating step.

The third coating composition is also applied by a cold spray slurry process in the form of a dispersion in a suitable vaporizable lacquer. After this coating composition is applied to the composite, which comprises the refractory metal substrate having the silicide first coating zone, and the Sn- and Cb-aluminide second coating zone, the composite is again heat treated at from 1900 to 2000° F. for from 1 to 16 hours, and preferably from 1.5 to 4 hours, to produce an adherent third coating zone on the composite.

The third coating composition is preferably adhered to the composite in an amount of about 25 to 30 mg./cm.² of surface area, although this amount is not critical. The resulting product is coated refractory metal article having excellent resistance to oxidation and contamination at intermediate temperature ranges up to about 2000° F. for long periods of time.

Both the Cb- or other refractory metal-silicide of the first coating zone, and the Cb-trialuminide of the second

coating zone are oxidation resistant in themselves. The trialuminide outer coating is particularly effective at temperatures of about 1000 to 1800° F. while the inner silicide (or boride or beryllide) coating zone provides more effective oxidation resistance at higher temperatures. The oxidation resistance of this inner silicide coating zone is particularly important in the event of localized failure in the Cb-aluminide overcoat.

Conversely, the Sn and Al second coating zone effectively fills voids which are normally present or occur in the Cb-silicide first coating zone. Thus, the coating provides the good properties of both an Sn-Al coating and a silicide coating, and minimizes the bad characteristics of each of these types of coating.

The intermediate silicide coating zone prevents degradation of the mechanical and strength properties of the substrate by shielding the refractory metal substrate from Ti present in the second coating. However, this is not a great problem in the coatings of this invention, because the amounts of Ti present in the second (or second and third) coating zone are so small that the Ti is normally chemically tied in the coating, as an intermetallic compound or the like, and is not likely to migrate or diffuse into the substrate in an amount sufficient to cause any significant problems of degradation.

The final coating achieved on the Cb or other refractory metal-base substrate with the composition described above is a multi-zone coating having essentially the following compositions from the substrate to the outer surface:

Refractory metal substrate

Cb₅Si₃

CbSi₂

CbAl₃

Sn-Al envelope zone.

The structure of the coatings of this invention is clearly shown by the photomicrographs FIGS. 1 through 3, which illustrate a Cb-1Zr alloy coated in accordance with this invention and exposed in air at about 2000° F. for times up to 900 hours.

FIG. 1 is a photomicrograph enlarged 500 times and shows the coated substrate in the "as heated" condition, with a silicide zone immediately adjacent to the Cb-1Zr alloy matrix. The Cb-aluminide zone and the envelope zone are respectively superimposed on the Cb-silicide first coating zone.

FIG. 2 is a photomicrograph enlarged 500 times and shows the same alloy after exposure to air for about 100 hours at 2000° F. FIG. 2 reveals that oxidation for this period produced interaction and redistribution of the aluminide and envelope zones and produced secondary phases in the CbSi₂ layer. It also evidences the formation of a Cr-rich phase and the formation of a Sn-rich phase in the silicide zone.

X-ray distribution density photomicrographs showed that Cr had diffused from the envelope zone into the aluminide zone, where it altered the Cb-aluminide phase and formed new compounds at the silicide-aluminide interface. This shows up in FIG. 2 as the Cr-rich phase.

After the 100 hours of exposure, it was impossible to confirm that the CbSi₂ phase was still present. This was not unexpected, however, since it was established that Al, Cr, and Sn had diffused into this phase, and these modifiers presumably changed the structure of the phase. The major oxide phase present on the surface was identified as Al₂O₃. Secondary oxide phases were also present but could not be identified.

FIG. 3 is a photomicrograph enlarged 500 times and shows the coating of this invention on the Cb-1Zr alloy substrate after exposure in static air for about 900 hours at 2000° F. After this length of time, phases rich in Sn, Cr, and Al had penetrated the Cb₅Si₃ protective silicide layer and entered the Cb-1Zr alloy substrate. Diffractograms and X-ray density photomicrographs indicated

that the major phase shown in FIG. 4 immediately beneath the Cb_5Si_3 alloy interface was probably Cb_3Sn_2 , modified by Al, Ti, and Cr. Secondary phases were also present, but could not be identified.

The above photographs and discussion and other available data clearly illustrate the mode of ultimate failure of the coatings of this invention when applied to a Cb-base substrate. This failure is believed to take place through the following steps:

(1) The Al present in the Sn matrix and the intermetallic compound CbAl_3 reacts with the environment to form the protective oxide corundum, Al_2O_3 . Secondary oxides TiO_2 and SnO_2 are formed during prolonged exposures.

(2) Cr and Ti diffuse from the third coating zone or envelope into the aluminide and silicide zones and form intermetallic compounds. Concurrent Sn diffusion may provide a liquid metal path for more rapid transport of the coating element constituents.

(3) After about 600 hours of exposure at 2000°F ., Sn penetrates the Cb_5Si_3 layer and forms a compound with Cb having the apparent structure— Cb_3Sn_2 .

(4) Oxygen diffuses through the liquid Sn path from the surface of the specimen to the base metal of the substrate resulting in the formation of CbO and CbO_2 , or other refractory metal oxides, depending on the refractory metal which forms the base of the substrate.

(5) Continued increase in oxygen content results in the formation of the voluminous Cb_2O_3 oxide which ruptures the coating and allows catastrophic oxidation of the base metal to occur.

The breakdown in protection afforded by the multi-zone coatings of this invention is thus ultimately brought about through penetration of the silicide barrier zone by Sn.

Each of the coating zones of this invention is preferably applied by a cold spray slurry process. This process is readily adaptable to scaling up from use on laboratory specimens to use on dimensionally large configurations without any sacrifice in coating performance. It is also amenable to application of coatings or repairs of coatings in the field. This coating procedure is further desirable in that it does not require excessively high temperatures and hence does not produce or contribute to thermal damage or interstitial contamination of the refractory metal substrate.

Moreover, the cold slurry spray process is useful in that it can produce multi-component composites of various combinations of a wide variety of elements and compounds. It also achieves a uniformity in both thickness and composition of coating from place to place on the work piece surface. All that is required for the cold spray slurry process to be effective is a clean surface, spray coating or brushing of the slurry onto the area to be coated with blending into any already coated surfaces, and inert-atmosphere heat treatment. The latter may be accomplished using portable apparatus which have been developed for annealing field welds.

Before coating, the surfaces of the substrate should be thoroughly cleaned of dust, dirt, or other foreign substances. This may be accomplished by water rinsing, liquid blasting, washing in suitable organic or inorganic solvents, or immersion in alkali cleaners or acid pickles. Care should be taken in cleaning the substrate to ensure removal of all foreign matter.

After the surface has been cleaned, a metal powder mixture of the first coating composition is dispersed in a suitable liquid diluent, and the resulting dispersion is applied to the substrate by spraying, brushing, dip-coating, or any other effective method. As pointed out above, spraying is generally preferred.

The diluent used in the preparation of the dispersion can be any compatible diluent. Any of the well-known diluents employed with resins and polymers in the paint industry may be used. Preferably, a readily volatilizable

organic solvent or mixture of solvents is used. Examples of solvents that may be used are lower aliphatic alcohols, lower aliphatic ketones, lower alkyl esters of lower aliphatic acids, and lower hydrocarbons such as benzene and lower alkyl substituted benzene. Non-limiting examples of such diluents are methyl, ethyl, propyl and butyl alcohols; acetone, methyl ethyl ketone, diethyl ketone, and octyl hexyl ketone; methyl acetate, butyl acetate, octyl acetate, methyl propionate, octyl hexanoate; benzene, toluene, xylene, ethyl benzene; and the like.

The organic solvents mentioned are illustrative only and are not to be considered limiting. The main requirement of the volatile liquid substance or diluent is that it be reasonably safe to use, inexpensive, and sufficiently liquid at ordinary temperatures to act as a dispersant for the metallic powders so that the dispersant can be sprayed or suitably coated on the specimen, and at the same time be sufficiently volatile to evaporate when exposed to atmospheric or other conditions as will be described below.

If desired, a binding or sticking agent can be added to the liquid diluent to hold the powder mixture to the surface of the substrate after evaporation of the solvent. Use of a binder enables the powders to adhere to the substrate for prolonged periods of time, thereby precluding the necessity of heat treating immediately after application of powder or of taking special precautions in handling the treated substrate to avoid loss of powders.

The binder should be one that will substantially completely decompose during heat treatment and that will preferably decompose at a temperature below the melting point of the lowest melting metal or combination of metals used. Suitable binders or sticking agents that may be mentioned include nitrocellulose, naphthalene, and stearates. Other sticking or binding agents will be readily apparent to those skilled in the art.

Suitable wetting agents may also be added to the diluent if required. Moreover, low boiling organic compounds in small amounts can be added to the diluent to enhance its rapid evaporation.

In accordance with the invention, a dispersion of metal powders, such as, for example, Mg and Si in a liquid diluent, or preferably in a lacquer—a diluent containing a binder or sticking agent—is deposited on the surface of a substrate to be coated in the manner already described. After application the solvent is allowed to evaporate and a mixture of metal powders is left on the substrate. If a sticking agent is added to the diluent, upon evaporation of the solvent the sticking agent will remain dispersed throughout the powder mixture in the coating, and will serve to hold the powder or dust on the substrate before heat treatment begins.

Evaporation of the volatile solvent, or a volatile portion of the lacquer, containing a sticking agent, may be conveniently brought about by allowing the coated substrate to be stored in an atmospheric environment at room temperature. If desired, suction or vacuum and elevated temperatures may be used to accelerate evaporation of the volatile solvent. Evaporation of the solvent leaves a fine layer of metallic powder mixture, such as Mg and Si, on the surface of the substrate to be heat treated.

The ratio of metallic powders to liquid diluent may vary from about 1:1 to 1:10, or higher, with the amount of diluent being adjusted to suit the particular method of application. A ratio of powder to diluent of 1:1 is satisfactory when it is desired to use a spatula to spread the coating on the surface to be protected. For spray application, however, the coating composition will be of proper consistency when the ratio of powders to diluent is about 1:10. Still larger amounts of diluent may be used if desired; however, amounts of diluent in excess of a powder to diluent ratio of about 1:10 are of no particular advantage and increase the amount of diluent that must be evaporated from the coating.

The metallic powders may be mixed in the diluent or

lacquer by any of the arts well known in the paint industry, or simply by using a Waring Blendor or a ball mill.

A preferred lacquer or diluent with binding or sticking agent for use with the coating compositions of this invention is nitrocellulose lacquer or nitrocellulose dissolved in an organic solvent such as amyl acetate.

After the solvent has been allowed to evaporate from the surface of the substrate, the resulting specimen is ready for heat treatment in a suitable furnace or oven, to complete the formation of the Cb silicide first coating zone.

It has been unexpectedly found that an In-Si mixture can be advantageously used to produce the first coating zone of this invention. Normally during heat treatment of the first coating composition, following its application to the refractory metal substrate, the Mg, Ca, or like metal is removed from the substrate by evaporation. However, when In is used in the production of the first coating zone, it is not removed during this heat treatment and remains as a component of the first coating zone.

It has been found that when the first coating zone is produced using an In-Si mixture the reliability of the resulting coating is markedly improved. Thus, the mean lifetime of the coatings produced in accordance with this invention using Mg and Si in the production of the Cb-silicide first coating zone was 820 hours at 2000° F. When an In-Si mixture was substituted for the Mg-Si mixture, coatings were produced which had a mean lifetime of 1460 hours at 2000° F.

This improved result is believed to be due to the presence of In in a liquid phase during subjugation of the coating to oxidation at elevated temperatures. This liquid phase In promotes self-healing in the coating. The marked coating improvement resulting from the use of In is also believed to be attributable in part to In's retarding effect on reactions within the coating. In thus serves to retard Sn penetration to the substrate which, as discussed above, is the normal mode of ultimate failure of the coatings of this invention.

The mechanics of application of the In-Si mixture to the refractory alloy substrate are the same as those used in producing the refractory metal silicide first coating zone by the application of a Mg-Si mixture to the substrate. Of course, a greater amount by weight of the In-Si mixture must be applied to the substrate to produce a first coating zone of the desired thickness (0.5 to 2 mils) because of the much greater atomic weight of In compared to Mg. For this reason, about 40 to 50 mg./cm.² of surface area of the In-Si mixture is applied to the refractory metal substrate.

Heat treatment of the In-Si first coating zone is preferably carried out at about 1950° F. for 16 hours; however, the general limits on heat treatment times and temperatures are the same as those used for the Mg-Si first coating compositions.

The relative amounts of In and Si present in the first coating composition are considerably different than the relative amounts of Mg and Si when Mg is used in the first coating composition. With the In-Si system, the first coating composition will consist essentially of from 90 to 97% In and from 3 to 10% Si. In a preferred embodiment, the first coating composition consists essentially of about 95% In and about 5% Si.

The relatively greater proportion of In to Si in the preferred first coating composition of this invention, when compared to the proportion of Mg to Si, is not completely explained by the greater molecular weight of In. It is known that the proportion of Mg to Si in the first coating compositions using these elements are based substantially on proportions of Mg to Si within $\pm 10\%$ by weight of a eutectic point in the Mg-Si binary system. It is believed that the proportions of In to Si which are useful in preparation of the preferred first coating composition of this invention are probably also based on a eutectic relationship. Not enough is yet known about the In-Si

equilibrium diagram to reach a positive conclusion on this point. It is known, however, that the proportions of In to Si set forth above are necessary to the production of the desired first coating composition of this invention.

As in the other embodiments of this invention, B or Be can be substituted for Si in the first coating composition when that composition also contains In.

FIG. 4 is a photomicrograph enlarged 500 times, and shows a coating prepared in accordance with this invention in which the first coating composition consisted essentially of 95% by weight of In and 5% by weight of Si. This coating was quite similar to that formed by using the Mg-Si first coating composition as illustrated in FIG. 1. The region of this first coating zone directly adjacent the base metal was Cb_5Si_3 ; the next region was CbSi_2 , but, in addition, in the coating illustrated in FIG. 5 there was a third region on the substrate surface which was identified as In.

The second and third coating compositions of this invention are applied in the same manner, as described above, regardless of whether an In-Si or a Mg-Si mixture is used as the first coating composition.

The foregoing description of the various suitable diluents and methods of application for the first coating composition also apply to the preparation and application of the second and the third coating compositions. In other words, diluents suitable for use with the first coating compositions are also suitable for use with the second and third coating compositions, and the methods of application suitable for use with the first coating composition are also suitable for use with the second and third coating compositions.

The metal powders used in the coating compositions of this invention preferably have a size range that will permit them to pass through a 200 mesh screen, although coarser particles up to a size that will pass through a 100 mesh screen may also be used. Especially good results are obtained when the size range of metal powders is reduced to a size that will pass through a 325 mesh screen (43 microns), or between about 0 to 43 microns, and preferably between about 0 to 10 microns. As a general rule, it can be said that the finer the particles, the better will be the final coating produced. The mesh sizes referred to above are Tyler standard.

The use of a fine mesh metal powder helps to keep the powders in suspension and in a slurry and hence is desirable. The larger the particles are, the more differences in specific gravity of the powders produce tendencies to separation and make dispersion of the powders in liquid carriers more difficult. Further, as the particle size decreases, the surface area per unit weight increases and reaction is thus promoted by having powders of small particle size.

It should be noted, however, that the above advantages of fine particle size must be balanced against the increase in oxygen content of the coating that can result from the use of small particles having a larger total oxidized surface area.

The metal and halide activator dust or powders can be applied to the refractory metal substrates in any suitable manner. As pointed out above, the application of these powders in the form of a dispersion in a diluent is preferred. However, a fine film of the powders may be blasted or dusted onto the substrate, or any other suitable means can be used.

A preferred halide activator for use with the second coating composition is LiF. LiF is soluble in many of the organic solvents mentioned above, and when it is used as the activator, an organic solvent is selected in which it will readily dissolve. Similarly, when other halides of alkali metals and alkaline earth metals are used as activators, the particular halide used should be soluble in the particular organic solvent selected for use as the diluent.

For a clearer understanding of the invention specific examples of it are set forth below. These examples are

merely illustrative and are not to be understood as limiting the scope and underlying principles of the invention in any way.

EXAMPLE 1

The specimen blanks used in this and many of the following examples were cut from a Cb-1Zr alloy sheet to a nominal size of 0.625 inch x 0.625 inch x 0.030 inch, and a 0.125 inch diameter hole was punched at one end of each sample to facilitate handling. The blanks were tumbled in a ball mill using porcelain balls and alumina grit, for 100 hours to relieve the edges of the specimens. The blanks were then etched for 5 minutes in an acid solution consisting of 10% HF, 28% HNO₃, and 62% H₂O to remove surface contamination and were subsequently vacuum heat treated to stress relieve the blanks. A typical heat treatment for the Cb-1Zr alloy specimens was 2 hours at 981° C.

Immediately prior to application of the coating, the specimen blanks were degreased in trichloroethylene vapor, immersed for 5 minutes in a heavy-duty alkali cleaning solution at 65° C., rinsed in water, etched for 3 additional minutes in the above described acid etching solution at room temperature, rinsed again in tap water, and then in deionized water, dried and placed on spraying racks.

The first coating composition was prepared by mixing high purity metallic powders in the following proportions:

42% by weight of Mg powder (−325 mesh; 99+% purity),
58% by weight of Si powder (−325 mesh; 99.6+% purity).

This metal powder mixture was suspended in nitrocellulose lacquer (nitrocellulose dissolved in amyl acetate) by mixing in a Waring Blendor. to provide a quantity of first coating composition suitable for spraying, approximately 50 grams of dry powder per 40 cc. of lacquer were mixed together. This provided a proper consistency for spraying. After mixing, the first coating composition was applied to the refractory alloy blank by spraying at a rate of 23 mg. of coating composition per cm.² of substrate surface. The coating thus applied had a sprayed-on thickness of about 3 mils. This first coating composition was then permitted to dry in air for 1 hour at about 70° F.

At the end of this time substantially all of the organic solvent had evaporated from the nitrocellulose lacquer leaving a coating composition on the specimen blank of metal powders and nitrocellulose as a binder sticking agent.

The specimens were then suspended by means of hooks made from stranded tungsten wire, the hooks attached to a boat, and the boat and samples placed in the cold zone of an argon atmosphere furnace. After a 1 hour purge, the specimens were moved to the hot zone of the furnace, and heated for 16 hours at 2200° F. After this heat treatment, the samples were withdrawn to the cold zone of the furnace and allowed to cool to room temperature before being removed from the furnace.

The thin, friable Mg silicide scale was then removed by wire brushing, and the specimens were weighed and then coated with the second coating composition. This second coating composition was prepared by mixing the following metal powders in the proportions indicated:

53% by weight of Sn powder (−325 mesh; 99.9+% purity),
24% by weight of Cb powder (−325 mesh),
10% by weight of Al powder (pigment grade Al paste or finer),
7% by weight of Ti powder (−325 mesh; 99+% purity),

3% by weight of Cr powder (−325 mesh; 99+% purity),
1.5% by weight of Zn powder (−325 mesh; 97+% purity), and
1.5% by weight of LiF powder (finest powder available; 99.9+% purity).

This metal powder mixture was also suspended in a nitrocellulose lacquer (as described above) by mixing in a Waring Blendor. To provide a quantity of second coating composition suitable for spraying, approximately 50 grams of dry powder per 40 cc. of lacquer were mixed together. After mixing, the coating was applied to the specimen blanks by spraying at a rate of about 33 mg./cm.² of surface area. The second coating composition thus applied had a spray-on thickness of about 3 mils. This coating composition was then permitted to dry in air for 1 hour at about 70° F.

At the end of this time substantially all of the organic solvent had evaporated from the nitrocellulose lacquer leaving a coating composition on the specimen blanks of metal powders, LiF and nitrocellulose as a binder sticking agent. The LiF powder in the coating composition dissolved in the nitrocellulose lacquer when the powder was mixed with the lacquer to form the composition. When the solvent evaporated the LiF precipitated out and remained substantially evenly distributed throughout the coating composition.

The specimen was then subjected to heating in an argon atmosphere furnace, in the same manner as the heat treatment used following application of the first coating composition, except that the second coating was heated for a period of 2 hours at 1950° F. in the furnace. Following this heat treatment, the specimens were ultrasonically cleaned to remove any powder deposit remaining on their surfaces, and the third coating composition was applied.

This third coating composition was prepared by mixing high purity metallic powders in the following proportions:

45% by weight of Sn powder (−325 mesh; 99.9+% purity),
30% by weight of Cr powder (−325 mesh; 99+% purity),
16% by weight of Al powder (pigment grade Al paste),
9% by weight of Ti powder (−325 mesh; 99+% purity).

This metal powder mixture was also suspended in a nitrocellulose lacquer of the type described above by mixing in a Waring Blendor. To provide a quantity of this third coating composition suitable for spraying, approximately 50 grams of dry powder per 40 cc. of lacquer were mixed together. After mixing, the coating was applied to the specimen blanks by spraying at the rate of 25 mg./cm.² of specimen surface. The third coating composition thus applied had a sprayed-on thickness of about 3 mils.

This third coating composition was then permitted to dry in air for 1 hour at about 70° F. This resulted in evaporation of substantially all of the organic solvent from the coating. The composite was then heat treated in an argon atmosphere furnace, in the manner described above, for a period of 2 hours at 1950° F. After this heat treatment the specimen blanks were tested to determine their resistance to oxidation at elevated temperatures.

Coated specimens produced in the above manner (on Cb-1Zr alloy substrates) were endurance tested to determine their air exposure lifetime at 650° C. (1200° F.) and 1100° C. (2000° F.). The endurance test specimens were placed on slotted ceramic supports and inserted in pre-heated furnaces at the testing temperatures. The specimens were thermal-cycled to room temperature five (5) times each week, to permit their inspection. Failure criterion was the first appearance of Cb-oxide on the specimens.

A total of 110 Cb-1Zr alloy specimens coated in the above manner were tested to failure at 1200° F. in the

manner described above. The median coating life of these specimens was 2244 hours, and 44 of the 110 specimens exhibited coating lifetimes in excess of 5000 hours. In many instances protection for over 6000 hours was obtained.

A total of 86 Cb-1Zr alloy specimens, prepared in the above manner, were endurance tested by the same procedure in air at 2000° F. These specimens were also thermal-cycled to room temperature five (5) times per week. The median coating life of these specimens was 716 hours, and in some cases protection for over 1500 hours was obtained.

Failure was again determined by the first appearance of Cb-oxide on the specimens.

In the testing at both 1200° F. and 2000° F., all failures were either at the edges of the specimen or at a small area on the face of the specimen. There was no case of failure due to total degradation of the coating.

The performance of the above coatings on Cb-1Zr alloys was also evaluated at various temperatures between 1200° F. and 2000° F. in order to detect anomalies in the oxidation protection afforded by the coating. Five specimen blanks were exposed to air at 1382° F., with no failure to 5000 hours, 4 specimens were exposed to air at 1600° F., with no failures to 5000 hours, 5 specimens were exposed to air at 1800° F., with 3 failures at 2640 hours and 2 failures at 2808 hours. These results indicated no anomalous behavior between 1200° F. and 2000° F.

EXAMPLE 2

In this example seven (7) specimens of Cb-1Zr alloy, coated in accordance with the procedure of Example 1, were exposed to air at 2000° F. for various time periods up to 900 hours. The resulting specimens were chemically analyzed for oxygen and nitrogen content. The results of these analyses are presented in Table 1.

TABLE 1

Treatment of specimen	Oxygen content, p.p.m.	Nitrogen content, p.p.m.
Uncoated.....	185	150±35
As coated.....	150	140±45
100 hour exposure.....	230	115±40
400 hour exposure.....	300	185±35
550 hour exposure.....	270	115±55
700 hour exposure.....	250	120±25
900 hour exposure.....	250	130±15

These results show that no significant contamination of the base metal occurred during exposure in air for time durations up to 900 hours at temperatures of 2000° F. Thus, the coatings of Example 1 were shown to serve as effective barriers to the penetration of oxygen and nitrogen.

EXAMPLE 3

The procedure of Example 1 was repeated in this example, except that a second coating composition was used which contained no Cb. The second coating composition used in this example was:

	Percent by wt.
Sn	70
Al	13
Ti	9
Cr	4
Zn	2
LiF	2

This composition produced a uniform coating on the specimens; however, the oxidation resistance of these coatings at 2000° F. was poor. All of the specimens tested at 2000° F. in the manner set forth in Example 1 failed catastrophically within 48 hours.

These test results indicate the importance of the presence of Cb in the second coating composition of this invention.

EXAMPLE 4

A Cb alloy specimen blank consisting essentially of 1% by weight of Zr, 0.1% by weight of carbon, and balance essentially all Cb was prepared and coated in accordance with the procedure set forth in Example 1. First, second, and third coating compositions having the same ingredients as in Example 1 were applied to the Cb-base alloy specimen blank in the same manner set forth in Example 1, with heat treatment after the application of each coating, in the manner described in that example. This procedure produced a metal article having a coating of the desired properties on the surface of the Cb-1Zr-0.1C alloy substrate.

EXAMPLE 5

A Cb-base alloy specimen blank consisting essentially of 10% by weight of W, 1% by weight of Zr, 0.1% by weight of carbon, and balance essentially all Cb, was coated in accordance with the procedure set forth in Example 1. First, second, and third coating compositions of the same ingredients as in Example 1 were applied to the Cb-base alloy specimen blank in the same manner set forth in Example 1, with heat treatment of the character described in that example following the application of each coating composition. The resulting product had a coating of the desired properties on the surface of the Cb-10W-1Zr-0.1C alloy substrate.

EXAMPLE 6

A Cb-base alloy specimen blank consisting essentially of 18% by weight of W, 8% by weight of Hf, and balance essentially all Cb was prepared in accordance with the procedures set forth in Example 1. First, second, and third coating compositions of the same ingredients as in Example 1 were applied to the Cb-base alloy specimen in the same manner set forth in Example 1, with heat treatment following the application of each coating composition, in accordance with the procedure of that example. The resulting product had a coating of the desired properties on the surface of the Cb-18W-8Hf alloy substrate.

EXAMPLE 7

A Cb-base alloy specimen blank consisting essentially by weight of 27% Ta, 10% W, 1% Zr, and balance essentially all Cb was prepared in accordance with the procedures set forth in Example 1. First, second, and third coating compositions of the same ingredients as in Example 1 were applied to the Cb-base alloy specimen in the same manner set forth in Example 1 with heat treatment, in the manner set forth in that example, following the application of each of the coating compositions. The resultant product had a coating of the desired properties formed on the Cb-27Ta-10W-1Zr alloy substrate.

EXAMPLE 8

A Ta-base alloy specimen blank consisting essentially of 8% by weight of W, 2% by weight of Hf, and balance essentially all Ta was prepared in accordance with the procedures set forth in Example 1. First, second, and third coating compositions of the same ingredients as in Example 1 were applied to the Ta-base alloy specimen, in the manner set forth in Example 1, with each coating being heat treated on the substrate following its application in accordance with the procedure of Example 1. The resulting product had a coating of the desired properties formed on the surface of the Ta-8W-2Hf alloy substrate.

EXAMPLE 9

A Ta-base alloy specimen blank consisting essentially of 9.5% by weight of W, 2.5% by weight of Hf, 0.1% by weight of carbon, and balance essentially all Ta was prepared in accordance with the procedures set forth in

Example 1. First, second, and third coating compositions of the same ingredients as in Example 1 were applied to the Ta-base alloy specimen in the same manner set forth in Example 1, with heat treatment of each coating composition following its application to the specimen, in accordance with the procedure of that example. The resulting product had a coating of the desired properties formed on the surface of the Ta-9.5W-2.5Hf-0.1C alloy substrate.

EXAMPLE 10

In this example a number of Cb-1Zr specimens, prepared in accordance with the procedure of Example 1, were coated with a first coating composition comprising 95% by weight of In and 5% by weight of Si. His coating composition was applied to the specimen blanks in exactly the same manner used to apply the Mg-Si first coating composition in Example 1. The slurry was prepared using In in the form of a fine powder (-325 mesh; 99+-% purity) and Si in the same fine powder used in Example 1. After the first coating composition had been applied, the coated specimens were allowed to stand at room temperature for 1 hour to allow evaporation of the solvent, and the coated specimens were then heat treated in an argon atmosphere for 2 hours at 1950° F.

The second and third coating compositions described in Example 1 were then applied to the In-Si coated Cb-1Zr substrate in exactly the same manner as the second and third coatings were applied to the specimens of Example 1. The resulting specimens were endurance tested in air at 1200° F. and 2000° F. to evaluate the oxidation protection afforded by the coatings of this example.

Each of the six (6) specimens tested at 2000° F. had an exposure lifetime at that temperature in excess of 1200 hours, and the mean lifetime of the samples was 1460 hours. This compares to a mean lifetime of 820 hours at 2000° F. for the coatings of Example 1, applied using a Mg-Si first coating composition rather than the In-Si first coating composition of this example.

The specimens coated in accordance with this example also exhibited excellent oxidation resistance at 1200° F. Four of the five specimens tested at 1200° F. exhibited exposure lifetimes at that temperature in excess of 4000 hours. In each of these four instances, the test was terminated after 4104 hours, with no failures being observed.

EXAMPLE 11

A Cb-base alloy specimen consisting of essentially 1% by weight of Zr, 0.1% by weight of carbon, and balance essentially all Cb was prepared in accordance with the procedures set forth in Example 10. First, second, and third coating compositions of the same ingredients as in Example 10 were applied to the Cb-base alloy specimen in the same manner set forth in Example 10, with heat treatment following the application of each coating composition, in accordance with the procedures set forth in that example. The resulting product had a coating of the desired properties formed on the surface of the Cb-1Zr-0.1C alloy substrate.

EXAMPLE 12

A Cb-base alloy specimen blank consisting of essentially 10% by weight of W, 1% by weight of Zr, 0.1% by weight of carbon, and balance essentially all Cb, was prepared in accordance with the procedures set forth in Example 10. First, second, and third coating compositions of the same ingredients as in Example 10 were applied to the Cb-base alloy specimen in the same manner set forth in Example 10, with heat treatment following the application of each coating composition in the manner set forth in that example. The resulting product had a coating of the desired properties formed on the surface of the Cb-10W-1Zr-0.1C alloy substrate.

EXAMPLE 13

A Cb-base alloy specimen blank consisting essentially of 18% by weight of W, 8% by weight of Hf, and balance

essentially all Cb was prepared in accordance with the procedures set forth in Example 10. First, second, and third coating compositions of the same ingredients set forth in Example 10 were applied to the Cb-base alloy specimen in the same manner set forth in Example 10, with heat treatment following the application of each coating composition in the manner set forth in that example. The resulting product had a coating of the desired properties formed on the surface of the Cb-18W-8Hf alloy substrate.

EXAMPLE 14

A Ta-base alloy specimen blank consisting essentially of 8% by weight of W, 2% by weight of Hf, and balance essentially all Ta was prepared in accordance with the procedures set forth in Example 10. First, second, and third coating compositions of the same ingredients as in Example 10 were applied to the Ta-base alloy specimen, in the same manner set forth in Example 10, with heat treatment following the application of each coating composition in the manner set forth in that example. The resulting product had a coating of the desired properties formed on the surface of the Ta-8W-2Hf alloy substrate.

EXAMPLE 15

A Ta-base alloy specimen blank consisting essentially of 9.5% by weight of W, 2.5% by weight of Hf, 0.1% by weight of carbon, and balance essentially all Ta was prepared in accordance with the procedures set forth in Example 10. First, second, and third coating compositions of the same ingredients as in Example 10 were applied to the Ta-base alloy specimen in the same manner set forth in Example 10, with heat treatment following the application of each coating composition, in the same manner described in that example. The resulting product had a coating of the desired properties formed on the surface of the Ta-9.5W-2.5Hf-0.1C alloy substrate.

In addition to the foregoing examples, the desired articles of this invention can also be obtained by applying the coatings of this invention, as specifically illustrated by Examples 1 and 10 above, to the substrates of the following examples.

EXAMPLE 16

A Mo-base alloy consisting essentially of 0.5% by weight of Ti and balance essentially all Mo.

EXAMPLE 17

A Mo-base alloy consisting essentially of 0.5% by weight of Ti, 0.5% by weight of Zr, 0.1% by weight of carbon and balance essentially all Mo.

The invention in its broader aspects is not limited to the specific details shown and described, but departures may be made from such details within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

We claim:

1. A metal article having a substrate consisting essentially of a refractory metal selected from the group consisting of Cr, V, Hf, Cb, Mo, Ta, W, and alloys having one of said refractory metals as their base, and a coating superimposed on the substrate, the coating comprising an interior coating zone and an exterior coating zone; the interior coating zone consisting essentially of a silicide of the refractory-base metal of the substrate and the exterior coating zone having a surface region and a subsurface region; the surface region consisting essentially, by weight, of from 40 to 50% of Sn, from 27 to 33% of Cr, from 14 to 18% of Al, and from 7 to 11% of Ti; and the subsurface region consisting essentially, by weight, of from 48 to 58% of Sn, from 20 to 28% of Cb, from 8 to 12% of Al, up to 10% of Ti, up to 5% of Cr, up to 1.5% of Zn, and up to 2% of a halide activator selected from the group consisting of alkali metal halides and alkaline earth metal halides.

2. The article of claim 1 in which the subsurface region of said exterior coating zone contains from 5 to 10% by weight of Ti, from 1 to 5% by weight of Cr, and from 1 to 2% by weight of the halide activator.

3. The article of claim 8 in which the substrate is selected from the group consisting of Cb and Cb-base alloys.

4. The article of claim 8 in which the substrate is selected from the group consisting of Ta and Ta-base alloys.

5. The article of claim 4 in which the substrate consists essentially of 1% by weight of Zr and balance essentially Cb.

6. The article of claim 1 in which the surface region of the exterior coating zone consists essentially, by weight, of about 45% Sn, about 30% Cr, about 16% Al, and about 9% Ti; and the subsurface region of the exterior coating zone consists essentially, by weight, of about 53% Sn, about 24% Cb, about 10% Al, about 7% Ti, about 3% Cr, about 1.5% Zn, and about 1.5% LiF.

7. A metal article having a refractory metal substrate selected from the group consisting of Cr, V, Hf, Cb, Mo, Ta, W, and alloys having one of said refractory metals as their base, and an oxidation resistant coating superimposed on the substrate; the coating comprising an interior coating zone adjacent to the substrate, and an exterior coating zone superimposed on the interior coating zone; the interior coating zone consisting essentially of a material selected from the group consisting of 3-10% by weight of silicides, borides, and beryllides of the refractory base metal of the substrate, and 90-97% by weight of In; and the exterior coating zone consisting essentially of Cb, Al, and Sn.

8. The article of claim 7 in which the interior coating zone consists essentially of a silicide of the refractory metal of the substrate, and In.

9. A metal article having a substrate consisting essentially of a refractory metal selected from the group consisting of Cr, V, Hf, Cb, Mo, Ta, and W and alloys having one of said refractory metals as their base, and a coating superimposed on the substrate, the coating comprising an interior coating zone and an exterior coating zone; the interior coating zone consisting essentially of a silicide of the refractory-base metal of the substrate and In; and the exterior coating zone comprising a surface region and a subsurface region; the surface region consisting essentially, by weight, of from 40 to 50% of Sn, from 27 to 33% of Cr, from 14 to 18% of Al, and from 7 to 11% of Ti; and the subsurface region consisting essentially, by weight, of from 48 to 58% of Sn, from 20 to 28% of Cb, from 8 to 12% of Al, up to 10% of Ti, up to 5% of Cr, up to 1.5% of Zn, and up to 2% of a halide activator selected from the group consisting of alkali metal halides and alkaline earth metal halides.

10. The article of claim 9 in which the weight ratio of In to Si in the interior coating zone is from 90:10 to 97:3.

11. The article of claim 10 in which the weight ratio of In to Si in the interior coating zone is about 95:5.

12. The article of claim 10 in which the substrate is selected from the group consisting of Cb and Cb-base alloys.

13. The article of claim 9 in which the subsurface region of said exterior coating zone contains from 5 to 10% by weight of Ti, from 1 to 5% of weight of Cr, and from 1 to 2% by weight of the halide activator.

14. The article of claim 7 in which the substrate is selected from the group consisting of Cb and Cb-base alloys.

15. The article of claim 7 in which the substrate is selected from the group consisting of Ta and Ta-base alloys.

16. A metal article having a substrate consisting essentially of a refractory metal selected from the group consisting of Cr, V, Hf, Cb, Mo, Ta, W, and alloys having one of said refractory metals as their base and an oxidation resistant coating superimposed on the substrate, the coating comprising an interior coating zone adjacent to the substrate, and an exterior coating zone superimposed on the interior coating zone; the interior coating zone consisting essentially of a member selected from the group consisting of silicides, borides and beryllides of the refractory base metal of the substrate and the exterior coating zone consisting essentially by weight of 20-28% Cb, 8-12% Al, 48-58% Sn, 0-10% Ti, 0-5% of Cr, 0-5% of Zn, and 0-2% of a halide activator selected from the group consisting of alkali metal halides and alkaline earth metal halides.

17. A metal article having a substrate consisting essentially of a refractory metal selected from the group consisting of Cr, V, Hf, Cb, Mo, Ta, W, and alloys having one of said refractory metals as their base, and a coating superimposed on the substrate, the coating comprising an interior coating zone and an exterior coating zone; the interior coating zone consisting essentially of a silicide of the refractory base metal of the substrate and the exterior coating zone consisting essentially, by weight of 20-28% Cb, 8-12% Al, 48-58% Sn, 1-5% Cr, 5-10% Ti, and 1-2% of at least one halide activator selected from the group consisting of alkali metal halides and alkaline earth metal halides.

18. The article of claim 16 in which the interior coating zone is a silicide of the refractory base metal of the substrate.

19. The article of claim 16 in which the substrate is selected from the group consisting of Cb and Cb-base alloys.

20. The article of claim 35 in which the substrate is selected from the group consisting of Ta and Ta-based alloys.

21. The article of claim 17 in which the substrate is selected from the group consisting of Cb and Cb-based alloys.

22. The article of claim 17 in which the substrate is selected from the group consisting of Ta and Ta-based alloys.

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HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R.

29-198

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,492,102 Dated January 27, 1970

Inventor(s) N. S. Bornstein et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 3, column 21, line 5, change "claim 8" to -- claim 1 --.

Claim 4, column 21, line 8, change "claim 8" to -- claim 1 --.

Claim 20, column 22, line 42, change "claim 35" to -- claim 16 --

SIGNED AND
SEALED
JUN 23 1970

(SEAL)

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