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PROCESS AND COMPOSITION FOR DIFFUSION COATING REFRACTORY METALS AND PRODUCT PRODUCED THEREBY

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This invention relates to the formation of oxidation resistant diffusion alloy coatings on refractory metals. More particularly, this invention relates to the diffusion coating of refractory metals with certain diffusing elements through a liquid-to-solid transfer process using Group IIA metals as transfer agents.

This application is a continuation-in-part of our copending application Serial No. 57,387, filed September 21, 1960, now abandoned.

Alloys based on the refractory metals, e.g., nickel, cobalt, niobium, molybdenum, tungsten, tantalum and, to a lesser extent, vanadium are used in a variety of applications where high temperatures are encountered. Specifically, turbine blades and buckets, furnace heating elements, jet and internal combustion engine parts of these metals and alloys thereof are characterized by being resistant to chemical attack and having high melting points with the additional characteristic of retaining their good mechanical properties at elevated temperatures. However, in order to prevent the oxidation of these metals at elevated temperatures, it is necessary to exclude oxygen or to protect the metal surfaces with oxidation resistant coatings.

Chromium is also considered to be a refractory metal although oxidation of this metal at high temperatures is not a serious problem. However, a protective coating on this metal serves to resist nitriding.

A number of methods for coating refractory metals are known. Specifically, it has been proposed to protect refractory metals by electroplating following by annealing, vapor or gaseous plating, annealing in pack treatments, dipping, spraying and painting on coatings that can be subsequently annealed. These prior art methods have serious disadvantages in that the protective coatings formed are not sufficiently adherent or they are non-uniform or excessively porous or thick. Frequently these coatings can only be formed under impractical operating conditions and only a limited number of alloys can be prepared.

Coatings can be prepared in accordance with the present invention that are uniform and exhibit excellent adhesion and virtually no porosity. Furthermore, these coatings can be formed on intricately shaped objects and complete coverage, even in the recesses, can be obtained. The large number of distinct alloy coatings that can be obtained as outlined herein is an added advantage.

It is an object of the present invention to provide diffusion alloy coatings on refractory metal articles that resist oxidation under high temperature surface conditions.

It is another object of the present invention to provide unique oxidation-resistant coatings using a novel liquid-to-solid diffusion process.

The diffusion coatings of the present invention are oxidation resistant alloys formed on refractory metal articles by diffusing into the articles one or more diffusing elements from either or both of the following groups: (1) silicon and aluminum and (2) the transition metals having at least one but less than 10 *d* electrons. Preferred oxidation resistant coatings contain aluminum with or without additional diffusing elements selected from the above-mentioned transition elements.

Aluminum and silicon have the property of being solu-

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ble to at least some extent in both the liquid transfer medium and the solid refractory article being coated under the conditions outlined herein. In addition, aluminum and silicon impart superior oxidation resistance to refractory metals and can be codiffused with the transition diffusing elements to form alloy rich coatings.

Diffusion of an element is considered to proceed when the concentration of the element in the liquid transfer agent is sufficiently high to favor the element's diffusion into the refractory article. Considering the mechanism as principally depending on the relative chemical activities of a particular element in both the transfer agent and the solid article, it is observed that a high concentration or a saturated solution of a diffusing element in a liquid melt of the transfer agent favors diffusion of the element into the refractory article when the element is soluble but not present in saturated amounts in the solid article.

Diffusion can be carried out by contacting, preferably by immersion, the refractory metal with a melt of the transfer agent containing one or more of the diffusing elements at a temperature of about 900–1450° C., preferably at about 1000–1400° C.

The preferred transfer agent is calcium although other Group IIA metals such as barium and strontium, and mixtures thereof, are suitable. The high vapor pressure of magnesium at operating temperatures makes it less desirable as a transfer agent. These metals, except for beryllium, have melting points below 900° C. and are comparatively inert toward all of the refractory metals except nickel. Where nickel-rich alloys are used as substrates, it is necessary to maintain sufficient nickel dissolved in the transfer agent to prevent dissolution of the substrate. The diffusing elements are all soluble to the extent that diffusion is favored when sufficient concentrations of the diffusing elements are incorporated in the IIA metal transfer agents.

At least about 25% by weight of the diffusion composition (transfer agent and diffusing elements) should be comprised of the transfer agent; up to 99.5% of the composition can be the transfer agent, but the preferred amount of the agent is about 35–65% by weight. When aluminum is being diffused from a Ca-Al composition, preferably about 35–65% of the diffusing composition should be calcium, the balance being aluminum or aluminum and up to about 30% additional diffusing elements. In general, only small amounts, about 0.5% by weight, of the diffusing elements need be present in the composition and up to about 75% can be used.

The second group of diffusing elements include those transition elements that have at least 1 but less than 10 *d* electrons. Specifically, titanium, manganese, iron, yttrium and zirconium are embraced within this group. In addition, this group of diffusing transition elements includes the refractory metals vanadium, chromium, cobalt, nickel, molybdenum, niobium, tantalum and tungsten which are preferably co-diffused with at least one other diffusing element, usually aluminum, to form oxidation resistant coatings on refractory metal articles.

It should be emphasized that the majority of the diffusing elements are sparingly soluble in melts of the transfer agents, the most notable exceptions being aluminum, silicon, and nickel. Introducing these slightly soluble diffusing elements as finely divided powders (preferably 100–400 mesh) and providing agitation during diffusion serve to facilitate the formation of the coating. It should also be noted that during diffusion, multiple component systems exist in both the coated article and in the diffusion composition. These systems have characteristic melting points and solubilities that are distinct from those of the starting materials.

Frequently, these distinct melting points and solubility changes can be advantageous. For instance, some coat-

ings are formed to an appreciable extent only in the presence of certain other metals. Chromium rich coatings can be formed on niobium when other diffusing elements such as Al, Ni or Co are present in the diffusion mixture; when calcium-chromium diffusion mixtures are used without additional metals, much, but not all, of the deposited Cr adheres without diffusing into the refractory metal substrate. Other elements such as yttrium, vanadium, molybdenum, titanium, and zirconium will form diffusion alloy coatings with aluminum on niobium in Ca-Al baths. The presence of aluminum apparently serves to increase the solubility of these comparatively insoluble elements in calcium or in the substrate. This is not to say, however, that these comparatively insoluble elements cannot be diffused to some extent into niobium and other refractory metal articles from a melt of calcium in the absence of aluminum. Rather, it is to state that these elements should be codiffused with aluminum in order to obtain coatings sufficiently alloy rich to impart appreciable resistance to oxidation at elevated temperatures; moreover, alloy coatings containing aluminum are preferred.

The following examples illustrate specific embodiments of the present invention.

EXAMPLE I

Samples of Mo and W were treated without stirring in a bath containing 60 g. Ca, 6 g. Cr, and 10 g. Ni in a carbon steel crucible. The samples were heated for about 1 hour at 1290° C. The coatings on the Mo and W samples both contained nearly the same concentrations of Cr (over 50%), Fe (over 10%), and Ni (over 10%). These coatings impart oxidation resistance to the refractory metal substrates, but the resistance to oxidation is not as high as those alloy coatings containing aluminum.

EXAMPLE II

Samples of Nb, Mo and W were treated without stirring in a bath containing 25 g. Ca, 3 g. Mn, 3 g. Co, and 5 g. Cr powder in a Mo crucible. They were heated at 1290° C. for about 2 hours. The Nb sample was coated with high concentrations of Ni, Co, and Mn (each > 10%) and with several percent of Cr. The Mo and W samples contained similar high concentrations of Ni, Co, and Mn and a lower concentration of Cr. The Ni was present as a contaminant in the Mo crucible from a previous run in which the Mo crucible was used to hold a Ca-Ni bath.

EXAMPLE III

When Nb, Mo, and W were treated without agitation in a bath containing 75 g. Ca, 10 g. Cu, and 10 g. Zn, and placed in a mild steel crucible, at 1290° C. for about 2 hours, the coatings on the samples contained iron but little, if any, Cu or Zn. Copper and zinc can be used with calcium and serve to dilute the diffusion composition since neither copper nor zinc diffuses into the refractory metal substrate to any extent and these metals remain substantially inert in the melt.

EXAMPLE IV

Samples of Nb, Mo and W were treated without agitation in a bath containing 15 g. Ca, 15 g. CaSi₂, and 5 g. Cr powder for 2 hours at 1300° C. The coatings on the Nb, Mo, and W samples contained both Cr and Si, identified by X-ray fluorescence. Alloy content and thicknesses of the various coatings obtained are determined by alternately examining the coated article with X-ray fluorescence and removing by polishing the portion examined (0.1–0.2 mil) and repeating the examination. The exact nature of some of the coatings, especially those alloys that are unreported in the literature, is difficult to establish. However, surface (the top 0.1–0.2 mil of the coating) concentrations have been determined in a number of the coatings obtained.

EXAMPLE V

Samples of Nb, Mo and W were treated in a bath containing 30 g. Ca, 5 g. Cr, 5 g. Co, and 3 g. Y for about 2 hours at 1300° C. The samples were not agitated in the bath. The Nb sample had a high concentration of Co, a few percent of Cr, and about 1% of Y at the surface of the coating. The Mo and W had a high concentration of Co, several percent of Cr, and about 2%–3% Y at the surface of the coating.

EXAMPLE VI

Nb was coated with V and Ni by treating it in a bath containing about 45 g. Ca, 3 g. Ni, and 5 g. V (20 mesh). The sample was heated for 3 hours at about 1200° C. in an induction furnace.

EXAMPLE VII

A niobium article was treated in a melt containing 54 g. of Ca-Al alloy, 73% Ca–27% Al, to which had been added 25 grams of Al. The melt was contained in a Mo crucible and the sample was treated for 4 hours at 1300° C. The Nb-Al alloy coating obtained withstood oxidation for more than 56 hours when heated to 1050° C. in air.

EXAMPLE VIII

A sample of Nb was coated with appreciable concentrations of Cr, Mn, Co, and Ni by treatment in a bath containing about 45 g. Ca and 0.5 g. Co, 0.5 g. Mn, 0.5 g. Ni, and 5 g. Cr at about 1300° C., heated in an induction furnace for 40 minutes.

EXAMPLE IX

Four samples of niobium were immersed in a melt comprised of 70 grams 50% Ca–50% Si for 4 hours at 1300° C. All samples gained appreciable weight and the coatings were 1.7–2.5 mils thick and multilayered with distinct alloys. When heated in air to 1050° C., the coatings began to fail only after 17 hours. Complete failure was not observed, but several spots appeared indicating that the coating was penetrated. In the oxidation test, breakdown of coating usually occurs at a corner or along the edge.

EXAMPLE X

A sample of Nb was coated with Ni by treatment in 45 g. Ca+5 g. Ni shot for 4 hours at 1300° C. The sample contained >30% Ni at the surface.

EXAMPLE XI

A sample of Nb was coated with Ni and Al by treatment for 4 hours in 54 g. 73–27% Ca-Al alloy, 15 g. Al, and 2 g. Ni. The temperature was 1300° C. The sample contained large concentration (>20%) each of Ni and Al.

EXAMPLE XII

A sample of Nb was treated in a Mo container holding a bath composition of 74 g. of 50% Ca–50% Al alloy and 3 g. Ti powder for 4 hours at 1300° C. in argon. The coating contained Al, Nb, Ti, and Mo. The concentration of Ti was greater than 20%. Some of the Mo from the container diffused into the Nb substrate.

EXAMPLE XIII

A sample of Nb was treated in a bath containing 74 g. 50% Ca–50% Al alloy and a 2 g. piece of zirconium for 4 hours at 1300° C. in argon. The diffusion coating that formed contained mainly Nb and Al with about 4–5% Mo, 2–3% Zr, and a trace of Fe. A different sample was treated in a bath containing 74 g. 50–50 Ca-Al and 3 g. Zr powder for 4 hours at 1300° C. in argon. The coating contained a high concentration of Al (20–30%), over 15% Zr, and about 5% Mo. The Fe was present as an impurity from the apparatus or in the starting material, probably the Ca-Al alloy, and the source of Mo was the crucible container.

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EXAMPLE XIV

A sample of Nb was treated in a bath containing 74 g. 50% Ca—50% Al and 5 g. Fe powder for 4 hours at 1300° C. in argon. A Mo crucible was the container. The coating on the Nb sample contained high concentrations (>20%) of Al and Fe, as well as over 10% Mo.

EXAMPLE XV

Samples of Nb, V, Ta, and Mo were treated in a bath containing 79 g. of 50% Ca—50% Al alloy in a Mo crucible for 3.5 hours at 1300° C. under argon. A coating of Al-Mo-Fe-Nb was obtained on Nb. The coating on V contained primarily Al, Mo, Nb, and smaller concentrations of Ta, V, and Fe. The coating on Ta contained Al and small concentrations of Mo, Nb, and Fe. The coating on Mo contained Al and small concentrations of Ta, Nb, and Fe. Fe was present in the system as an impurity.

EXAMPLE XVI

Samples of V, Ta, and Nb sheet were treated in a bath containing 45 g. Ca, 5 g. Cr powder, 2 g. Ni, 2 g. Co, and 2 g. Mn in a Mo crucible for 4 hours at 1300° C. in argon. The vanadium had a thick coating which contained appreciable concentrations (>10% by weight) of Cr, Mn, Co, Ni and smaller concentrations of V and Nb at the surface. The tantalum was coated with an alloy containing Cr, Mn, Co, Ni, and Nb. The Nb sample was coated with appreciable concentrations of Cr, Mn, Co, Ni and a trace of Ta.

EXAMPLE XVII

A sample of Nb was treated in a bath containing 32 g. Al, 27.5 g. Ba, and 52.5 g. Sr in a Mo crucible. The sample was heated for 4 hours at 1300° C. in argon. The coating was similar to that in Example XXIII. A small concentration of Sr was detected throughout the coating by X-ray fluorescence. For analytical purposes the coating was partially removed by electropolishing. Electropolishing was alternated with X-ray fluorescence in determining the depth to which Sr penetrated.

EXAMPLE XVIII

A sample of Nb-Mo-Ti alloy (80% Nb—10% Mo—10% Ti) was treated for 18 hours in 82 g. 50% Ca—50% Al alloy at 1100° C. in argon. The sample had a coating of 2.5 mils. The structure was nearly the same as that obtained in Example XXIII. However, the layer having the Nb₂Al structure was about 0.4 mil thick. The surface of the coating was poorer in Ti and richer in Mo than the starting alloy. The surface also contained Al and Nb and a trace of iron. This sample lasted for 42 hours at 1050° C. in air before rapid oxidation began.

EXAMPLE XIX

A sample of 95% Nb—5% Zr was treated in 82 g. 50% Ca—50% Al alloy for about 17 hours at 1100° C. in argon. The sample had a coating 2.5 to 2.8 mils thick with a Knoop hardness of 1050–1200. Its structure was similar to that obtained in Example XXIII. The sample lasted for 47 hours at 1050° C. in air without appreciable oxidation.

EXAMPLE XX

A sample of Nb was treated in a bath containing 82 g. of 50% Ca—50% Al alloy and 0.5 g. Ni as outlined in Example XXI. The coating, after about 18 hours of treatment, was 3.5±0.2 mils with a Knoop hardness of 725 to 840. The grains are mainly columnar and are extremely narrow. The coating's structure was similar to that obtained in Example XXIII. This sample resisted oxidation for 118 hours at 1050° C. in air.

EXAMPLE XXI

A sample of Nb was placed in a bath containing 82 g. of 50% Ca—50% Al alloy and 0.5 g. Co contained in

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a molybdenum crucible. The sample was treated for about 16 hours at 1100° C. in argon. The niobium was then removed, cleaned, and analyzed by X-ray fluorescence. The surface contained about 10% Mo, 0.5% Fe, 1–2% Co, 20–30% Al, and the balance niobium. The coating was 2.3±0.2 mils thick. Its structure was similar to that obtained in Example XXIII. The sample resisted oxidation at 1050° C. in air for 125 hours without any breakdown of the coating.

EXAMPLE XXII

When a sample of Nb was treated for 16 hours in 66 g. 61% Ca—39% Al alloy at 1100° C. in argon, the sample was similar to that in Example XXIII; that is, it had a relatively thick coating having the NbAl₃ structure and a thin layer having the structure of Nb₂Al.

EXAMPLE XXIII

A sample of pure Nb (about 1½" x ¾" x 0.04") was rotated in 82 g. 50% Ca—50% Al alloy for 18 hours at 1100° C. in an argon atmosphere. The bath was contained in a niobium crucible. The sample was removed, cooled, and cleaned in dilute HCl. A diffusion alloy coating of aluminum-niobium (about 3 mils thick) was present on the niobium substrate. This sample was heated in air at 1050° C. for 117 hours without appreciable oxidation and with no oxygen penetration. The sample gained 56 mg. in 117 hours due to oxidation, or less than 0.1 mg./cm.² per hour.

Another sample of niobium, which had a similar treatment in 50% Ca—50% Al alloy, was cross-sectioned, polished, etched, and photographed. Two layers were revealed: (1) the upper layer, about 2.7 mils thick, had the crystal structure of NbAl₃, determined by using an X-ray diffractometer and (2) a thin layer, 0.2–0.3 mil, appeared between the top layer and the niobium substrate. This layer has the structure of Nb₂Al.

EXAMPLE XXIV

A melt of a diffusion composition containing 81 g. Ca, 3 g. Mn, 3 g. Fe, 3 g. Co, and 10 g. Ni was heated to about 1100° C. A sample of Cr was rotated for 2.5 hours in the bath, contained in a carbon steel liner. The Cr was coated with Fe, Ni, Co, and Mn and the coating was about 0.002" thick.

The processes described in the above examples were carried out in an inert atmosphere of argon. Although diffusion can be carried out without the protection afforded by an inert atmosphere, it is preferred to exclude oxygen, nitrogen, and other contaminants, particularly at temperatures higher than 1100° C. and when the diffusion composition is comprised of aluminum and calcium. A practical method of carrying out the process at high temperatures is to enclose the melt within a container. The air can be exhausted from the container or simply permitted to become "dead" without replenishment during operation. It is to be understood, however, that diffusion can be carried out in the absence of the above measures and one skilled in the art can readily determine the most feasible conditions under which a particular refractory metal substrate can be coated with a particular alloy coating. In the event an inert atmosphere is desired, other gasses such as helium will suggest themselves. After the treated articles are removed, it is preferred to dissolve away the melt residue with dilute HCl or other suitable reagent.

EXAMPLE XXV

A series of experiments was conducted in which base refractory metals having the compositions indicated in Table 1 which follows were immersed in a stirred molten metal bath under an inert argon atmosphere. The bath consisted of calcium and one or more diffusing elements as indicated in the table. Upon removal of the coated article from the bath, quenching was accomplished by

either exposure to air at room temperature or immersing the article in an oil bath. Each of the coated articles was cleaned and then analyzed to determine its composition. The final percentage of diffusing elements in the surface of the coated article is recited in the table. The determination of the surface composition in this and the foregoing examples was accomplished in the usual manner as described in Example IV. It will be noted that in each experiment there was an increase in the percentage of at least one of the diffusing elements in the surface coating.

From the data in the table which follows, it will be noted that even with alloys containing as much as 50% cobalt or nickel, the cobalt or nickel content can be increased by the process of this invention. Generally speaking, the surface concentration of a diffusing element can be either increased or decreased by varying the composition of the coating bath.

Table 1

Experiment	Base Metal Composition (percent)						Molten Bath Composition (gms.)					Coating Operation		Quenching Medium	Percent Diffusing Elements in Coated Article Surface			
	Ni	Co	Cr	Mo	W	Fe	Ca	Ni	Co ¹	Cr ¹	Al	Time (min.)	Temp. (° C.)		Ni	Co	Cr	Al
1	10	50	20	---	15	3	2,300	79	200	---	---	15	1,150	Oil	14	68	---	---
2	10	50	20	---	15	3	2,300	167	200	---	---	15	1,500	Oil	16	70	---	---
3	10	50	20	---	15	3	2,300	167	200	23	---	15	1,500	Oil	15	66	6	---
4	54	2	16	16	4	5	1,500	1,833	75	230	---	15	1,150	Air	74	---	6	---
5	10	50	20	---	15	3	2,300	---	---	---	46	60	1,150	Oil	---	50	---	5-10

¹ -325 mesh powder.

It is to be noted that a great number of the coatings formed are novel in terms of alloy content and, in general, it can be said that the oxidation resistance of the refractory metals is enhanced by the great majority of the diffusion coatings obtained although the degree of resistance of individual coatings will vary considerably. Isolated instances where low melting alloys are formed or where the oxidation resistance of the coated refractory metal is not significantly increased can probably be cited. By following the examples, however, one skilled in the art can determine the conditions under which suitable coatings can be obtained.

The best coatings obtained in terms of oxidation resistance were those containing aluminum and, to a less extent, silicon. From the standpoint of refractory materials treated, undoubtedly those articles formed of niobium, molybdenum and tungsten or alloys of these metals have the greatest utility and will be more widely used than other refractory metals. In particular, coatings containing aluminum on niobium or alloys of niobium are outstanding in terms of oxidation resistance, and the base metal remains ductile because oxygen does not penetrate through the coatings.

The nature of the superior oxidation resistant coatings obtained in Example XXIII and similar coatings has been extensively investigated. As noted above, these coatings are comprised of layers having distinct phase structures; the thicker upper layer having a structure corresponding to NbAl₃ and the relatively thin bottom layer having a structure corresponding to Nb₂Al. Throughout the entire coatings and in both layers the aluminum and niobium are present in concentration gradients. In the NbAl₃ phase layer the concentration of aluminum decreases slowly with increasing depth until the thin inner layer is reached. Thereafter the concentration of aluminum decreases more rapidly and the concentration gradient is steep. Conversely, the increase in concentration of niobium in the layer having the structure of NbAl₃ is less abrupt than the increasing concentration of niobium in the thinner layer having the phase structure of Nb₂Al.

We have found that appreciable concentration of codiffusing elements, including W, Fe, Mo, Co, Ni and others, do not change the structures of the phases of the

coating. Thus the oxidation resistance conferred by these superior phase structures can be supplemented by further benefits derived from specific codiffusing elements. Furthermore, these desirable phase structures can be maintained on niobium base alloys despite the outward diffusion of alloying elements present in the basis metal. Concentration gradient analysis has shown that these codiffusing elements are likewise present in concentration gradients that decrease toward the interior of the coating.

Apparently the relatively thin Nb₂Al layer is a diffusion barrier and the rate of diffusion is slower through this layer than in the relatively thick layer of NbAl₃. The fact that this thin layer is a diffusion barrier accounts in part for the superior oxidation resistance of the Nb-Al coatings. This is evident because when heated in air at 1050° C. the aluminum in the coatings diffuses

very slowly, even more slowly than the rate of coating formation. In other words, the coating remains alloy rich and relatively fixed in content and structure. Photomicrographs and microhardnesses of these multilayered coatings that have been subjected to the oxidation test show that oxygen penetration is arrested in the NbAl₃ layer.

In addition to alternately scanning the surfaces of the coatings with a diffractometer and polishing to remove that area examined, a careful examination of photomicrographs has established that these two layers having distinct phase structures exist. The photomicrographs show that many of the grains are extremely narrow and columnar. Examination with the diffractometer establishes the structure of the thick outer layer as corresponding to that reported in the literature for NbAl₃. As the coating is polished and examined, the change of intensity of X-ray diffraction peaks indicates that a wide range of solid solubility exists in the Nb-Al coating. Also the results of X-ray investigations reveal the shifting of position of peaks as one probes deeper into the coatings. Under similar examination, the thin inner layer has been identified by X-ray refraction as having the same structure as Nb₂Al which is also reported in the literature in the form of bulk or substantially homogeneous alloys.

The multi-phase coating is obtained in accordance with the preferred process wherein about 35-65% by weight of the diffusion composition is calcium and about 35-65% by weight is aluminum. As the concentration of calcium is increased beyond approximately 65% by weight, the coatings are comparatively thin and have the phase structure of Nb₂Al. Since this structure acts as a diffusion barrier, it is understandable that the coatings are thin. These thin coatings which are comprised of a single layer having the structure of Nb₂Al do not have the outstanding oxidation resistance that the thicker multi-layered coatings have, although considerable resistance to oxidation is evident.

The diffusion coatings of the present invention are alloys of the refractory metals with the diffusing elements and are characterized by having concentration gradients of the diffused elements, the highest concentrations being

present in the outer portions of the coatings. The coatings also contain small amounts of the transfer agents which are present in a similar gradient. Generally, the amount of transfer agent is very small, less than 0.1% by weight, but even small amounts of Ca, Ba, and Sr have been reported to augment resistance to oxidation.

In the foregoing description and examples, parts and percentages are by weight unless otherwise indicated.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for diffusion coating a base refractory metal comprising contacting said metal with a molten composition containing at least about 25% by weight of a member selected from the group consisting of calcium, barium, strontium, and mixtures thereof, as a transfer agent, and from 0.5% up to 75% by weight of at least one diffusing element selected from the group consisting of aluminum, silicon, and transition elements having 1 to 9 *d* electrons, said process being carried out at a temperature of about 900–1450° C. for a time sufficient to form a diffusion alloy coating.

2. A process for diffusion coating a molybdenum base refractory metal comprising contacting said metal with a molten composition containing about 35–65% by weight calcium, about 35–65% by weight aluminum, and up to about 30% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, said process being carried out at about 900–1450° C. for a time sufficient to form a diffusion alloy coating.

3. A process for diffusion coating a base refractory metal comprising contacting said metal with a molten composition containing at least about 25% by weight of a member selected from the group consisting of calcium, barium, strontium, and mixtures thereof, as a transfer agent, up to about 75% by weight of at least one diffusing element selected from the group consisting of aluminum and silicon and up to about 75% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, the total amount of diffusing material exceeding 0.5% by weight, said process being carried out at about 900–1450° C. for a time sufficient to form a diffusion alloy coating.

4. A process for diffusion coating a niobium base refractory metal comprising contacting said metal with a molten composition containing at least about 25% by weight of a member selected from the group consisting of calcium, barium, strontium, and mixtures thereof, as a transfer agent, up to about 75% by weight of at least one diffusing element selected from the group consisting of aluminum and silicon and up to about 75% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, the total amount of diffusing material exceeding 0.5% by weight, said process being carried out at about 900–1450° C. for a time sufficient to form a diffusion alloy coating.

5. A process for diffusion coating a tungsten base refractory metal comprising contacting said metal with a molten composition containing at least about 25% by weight of a member selected from the group consisting of calcium, barium, strontium, and mixtures thereof, as a transfer agent, up to about 75% by weight of at least one diffusing element selected from the group consisting of aluminum and silicon and up to about 75% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, the total amount of diffusing material exceeding 0.5% by weight, said process being carried out at about 900–1450° C. for a time sufficient to form a diffusion alloy coating.

6. A process for diffusion coating a molybdenum base refractory metal comprising contacting said metal with a molten composition containing at least about 25% by weight of a member selected from the group consisting of calcium, barium, strontium, and mixtures thereof, as a transfer agent, up to about 75% by weight of at least

one diffusing element selected from the group consisting of aluminum and silicon and up to about 75% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, the total amount of diffusing material exceeding 0.5% by weight, said process being carried out at about 900–1450° C. for a time sufficient to form a diffusion alloy coating.

7. A process for diffusion coating a base refractory metal comprising contacting said metal with a molten composition containing at least about 25% by weight calcium, up to about 75% by weight of at least one diffusing element selected from the group consisting of aluminum and silicon, and up to about 75% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, the total amount of diffusion material exceeding 0.5% by weight, said process being carried out at about 1000–1400° C. for a time sufficient to form a diffusion alloy coating.

8. A process for diffusion coating a base refractory metal comprising contacting said metal with a molten composition containing at least about 25% by weight calcium, up to about 75% by weight of at least one diffusing element selected from the group consisting of aluminum and silicon, and up to about 75% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, the total amount of diffusion material exceeding 0.5% by weight, said process being carried out at about 900–1450° C. for a time sufficient to form a diffusion alloy coating.

9. A process for diffusion coating a niobium base refractory metal comprising contacting said metal with a molten composition containing at least about 25% by weight calcium, up to about 75% by weight of at least one diffusing element selected from the group consisting of aluminum and silicon, and up to about 75% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, the total amount of diffusion material exceeding 0.5% by weight, said process being carried out at about 1000–1400° C. for a time sufficient to form a diffusion alloy coating.

10. A process for diffusion coating a base refractory metal comprising contacting said metal with a molten composition containing at least about 25% by weight calcium, up to about 75% by weight of aluminum, and up to about 75% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, the total amount of diffusion material exceeding 0.5% by weight, said process being carried out at about 1000–1400° C. for a time sufficient to form a diffusion alloy coating.

11. A process for diffusion coating a base refractory metal comprising contacting said metal with a molten composition containing about 35–65% by weight calcium, about 35–65% by weight of at least one diffusing element selected from the group consisting of aluminum and silicon, and up to about 30% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, said process being carried out at about 1000–1400° C. for a time sufficient to form a diffusion alloy coating.

12. A process for diffusion coating a base refractory metal comprising contacting said metal with a molten composition containing about 35–65% by weight calcium, about 35–65% by weight aluminum, and up to about 30% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, said process being carried out at about 1000–1400° C. for a time sufficient to form a diffusion alloy coating.

13. A process for diffusion coating a niobium base refractory metal comprising contacting said metal with a molten composition containing about 35–65% by weight calcium, about 35–65% by weight aluminum, and up to about 30% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, said process being carried out at about 900–1450° C. for a time sufficient to form a diffusion alloy coating.

14. A process for diffusion coating a tungsten base re-

fractory metal comprising contacting said metal with a molten composition containing about 35-65% by weight calcium, about 35-65% by weight aluminum, and up to about 30% by weight of at least one diffusing transition element having 1 to 9 *d* electrons, said process being carried out at about 900-1450° C. for a time sufficient to form a diffusion alloy coating.

15. A diffusion composition comprising a melt of about 35-65% by weight calcium, about 35-65% by weight of aluminum, and 0.5% to about 30% by weight of at least one diffusing transition element having 1 to 9 *d* electrons.

16. A refractory metal article having an oxidation resistant coating comprising a refractory metal alloy containing at least one diffused element selected from the group consisting of aluminum, silicon, and transition elements having 1 to 9 *d* electrons, said coating having increasing concentrations of said diffused elements and a transfer agent toward the outer portion thereof, said transfer agent being selected from the group consisting of calcium, strontium, and barium.

17. A refractory metal article having an oxidation resistant diffusion coating comprising a refractory metal alloy containing aluminum and a transfer agent selected from the group consisting of calcium, strontium, and barium, said coating having increasing concentrations of said aluminum and said transfer agent toward the outer portions thereof.

18. A refractory metal article having an oxidation resistant coating comprising a refractory metal alloy containing at least one diffused element selected from the group consisting of aluminum and silicon, said coating having increasing concentrations of said diffused material and a transfer agent toward the outer portion thereof, said transfer agent being selected from the group consisting of calcium, strontium, and barium.

19. A niobium base refractory metal article having an oxidation resistant coating comprising a niobium refrac-

tory metal alloy containing at least one diffused element selected from the group consisting of aluminum and silicon, said coating having increasing concentrations of said diffused material and a transfer agent toward the outer portion thereof, said transfer agent being selected from the group consisting of calcium, strontium, and barium.

20. A niobium base refractory metal article having an oxidation resistant diffusion coating comprising a niobium refractory metal alloy containing aluminum and a transfer agent selected from the group consisting of calcium, strontium, and barium, said coating having increasing concentrations of said aluminum and said transfer agent toward the outer portions thereof.

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