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PROCESS FOR ZIRCONIDING AND HAFNIDING BASE METAL COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

A zirconide or hafnide coating is formed on specified base metal compositions by making the base metal the cathode joined through an external electrical circuit to a zirconium or hafnium anode in an electric cell having a specified fused salt electrolyte at a temperature of at least 900° C., but below the melting point of the metal composition. Such a combination is a self-generating cell producing electricity, but an external E.M.F. may be impressed providing the current density does not exceed 10 amperes/dm.^{2}. The process is useful in making tight adherent coatings composed of zirconium or hafnium and the base metal on the surface of the substrate.

This invention relates to a method for metalliding a base metal composition. More particularly, this invention is concerned with a process for zirconiding and hafniding a base metal composition in a fused salt bath.

It is known that zirconium can be electrodeposited on a metal composition having a melting point above 1000° C. to form a firmly adherent layer of zirconium joined to the metal composition by a metal-to-metal bond by electrodeposition in a fused salt bath. This method requires, however, that high current densities be employed together with high temperatures. Current densities in the range of 25–200 amperes/dm.^{2} are not unusual.

I have now discovered that uniform tough, adherent coatings of zirconium or hafnium can be formed on a base metal composition employing low current densities, that is, current densities in the range of 0.05–10 amperes/dm.^{2}. This electrodeposition of zirconium or hafnium is possible if certain critical steps are taken to insure the substantial absence of oxygen and oxide salts in the fused salt bath.

In accordance with the process of this invention, the zirconium or hafnium metal is employed as the anode and is immersed in a fused salt bath composed essentially of a member of the class consisting of the alkali metal fluorides and mixtures thereof and mixtures of the alkali metal fluorides with strontium or barium fluoride and containing from 0.01–5 mole percent of zirconium or hafnium fluoride. Higher concentrations of the zirconium or hafnium fluoride may be employed but no commensurate advantages are obtained thereby. The cathode employed is the base metal upon which the deposit is to be made. I have found that such a combination is an electric cell in which an electric current will be generated when an electrical connection, which is external to the fused bath, is made between the base metal cathode and the anode. Under such conditions, the metal in the anode dissolves in the fused salt bath and the metal ions are discharged at the surface of the base metal cathode where they form a deposit of zirconium or hafnium which immediately diffuses into and reacts with the base metal to form a metallide coating.

The alkali metal fluorides which can be used in accordance with the process of this invention include the fluorides of lithium, sodium, potassium, rubidium and cesium, and mixtures thereof. However, it is preferred to employ a eutectic mixture of sodium fluoride and lithium fluoride or lithium fluoride alone because some free alkali is generated and at the higher temperatures, i.e., 800°–1100° C., at which the process is normally conducted, the other alkali metal fluorides (potassium, rubidium and cesium) are volatilized with the obvious disadvantages. Mixtures of the alkali metal fluorides with strontium fluoride or barium fluoride can also be employed as a fused salt in the process of this invention. Calcium and magnesium fluorides can also be mixed with the alkali metal fluorides, but these salts often permit the incorporation of small amounts of calcium and magnesium in the diffusion coating and thus are not usually desirable.

The chemical composition of the fused salt bath is critical for optimum metalliding results. The starting salt should be as anhydrous and free of all impurities as is possible or should be easily dried or purified by simply heating during the fusion step. The process must be carried out in the substantial absence of oxygen since oxygen interferes with the process by forming zirconium or hafnium oxide and thereby preventing a firmly adhering film of zirconium or hafnium from being deposited on the base metal cathode. Thus, for example, the process can be carried out in an inert gas atmosphere or in a vacuum. By the term "substantial absence of oxygen" it is meant that neither atmospheric oxygen nor oxides of metals are present in the fused salt bath. The best results are obtained by starting with reagent grade salts and by carrying out the process under vacuum or in an inert gas atmosphere, for example, in an atmosphere of argon, helium, neon, krypton or xenon.

I have sometimes found that even commercially available reagent grade salts must be purified further in order to operate satisfactorily in my process. This purification can be readily done by utilizing scrap metal articles as the cathodes and carrying out the initial metalliding runs with or without additional applied voltage, thereby plating out and removing from the bath those impurities which interfere with the formation of high quality metallide coatings.

I have found that in order for the electrolytic cell of this process to work properly and to form a proper metallide coating which is not scaly due to the presence of the metal oxide, it is necessary to remove the last traces of oxygen and oxide compounds from the fused salt bath and to employ an inert atmosphere or a vacuum over the salt bath at all times to prevent the diffusion of oxygen into the salt bath. The oxygen can be removed from the fused salt bath by employing a carbon anode and running the bath as an electrolytic cell to remove the oxides and oxygen by means of the carbon anode. I have also found that the last traces of oxygen and oxides can be removed from the fused salt bath by maintaining the fused salt bath under an inert atmosphere and placing in the bath, strips or chips or zirconium or hafnium for a period of time until the strips or chips upon removal from the bath showed no evidence of pitting or other deterioration of the glossy, shiny surface of the metal due to the reaction of the zirconium or hafnium with oxygen.

I have also found that when the metal to be zirconided or hafnided is vanadium, niobium, tantalum, chromium, molybdenum or tungsten, it is necessary to

conduct the zirconiding or hafniding process in the absence of carbon and carbon compounds because carbon forms a very stable metal carbide on the surface of such base metals thereby rendering it impossible to further metallide the base metal and giving less firmly adhering deposits. I have found that carbon can be removed from the fused salt bath by operating it as a cell employing as a cathode, the base metals such as vanadium or niobium, until the carbide coating is no longer formed on the surface of the metal.

The base metals which can be zirconided or hafnided in accordance with the process of this invention includes the metals having atomic numbers 22–29, 40–47 and 72–79 inclusive. These metals are, for example, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, tantalum, tungsten, rhenium, iridium, platinum and gold. Alloys of these metals with each other or alloys containing these metals as the major constituent, that is, over 50 mole percent, alloyed with other metals as a minor constituent, that is less than 50 mole percent, can also be metallided in accordance with my process, providing the melting point of the resulting alloy is not lower than the temperature at which the fused salt bath is being operated.

In order to produce a reasonably fast plating rate and to insure the diffusion of the metal into the base metal to form a zirconide or hafnide, I have found it desirable to operate my process at a temperature no lower than about 900° C. It is usually preferred to operate at temperatures of from 900° C. to 1100° C. In this temperature range, I prefer to employ lithium fluoride as the fused salt in the bath.

When an electrical circuit is formed external to the fused salt bath by joining the anode to the base metal cathode by means of a conductor, an electric current will flow through the circuit without any applied electromotive force. The anode acts by dissolving in the fused salt bath to produce electrons and the metal ions. The electrons flow through the external circuit formed by the conductor and the metal ions migrate through the fused salt bath to the base metal cathode to be metallided, where the electrons discharge the metal ions, forming a metallide coating. The amount of current can be measured with an ammeter which enables one to readily calculate the amount of metal being deposited on the base metal cathode and being converted to the metallided layer. Knowing the area of the article being plated, it is possible to calculate the thickness of the metallide coating formed, thereby permitting accurate control of the process to obtain any desired thickness of the metallide layer.

Although the process operates very satisfactorily without impressing any additional electromotive force on the electrical circuit, I have found it possible to apply a small voltage when it is desired to obtain constant current densities during the reaction and to increase the deposition rate of the metal being deposited without exceeding the diffusion rate of the metal into the base metal cathode. The additional E.M.F. should not exceed 1.0 volts and preferably should fall between 0.1 and 0.5 volts.

When it is desirable to apply additional voltage to the circuit in order to shorten the time of operation, the total current density should not exceed 10 amperes/dm.^{2}. At current densities above 10 amperes/dm.^{2} the zirconium or hafnium deposition rate exceeds the diffusion rate and the base metal cathode becomes coated with a plate of zirconium or hafnium.

Since the diffusion rate of zirconium and hafnium into the cathode article varies from one material to another, with temperature, and with the thickness of the coating being formed, there is always a variation in the upper limits of the current densities that may be employed. Therefore, the deposition rate of the iding agent must always be adjusted so as not to exceed the diffusion rate of the iding agent into the substrate material if high efficiency and high quality diffusion coatings are to be obtained. The maximum current density for good zirconiding or hafniding is 10 amperes/dm.^{2}, when operating within the preferred temperature ranges of this disclosure. Higher current densities can sometimes be used to form coatings with zirconium or hafnium but in addition to the formation of a metallide coating, plating of the iding agent occurs over the diffusion layer.

Very low current densities (0.01–0.1 amp./dm.^{2}) are often employed when diffusion rates are correspondingly low, and when very dilute surface solutions or very thin coatings are desired. Often the composition of the diffusion coating can be changed by varying the current density, producing under one condition a composition suitable for one application and under another condition a composition suitable for another application. Generally, however, current densities to form good quality zirconide or hafnide coatings fall between 0.5 and 5 amperes per dm.^{2} for the preferred temperature ranges of this disclosure.

If an applied E.M.F. is used, the source, for example, a battery or other source of direct current, should be connected in series with the external circuit so that the negative terminal is connected to the external circuit, terminating at the metal being metallided and the positive terminal is connected to the external circuit terminating at the metal anode. In this way, the voltages of both sources are alegbraically additive.

As will be readily apparent to those skilled in the art, measuring instruments such as voltmeters, ammeters, resistances, timers, etc., may be included in the external circuit to aid in the control of the process.

Because the tough adherent corrosion resistant properties of the zirconide or hafnide coatings are uniform over the entire treated area, the coated metal compositions prepared by my process have a wide variety of uses. They can be used to fabricate reaction vessels for chemical reactions, to make gears, bearings, and other articles requiring hard, wear-resistant surfaces, and to prevent corrosion at high temperatures on gas turbine material, heating elements etc. Other uses will be readily apparent to those skilled in the art as well as other modifications and variations of the present invention in light of the above teachings.

In the specification and claims I use the term zirconide to designate any solid solution or alloy of zirconium and the base metal regardless of whether the base metal does or does not form an intermetallic compound with zirconium in definite stoichiometric proportions which can be represented by a chemical formula.

The following examples serve to further illustrate my invention. All parts are by weight unless otherwise stated.

EXAMPLE 1

Into a mild steel vessel (6" in diameter x 18" deep) fitted with a monel liner (5½" in diameter x 17¾" deep) was placed lithium fluoride (4680 grams) and sodium fluoride (5040 grams). The steel vessel was placed in an electric furnace. The vessel was fitted with a nickel plated steel top which contained a water channel for cooling, 2 ports for electrodes and another port for a thermocouple well and vacuum connections. The salts were then melted under vacuum. Argon was introduced into the cell and with an argon bypass to keep air excluded, zirconium tetrafluoride (160 grams), was then added to the molten salt (temp. 700° C.) through an electrode port.

A ⅛" diameter zirconium rod was immersed 6" into the salt and the voltage of the cell between the monel liner and zirconium rod measured at 1.1 volts. After 1½ hours in the cell at 800° C., 0.60 gram of zirconium was lost from the rod, and after another hour, only 0.14 gram was lost. These small losses indicated that the zirconium rod was not reducing Zr^{+4} ions to a lower valence state and valence change for electrochemical reduction should be 4.

The cell impurities in these were removed by operating the cell at 800° C. for using four different nickel cathodes (6" x 1" x 0.020") and a ⅛" zirconium rod as the anode. The results obtained are as given in the following table.

TABLE I

	Time (mins.)	Volts (anode polarity)	Current density amps./dm.²	Wt. gain grams	Percent coulombic efficiency
Run:					
1	30	−0.5	0.2	0.030	45
2	11	−0.03	0.6	0.047	65
3	80	−0.3	0.25	0.057	25
4	20	−0.2	0.25	0.065	98

The yields of zirconium collected on the nickel strips improved from 25 to 98%. However, it was noted that the zirconium anode was deteriorating much more rapidly than anodic solution could account for. It was also noted that when the zirconium electrode was pulled from the fluoride melt into the glass anode tower, "flame" surrounded the electrode for 1 to 2 minutes, although it was in an argon atmosphere. It is believed that this was due to the anodic formation of volatile $ZrOF_2$ which disproportionated to ZrF_4 and ZrO_2 when withdrawn from the liberation of enough heat and light to give the appearance of a flame. The oxygen in the electrolytic cell was removed by employing a carbon anode as described below.

A carbon anode was placed in the cell and the cell was run employing a nickel cathode for 41 hours at 0.5 amperes. The voltage stayed at 1.9 volts for 30 hours and then gradually increased to 3.0 volts at which point it leveled off, which indicated that the oxygen had been depleted from the bath.

After the clean-up by the use of the carbon anode in the cell, an attempt was made to zirconide a niobium strip. It was then discovered that metals such as niobium, tantalum, molybdenum and vanadium which form refractory carbides cannot be zirconided in a bath which contains carbon particles, which evidently disintegrated from the carbon anode. In order to zirconide such metals, it is necessary to further clean up the cell to remove the carbon present. Other materials like nickel and platinum which do not form stable carbides, can be zirconided even in the presence of impurities such as carbon. A series of metals were zirconided in the cell at 980° C. as shown in the following table.

TABLE II

Material	Time (mins.)	Current density amps./dm.²	Wt. gain grams	Coulombic efficiencies, percent
Ni	16	2.5	0.400	90
Ni	20	1.2	0.254	94
C.R. Steel (1015)	60	0.3	0.094	45
Pt	[1] 8	1.0	0.024	90
18-8S.S.	60	0.3	0.083	40
Cu	12	1.0	0.110	79
Silicided molybdenum	60	0.2	0.015	12

[1] 4 mins. as a battery.

At the temperature of 980° where the experiments given in the above table were operated, considerable sodium vapor (formed by zirconium through displacement) was continuously being evolved from the cell due to its volatility at the elevated temperature. This volatility makes it more desirable to employ pure lithium fluoride as the solvent in this process than to use mixtures containing alkali fluorides which can evolve volatile alkali metals at elevated temperatures.

When it was attempted to use sodium and calcium fluoride in this bath, it was discovered that the calcium contaminated the zirconide coatings. Thus, calcium salts can be used only where it is permissible or desirable to have calcium in the diffusion coating.

EXAMPLE 2

Lithium fluoride (7600 grams) was charged into the monel liner as described in Example 1 and the liner then fitted into the steel pot which was placed in a furnace.

The cover plate was attached to the pot and two glass electrode towers attached to the plate. The lithium fluoride was then melted (M.P. 846° C.) under vacuum (0.1 mm.) during a period of seven hours, forming 10" of molten salt. The salt was cooled to 650° C. and a mixture of lithium fluoride (600 grams) and zirconium fluoride (200 grams) was added to the pot. Nitrogen was swept over the salt for 10 minutes to flush out moisture and air and the salt was then remelted in a nitrogen atmosphere. Argon was then introduced into this cell and after flushing to remove the nitrogen, a zirconium anode (⅛" rod) was immersed 2" into the salt and a nickel cathode (6" x 1" x 0.020" strip) was positioned in the electrode towers. Current was supplied from a commercial battery charger and the nickel strip was treated as follows:

TABLE III

	Temperature, ° C.	Volts (anode polarity)	Current density, amps./dm.²
Time (mins.):			
0	980	−1.0	0
4	990	−1.0	0
9	990	−0.6	[1] 0.5
26	990	−0.57	0.35
44	990	−0.57	[2] 0.35

[1] Circuit closed as a battery.
[2] Circuit opened.

The nickel strip was withdrawn from the salt bath, allowed to cool in the argon atmosphere in the glass tower and then removed. After washing off the salts, the strip was found to have gained 168 mg. of a theoretical 185 mg. and to have increased 0.8 mils in thickness. Microscopic examination showed a diffusion coating approximately 1 mil thick that was considerably harder than the nickel and which strongly resisted the corrosive action of concentrated nitric acid. The strip could be bent through a ½" radius without cracking. X-ray emission spectroscopy showed high concentrations of zirconium in the coating.

EXAMPLE 3

After completion of Example 2, another nickel strip (5" x 1" x 0.020") was zirconided at 1000° C. in the same salt bath and under the conditions given in the following table.

TABLE IV

	Volts (anode polarity)	Current density, amps./dm.²
Time (mins.):		
0	−0.450	0.050 as a battery.
1	−0.400	0.020 as a battery.
2	−0.100	2.0 ext. emf. applied.
5	+0.100	Do.
30	+0.215	2.0.
45	+0.230	2.0 current off.
45:10	+0.030	0.
46	−0.017	0.
49	−0.000	0.
52	−0.005	0 sample out.

Only a few particles of salt adhered to the nickel strip when it was removed from the salt, and this was easily removed with scraping. The strip was very smooth and had gained 1.01 grams of a theoretical 1.21 grams and had increased 2.5 mils, in thickness. The 2.5 mils coating was very hard and markedly resisted the corrosive action of nitric acid.

EXAMPLE 4

The temperature of the salt bath in Examples 2 and 3 was increased to 1080° C. and another strip of nickel,

identical to the two previous samples was zirconided in a similar manner with the following results:

TABLE V

	Volts (anode polarity)	Current density, amps./dm.^{2}
Time (mins.):		
0	−0.450	0.05.
1	−0.220	2.0.
5	−0.110	2.0.
7	+0.068	2.0 current off.
15	−0.093	0.
16	−0.105	0 sample out.

As indicated in Table V, the rapid recovery of the anode to a negative polarity showed that the diffusion was exceedingly the deposition rate. The surface of the sample was very hard and smooth except near the edges where melting had begun to occur. The sample had gain −0.415 gram of a theoretical 0.425 mg. The properties were the same as the two previous samples. The melting indicates that the zirconium concentration on the surface of the nickel is between 20 to 40 atomic percent.

EXAMPLE 5

A strip of niobium (3.5" x 0.75" x 0.020") was immersed in the salt bath described in Example 2 and zirconided at 1080° C. according to the following conditions:

TABLE VI

	Volts (anode (polarity)	Amps.
Time (mins.):		
0	−0.500	0.11 as a battery.
4	−0.455	0.05 as a battery.
5	−0.035	0.2 current applied.
8	−0.002	0.2.
11	+0.009	0.2.
16	+0.022	0.2.
65	+0.029	0.2 current off.
65:10	−0.010	0.
66	−0.020	0.

The sample had gained 32 mg. of a theoretical 172 mg. and an X-ray emission analysis showed the presence of high concentrations of zirconium on the surface.

Three additional runs were made on an identical size niobium sample for 1 hour at a current density of 0.10 amps./dm.^{2}. These samples developed a deep gold color on the niobium surface and showed negligible weight gains. No zirconium was detected on the surfaces. The golden coating appeared to be niobium carbide and was a result of trace amounts of carbon in the bath which were electrolytically deposited on the surface and formed a barrier through which the zirconium could not diffuse.

The slow deposition rate in these latter three runs compared to that of the run of Table VI, allowed the niobium to become covered with carbon appreciable zirconium could be accumulated.

After additionally running the bath with niobium samples whereby the carbon was depleted, subsequent runs at both high and low densities showed increasing yields of zirconiding until both high and low current density runs gave substantially the same results. Typical examples of these high and low current density runs at 1100° C. are given in the following two tables which were made on niobium strips of 250 cm.^{2} each.

TABLE VII

	Volts (anode polarity)	Amps.
Time (mins.):		
0	−0.062	0 current on.
1	+1.43	20.
3	+1.40	20 current off.
3:10	+0.038	0.
4	+0.010	0.

The sample gained 634 mg. of theoretical 850, was very shiny and slightly granular in appearance.

TABLE VIII

	Volts (anode polarity)	Amps.
Time (mins.):		
0	−0.058	0 current on.
1	+0.245	2.5.
12	+0.250	2.5.
24	+0.250	2.5 current off.
24:10	+0.013	0.
25	+0.007	0.

The sample gained 851 mg. of a theoretical 850 mg. and was very shiny and smooth.

A series of metals and alloys was then zirconided at different temperatures in the lithium fluoride salt with the results shown in the following table:

TABLE IX

Metal	Temp., ° C.	Time, mins.	Current density, amps./dm.^{2}	Wt. gain, grams	Percent coulombic efficiences	Description of coating
Cobalt	1,100	60	1.0	0.185	100	Very shiny, smooth, fair flexibility, 1 mil thick, diffusion only, KHN 700–1,400.
Vanadium	1,100	30	1.2	0.046	54	Very shiny, smooth and flexible, 0.4 mil thick, diffusion plus dense plate.
Platinum	1,100	30	1.2	0.090	100	Very shiny, smooth, flexible, hard, 1 mil thick, diffusion only.
Mild Steel 1015	980	300	0.1	0.233	55	Very shiny, smooth, hard fair flexibility, 0.5 mil coat, diffusion only, very resistant to HNO_3.
Copper	980	10	1.2	0.110	79	Coating partially melted, moderately hard and flexible, improved resistance to HNO_3.
Molybdenum	1,100	60	0.5	0.170	89	Shiny, smooth, flexible, 0.5 mil thick, KHN 700–1,000, diffusion coating plus plating.
Tungsten	1,100	60	~0.2	0.038	22	Slightly granular surface especially at edges, mostly plating.
Tantalum	1,100	60	~0.2	0.056	66	Shiny, smooth, flexible, 0.25 mil thick, diffusion coat plus plating.
Rodar (Fe,Co,Ni)	1,100	60	0.5	0.168	100	Shiny, smooth, fair flexibility, hard, 0.5 mil thick, diffusion only, very resistant to HNO_3.
Inconel	(a) 1,100	120	1.0	0.149	88	(a) Some melting had occurred, ~1 mil coat. (b) Shiny, smooth, hard, 1 mil thick.
	(b) 1,000	120	1.0	0.129	76	
304 Stainless Steel	1,100	125	0.3	0.152	90	Very shiny, smooth, flexible, moderately hard, 0.5 mil coat, diffusion only, resistant to HNO_3.
Nb,Ti(5%)	1,100	60	0.5	0.085	100	Shiny, smooth, flexible, 0.6 mil thick, diffusion plus dense plating, KHN>1,000.
Nb,Ti,(25),Cr (5)	1,100	60	1.0	0.085	100	Shiny, smooth, flexible, 0.8 mil thick, diffusion plus dense plating KHN>1,000.
Borided Mild Steel (0.2% Ti)	1,100	60	0.6	0.134	79	Shiny, slightly granular, fairly flexible, very hard, 0.5 mil coat, diffusion only, very resistant to HNO_3.
Chromided Mild Steel (0.2% Ti)	1,100	60	0.3	0.078	92	Shiny, smooth, very flexible, 0.3 mil coat, hard diffusion layer plus soft outer plate.
Silicided Molybdenum	1,100	60	0.5	0.175	100	Shiny, smooth, fair flexibility, hard, mostly diffusion, very resistant to high temperature oxidation.

EXAMPLE 6

A sample of titanium, 24 cm.² in area was zirconided in the cell described in Example 2 at 1100° C. in accordance with the following procedure:

TABLE A

	Volts (anode polarity)	Amps.
Time (mins.):		
0	+0.088	0.2
1	+0.124	0.2
71	+0.125	0.2
71:10	+0.104	0
72	+0.100	0

The sample gained 566 grams in weight, whereas the theoretical weight gain would be 204 grams. A metallographic inspection of the coating showed a coating which varied from 0.5 to 1.2 mils. in thickness and with a Knoop hardness number of approximately 1000. Microscopic examination of the surface of the sample showed it had an etched appearance indicating that titanium had been going into the solution from the surface and that the titanium ions displaced zirconium ions which then dissolved in the titanium surface, causing it to gain in weight. An X-ray emission examination of the sample showed high concentrations of both titanium and zirconium on the surface, but no other metals.

A second run at 1100° C. to check the displacement reaction was made employing ⅛" diameter rods of zirconium and titanium to a depth of 3" in the salt in accordance with the followings results:

TABLE B

	Zr-rods, volts	Amps.
Time (mins.):		
0	−0.001	No current.
2	−0.004	Was allowed.
5	−0.007	To flow.
17	−0.009	Through-out.
93	−0.010	This reaction.
120	−0.009	

As is indicated in the table, no current was allowed to flow during this reaction. The titanium gained 135 mg. (over 7.5 cm.² area) and 3 mils. in thickness and had a hardness greater than 700 (Knoop) to a depth of 8–10 mils. X-ray emission examination of the surface showed high concentrations of zirconium and titanium, but no other elements.

This example shows that although zirconium is slightly above titanium in the electromotive series, the difference is so low that titanium establishes an equilibration reaction with the zirconium solution, forming zirconium metal which then dissolves into the titanium metal surface. A hard zirconium-titanium alloy diffusion coating is thus formed on the titanium structure. The latter run shows that this can be done without the benefit of any applied current.

EXAMPLE 7

A halfnium anode can be substituted for the zirconium anode and hafnium fluoride for the zirconium fluoride in the lithium fluoride bath and the cell operated as given in the above examples to give hafnium diffusion coatings on the various base metal cathodes discussed above.

It will, of course, be apparent to those skilled in the art that conditions other than those set forth in the above examples can be employed in the process of this invention without departing from the scope thereof.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method of forming a zirconide or hafnide coating on a metal composition having a melting point greater than 900° C., at least 50 mole percent of said metal composition being at least one of the metals selected from the class consisting of metals whose atomic numbers are 22–29, 41–47 and 73–79, said method comprising (1) forming an electric cell containing said metal composition as the cathode, joined through an external electrical circuit to a zirconium or hafnium anode and a fused salt electrolyte which consists essentially of a member of the class consisting of lithium fluoride, sodium fluoride, mixtures thereof, and mixtures of said fluorides with strontium fluoride or barium fluoride and from 0.01–5 mole percent of zirconium fluoride or hafnium fluoride, said electrolyte being maintained at a temperature of at least 900° C. but below the melting point of said metal composition in the substantial absence of oxygen, (2) controlling the current flowing in said electric cell so that the current density of the cathode does not exceed 10 amperes/dm.² during the formation of the zirconide or hafnide coating, and (3) interrupting the flow of electrical current after the desired thickness of the zirconide or hafnide coating is formed on the metal object.

2. The process of claim **1** wherein the fused salt electrolyte consists essentially of lithium fluoride and zirconium fluoride or hafnium fluoride.

3. The process of claim **1** which is also conducted in the substantial absence of carbon.

4. The process of claim **1** wherein the absence of oxygen is obtained by using an inert atmosphere and by allowing zirconium or hafnium metal to be in contact with the fused electrolyte prior to carrying out the process until the oxygen has been depleted from the electrolyte bath.

5. The method of claim **1** wherein the metal composition is nickel.

6. The method of claim **1** wherein the metal composition is cobalt.

7. The method of claim **1** wherein the metal composition is vanadium.

8. The method of claim **1** wherein the metal composition is niobium.

9. The method of claim **1** wherein the metal composition is molybdenum.

10. The method of claim **1** wherein the metal composition is iron.

11. The method of claim **1** wherein the metal composition is titanium.

12. A product produced in accordance with the process of claim **1**.

References Cited

UNITED STATES PATENTS

2,828,251 3/1958 Sibert et al. ---------- 204—39

FOREIGN PATENTS

563,495 9/1958 Canada.
742,190 9/1966 Canada.

OTHER REFERENCES

J. Electrochemical Soc. v. 112, No. 3, 1965, p. 266.
J. Electrochemical Soc. v. 113, No. 1, 1966, pp. 61–62.

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