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PROCESS FOR YTTRIDING AND RARE EARTHIDING

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ABSTRACT OF THE DISCLOSURE

A metallide coating of yttrium or rare earth metal is formed on certain specified base metals by forming an electric cell containing said base metal as a cathode and a carbon anode or the coating metal as an anode using a specified fused salt electrolyte maintained at a temperature of at least 500° C., but below the melting point of said metal composition and controlling the current flowing in said electric cell, so that the current density of the cathode does not exceed 30 amperes/dm.^{2}. The deposited metal diffuses into the substrate so that the metallided coating is the composition containing both the deposited metal and the metal of the substrate. This process is therefore useful in forming a diffusion coating of the deposited metal and the substrate 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 electrolytically yttriding and rare earthiding a base metal composition in a fused salt bath, containing a fluoride of the metal to be deposited. The process can either be operated as a battery generating its own electromotive force or as an electrolysis cell wherein a current is supplied from an outside direct current source.

I have discovered that a uniform tough, adherent yttride and rare earthide coatings can be formed on a specific group of metals and alloys employing current densities in the range of 0.10 to 30 amperes/dm.^{2}.

In accordance with one aspect of the process of this invention, the yttrium or rare earth 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, mixtures thereof, and mixtures of the alkali metal fluorides with strontium and barium fluorides and containing from 0.01–40 mole percent of yttrium or a rare earth metal fluoride. The cathode employed is the base metal upon which deposit is to be made. I have found that such a combination is an electric cell in which an electric current is generated when an electrical connection, which is external to the fused bath, is made between the base metal cathode and the metal anode. Under such conditions, the anode metal dissolves in the fused salt bath and anode metal ions are discharged at the surface of the base metal cathode where they form a deposit of the anode metal which immediately diffuses into and reacts with the base metal to form a metallide coating. In the specification and claims I use the term "yttriding," "rare earthiding" and

"metalliding" to designate any solid solution or alloy of yttrium or a rare earth metal and the base metal regardless of whether the base metal does or does not form an intermetallic compound with yttrium or the rare earth metal in definite stoichiometric proportions which can be represented by a chemical formula.

The rate of dissolution and deposition of the yttrium or rare earth is self regulating in that the rate of deposition is equal to the rate of diffusion of the yttrium or rare earth into the base metal cathode. The deposition rate can be decreased by inserting some resistance in the circuit. A faster rate can be obtained by impressing a limited amount of voltage into the circuit to supply additional direct current.

The amount of the yttrium or rare earth metal fluoride present in the bath can be from 0.01 to 40 or more mole percent. It is preferred however that the concentration of the yttrium or rare earth fluoride be from 0.1 to 10 mole percent of the fused salt bath. Higher concentrations of the yttrium or rare earth fluorides, i.e., 30 mole percent or more, are necessary only where in the particular instance the displacement of lithium ions by yttrium or rare earth metal is to be almost completely suppressed.

The alkali metal fluorides which can be used in accordance with the process of the invention include the fluorides of lithium, sodium, potassium, rubidium and cesium and mixtures thereof. However, it is preferred to employ an eutectic mixture of sodium fluoride and lithium fluoride because some free alkali metal is produced by a displacement reaction and potassium, rubidium and cesium are volatilized with the obvious disadvantages. It is particularly preferred to employ lithium fluoride as the fused salt bath in which the yttrium or rare earth fluoride is dissolved, because at the temperatures at which the cell is operated, lithium metal is not volatilized to any appreciable extent. 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.

The chemical composition of the fused salt bath is critical if good metallide coatings are to be obtained. The starting salt should be as anhydrous and as 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 anode metal oxides and thereby preventing a firmly adhering film of the anode metal 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 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 an additional applied voltage, thereby plating

out and removing from the bath those impurities which interfere with the formation of high quality metallide coatings.

The base metals which can be metallided in accordance with the process of this invention included the metals having atomic numbers of 4, 21, 22, 25 to 29, 40, 43 to 47, 72 and 75 to 79, inclusive. These metals are, for example, beryllium, scandium, titanium, manganese, iron, cobalt, nickel, copper, zirconium, technetium, ruthenium, rhodium, palladium, silver, hafnium, rhenium, osmium, 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. It is preferred that the alloy contain at least 75 mole percent of the metal and even more preferred, that the alloy contain 90 mole percent of the metal with correspondingly less of the alloying constituent.

Although it has been found that it is not possible to metallide the highly refractory metals such as vanadium, chromium, niobium, molybdenum, tantalum and tungsten, I have unexpectedly discovered that if such refractory metals are covered with a thin layer of one of several specific iding agents, that these metals can then be satisfactorily yttrided or rare earthided. The special iding agents which I have found useful are beryllium, boron and silicon. These alloys are hereinafter referred to as beryllides, borides and silicides, respectively. The beryllided compositions are produced in accordance with the process of United States Patent No. 3,024,175, the silicided compositions in accordance with United States Reissue Patent No. 25,630, the borided compositions in accordance with the process of United States Patent 3,024,176, which patents are made a part hereof.

I have also found that it is advantageous to conduct the metalliding process in the absence of carbon, because carbon forms a very stable metal carbide on the surface of the base metals thereby rendering it very difficult 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, until the carbide coating is no longer formed on the surface of the base metal.

The form of the anode is not critical. For example, I can employ as the anode pure yttrium or rare earth metal in the form of a rod or the yttrium or rare earth metal can be employed in the form of chips in porous metal baskets, such as niobium or tantalum. I have also found that a shielded carbon anode can be substituted for the metal anode and the cell operated as an electrolytic cell by impressing some electromotive force from an outside source as hereinafter described.

In order to produce reasonably fast plating rates and to insure the fusion of the yttrium or rare earth into the base metal to form a metallide, I have found it desirable to operate my process at a temperature in the range of from about 500° C. to 1100° C. It is preferred to operate at temperatures of from 900°–1100° C.

The temperature at which the process of this invention is conducted is dependent to some extent upon the particular fused salt bath employed. Thus, for example, when temperatures as low as 500° C. are desired, a eutectic of sodium, potassium and lithium fluoride can be employed. Inasmuch as the preferred operating range is from 900° C. to 1100° C., I prefer to employ lithium fluoride as the fused salt.

When an electrical circuit is formed external to the fused salt bath by joining the metal anode to the base cathode by means of a conductor, an electric current will flow through the circuit without any applied electromotive force. The metal anode acts by dissolving in the fused salt bath to produce electrons and anode metal ions. The electrons flow through the external circuit formed by the conductor and the anode metal ions migrate through the fused salt bath to the base metal cathode to be metallided, where the electrons discharge the 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 metallide 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 as a battery 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 volt and preferably should fall between 0.1 and 0.5 volt.

Since the diffusion rate of yttrium and rare earth metals 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 metalliding is 30 amperes/dm.^{2}, when operating within the preferred temperature ranges of this disclosure. Higher current densities can sometimes be used to form coatings with yttrium or the rare earth metals 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 ampere/dm.^{2}), employed when diffusion rates are correspondingly low, and when very dilute surface solutions or very thin coatings are desired, can only be used profitably when high concentrations of the iding ion (>5%) or lithium metals (~1%) are in the salt. Often the compositions 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 metallide coatings fall between 1 and 10 amperes per dm.^{2} for the preferred temperature ranges of this disclosure. The higher current densities (10–30 amps/dm.^{2}) can only be used on a few metals, such as nickel and cobalt, where diffusion is very rapid due to tremendous reactivity in the formation of intermetallic compounds.

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 base 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 algebraically 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.

I have found that when a base metal has been metallided in accordance with the process of this invention, that such metallided base metal should be removed from the fused salt electrolyte within a reasonable time. It has been found that if such metallided base metal composition is allowed to remain in contact with the fused salt

bath, that a displacement reaction takes place wherein the yttrium or rare earth in the metallided base metal reacts with the alkali metal fluoride to produce free alkali metal and the fluoride of the yttrium or the rare earth metal.

The description of the process of this invention as given hereinabove has been primarily described with reference to the employment of a yttrium or rare earth metal anode and operating the process as a battery. I have also found that a shielded carbon anode can be used in place of the yttrium or rare earth metal anode and the cell operated as an electrolysis cell wherein the electromotive force which allows the cell to operate is derived from an outside source of direct current such as a battery.

I have found that in the electrodeposition and metalliding with yttrium, or the rare earth fluorides, that the limitations on current density as set forth above should be maintained. It has been found however that the voltage applied to the electrolytic cell when a carbon anode is employed must be increased to from about 1 to 3.0 volts. If the carbon anode has insufficient surface area, voltage can, of course, go much higher.

When the cell is operated with a carbon anode, carbon tetrafluoride is produced at the anode and escapes as a gas, and the metal ions migrate to the cathode where they are deposited and diffuse into and react with the base metal to form a metallide coating. Extended operations with carbon anodes would obviously require the addition of yttrium or rare earth fluorides from time-to-time as the iding ions were depleted from the salt.

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

Example 1

Lithium fluoride (6810 grams) was charged into a Monel liner (5½" diameter x 12" deep) fitted into a mild steel pot (6" in diameter x 18" deep). The pot was placed in an electric furnace (6½" in diameter x 20" deep). The mild steel pot was flanged at the upper portion and sealed with a cover plate of nickel plated steel which contained a water channel for cooling, two ports (2½" in diameter) for glass electrode towers and two 1" ports for a thermocouple probe and a gas bubbler or vacuum connection. A vacuum was pulled on the cell and the lithium fluoride melted. Argon was then bled into the cell and yttrium fluoride (91 grams) was added to the molten lithium fluoride. A ¼" diameter graphite anode shielded with a Monel screen to prevent carbon particles from getting into the salt, was then immersed in the molten lithium fluoride to a depth of 4 inches. A nickel strip (1" x 5" x 0.02") was employed as a cathode and the temperature maintained at 1000° C. for the times, volts and amperes as set forth in the following table.

TABLE I

Time (min.)	Volts (anode polarity)	Amperes
0	+0.04	0.0
1	+1.90	0.5
11	+2.10	0.5
31	+2.50	0.5
32	+0.82	0.0

The nickel cathode had gained 0.014 gram in weight, (theoretical yield 0.270 gram, for cathode reaction of $Y^{+3}+3e \rightarrow y^0$) and was dull grey in color. An X-ray emission analysis showed the presence of large amounts of yttrium on the surface of the nickel.

Example 2

In this example an yttrium anode was employed in place of the shielded carbon anode described in Example 1. The cell was run at 1000° C. using a nickel strip, as in Example 1, for the cathode. Table II shows the results at low current densities.

TABLE II

Time (min.)	Volts (anode polarity)	Current density, amps/dm.²	
0	−0.410	0	
1	−0.300	0.60	Current on.
25	−0.150	0.60	
47	−0.100	0.60	Current off.
47:10	−0.210	0	
48	−0.260	0	Sample out.

The nickel cathode gained 0.129 gram of yttrium, which corresponds to a 60% yield, and developed a yttride coating 1 mil thick. The battery characteristics of the reaction are obvious from the negative polarity of the anode.

Table III gives the conditions of a high current density run at 1000° C. employing a nickel cathode and yttrium anode.

TABLE III

Time (min.)	Volts (anode polarity)	Current density, amps/dm.²	
0	−0.420	0	
1	+0.320	10	Current on.
4	+0.56	10	Current off.
4:10	−0.16	0	
5	−0.20	0	Sample out.

The nickel cathode gained 0.266 gram of yttrium, which corresponds to a 91% yield, and developed a 2 mil thick coating.

It was found that the yttrided samples should be removed from the cell immediately after removal of the current, because allowing the yttrided sample to remain in contact with the lithium fluoride bath permitted the yttrium to go into solution displacing lithium ions. This was demonstrated by placing two samples of yttrided nickel in a bath for different lengths of time. The first for 60 minutes and the second for 10 minutes respectively. The sample remaining in the bath for 60 minutes lost 0.062 gram whereas the sample remaining in the bath for 10 minutes lost only 0.020 gram. A nickel strip placed in the bath was unaffected.

Example 3

In a series of runs at 850° to 1100° C. using nickel strips as cathodes and shielded carbon rods as anodes, current density and yttrium fluoride concentration were found to have large effects on the yield of yttriding, as shown in Table IV.

TABLE IV

YF_3 concentration, mole percent	Volts, anode polarity	Current density, amps/dm.²	Average coulombic efficiency (percent)
0.23	+0.5–+2.5	0.05–1.0	15
0.59	+0.8–+3.5	0.1–2.0	25
1.12	+0.8–+3.5	0.1–2.0	35
1.79	+0.8–+3.5	0.1–2.0	40
2.31	+0.8–+3.5	0.1–2.20	45
2.31	+2.0–+5.0	5–10	90
6.7	+3.0–+10.0	5–30	>95

In all the runs shown in Table IV, shiny, smooth yttride coatings were produced on the nickel cathodes at all the different concentrations and current densities. The coatings were very flexible and quite hard (600–900 Knoop hardness). X-ray emission analyses showed both nickel and yttrium to be present on the surface of the yttrided strips, indicating that yttrium was diffusing into the nickel very rapidly. Crystallographic examination on the intermetallic compound coatings showed that YNi_5 was formed predominately at low current densities and YNi_2 at the higher current densities.

Example 4

A large number of runs employing base metal cathodes were made in a lithium fluoride cell as shown in the following table, which gives the conditions of the reaction together with the results.

TABLE V

Metal	Temp., ° C.	Time (min.)	Current Density, amps/dm.²	Weight gain, grams	Percent coulombic efficiency	Description of coating
Nickel	1,050	2	30.0	0.705	96	5 mil coat; shiny, smooth, flexible, hard (600-900 KHN).
Cobalt	900	2	16.7	0.140	95.5	1 mil coat
Do	900	16	2.1	0.105	71.5	0.7 mil coat } Shiny, smooth, flexible, hard, (500-800 KHN).
Do	900	32	1	0.058	39.4	0.4 mil coat
Ti-Namel	900	2	23.6	0.158	43	1 mil coat
Do	900	3	9.4	0.147	67	1 mil coat } Shiny, smooth, very flexible, hard (500-800 KHN).
Do	900	20	1.2	0.009	5	0.1 mil coat
Iron-chromium(28)	900	8	5.1	0.146	40	1 mil coat; shiny, grainy, flexible, soft, mainly plate plus some diffusion layer.
Zirconium	900	2	14.3	0.042	57	0.2 mil coat; shiny, smooth, very flexible.
Rhenium	900	3	1.3	0.085	17	~0.1 mil coat; shiny, smooth, flexible, surface softer than rhenium, some diffusion, mostly plating.
Platinum	900	3.5	1.3	0.095	100	2 mil coat; shiny, smooth, brittle, hard.
Palladium	900	12	3.3	0.018	100	1 mil coat; shiny, smooth, brittle, hard (~500 KHN).
Silicided molybdenum*	900	1	32	0.027	36	0.5 mil coat; shiny, smooth, fairly flexible, soft plated yttrium surface over hard ternary layer

*The molybdenum had been coated with a silicide coating in accordance with Reissued Patent No. 25,630, reissued Aug. 4, 1964.

Example 5

A carbon electrode was substituted for the yttrium anode in the previous example and some additional metals yttrided in accordance with the same general procedure with the results given in Table VI.

The cell was then run for 5 ampere hours against 7 different nickel cathodes to remove impurities from the cell. At the end of these runs, the nickel cathode strips came out shiny and smooth and the yield had increased to 70% of theoretical.

TABLE VI

Metal	Temp., ° C.	Time (min.)	Current density, amps/dm.²	Volts, anode polarity	Weight gain, grams	Percent coulombic efficiency	Description of coating
Borided niobium	940	3	26	+3-5	0.105	19	1 mil Y-B-Nb coat; shiny smooth, very flexible, soft plated yttrium surface over hard inner ternary layer.
Borided (304) stainless steel.	940	3	15	+2-3	0.153	56	1 mil Y-B-SS coat; shiny, bumpy (from surface melting) moderately flexible, soft yttrium surface over hard boride inner layer.
Stainless steel	980	10	8	+2-4	0.480	31	1 mil coat; shiny, bumpy (from surface melting), moderately flexible, hard (700-800 KHN).
Monel	1,100	10	8	+2-3	0.165	45	1.2 mil coat; shiny, smooth, moderately hard (400-500 KHN).
Borided nickel	940	3	25	+2-3	0.462	84	~3 mil Y-B-Ni coat; 3 mil B-Ni coat; smooth, shiny, very hard, flexible.

Example 6

To a melt of lithium fluoride (3178 grams) contained in the same equipment as described in Example 1, was added 110 grams of gadolinium trifluoride. A ¼" diameter shielded graphite anode was then immersed through one of the ports into the salt to a depth of four inches, and a nickel strip (6" x ¾" x 0.020") was immersed in the salt through the other port as a cathode. The cell was maintained at 945° C. and was run as indicated in the following table.

TABLE VII

Time	Volts, anode polarity	Current density, amps/dm.²	
0	−0.07	0	
1	+3.70	3.0	Current on.
5	+4.10	3.0	
31	+4.60	3.0	Current off.
32	+1.77	0	Sample out.

The nickel sample was covered with a black material which readily washed off, revealing a hard grey, flexible coating which was 2 mils thick. The nickel cathode sample had gained 0.835 gram as compared to a theoretical of 1.955 (for the reaction $Gd^{+3}+3e \rightarrow Gd°$) for a 43% yield. X-ray emission spectra showed the presence of large amounts of gadolinium in the surface of the nickel strip.

Example 7

A gadolinium anode was substituted for the carbon anode of Example 6 and the cell run employing a nickel strip as a cathode (4" x 1" x 0.020") at a temperature of 1000° C. in accordance with conditions set forth in the following table.

TABLE VIII

Time	Volts, anode polarity	Current density, amps/dm.²	
0	−0.250	0	
1	−0.540	0	
2	+1.03	10.0	Current on.
6	+1.02	10.0	Current off.
6:10	−0.16	0	Sample out.

The nickel cathode had gained 0.628 gram of a theoretical 0.652 gram and developed a coat that was shiny, smooth, hard and flexible and was 2 mils thick.

When the cell was operated employing a nickel cathode at lower current densities (1–3 amps./dm.²) yields of 40–50% were obtained.

The cell was then run employing the procedure of Example 5 with a gadolinium or carbon anode and a metal cathode under the conditions and with the results shown in the following table.

TABLE IX

Metal	Temp., °C.	Time, min.	Volts, anode polarity	Current density, amps/dm.[2]	Weight gain, grams	Percent coulombic efficiency	Description of coating
1015 steel [1]	1,000	5	+0.42	5	0.159	40	0.5 mil coat; shiny, smooth, flexible, moderately hard.
Cobalt [1]	1,000	4	+0.75	15	0.542	83	2 mil coat; shiny, smooth, flexible, hard.
Vanadium [1]	1,000	120	−0.11−−0.60	8	0.064	8	0.3 mil coat; shiny, smooth, flexible, hard.
Copper [1]	900	2	+1.0	5	0.060	90	Surface melted, shiny soft, flexible.
Palladium [1]	900	3	+0.4	12	0.149	38	2 mil coat; shiny, smooth, soft, flexible.
Kovar [1]	1,000	5	+0.3	8	0.095	29	0.5 mil coat; shiny, smooth, moderately hard, brittle.
Monel [1]	900	3	+1.15	12	0.600	77	1 mil coat; shiny, smooth, moderately flexible and hard.
β-Titanium,[1] 13% vanadium, 11% chromium, 3% aluminum.	1,000	5	1.85	20	0.231	15	0.5 mil coat; grey, smooth, flexible, soft; Cd plate overlaid inner layer.
Zirconided [2 3] Niobium.	1,000	15	+0.23	0.7	0.040	14	0.2 mil outer coat; shiny, smooth, hard over 1.5 mil soft inner layer; total coating flexible.
Borided [1] Ti-Namel	1,000	5	+0.33	4.0	0.153	47	0.5 mil outer coat, shiny, smooth, very hard over 1.5 mil inner coat; total coating flexible.
Scandided [1 4] nickel	1,000	60	−0.38−−0.08	0.75	0.864	88	1.5 mil outer layer, shiny, smooth, very hard, over 1 mil inner layer, moderately hard; total coating flexible.

[1] Gadolinium anode.
[2] Shielded carbon anode.
[3] The niobium was zirconided in accordance with the procedure set forth in my application Ser. No. 593,274, filed concurrently herewith.
[4] The nickel was scandided in accordance with the procedure set forth in my application Ser. No. 593,270, filed concurrently herewith.

It will, of course, be apparent to those skilled in the art that modifications 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 metallide coating of a metal of the group consisting of yttrium, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium thulium, ytterbium and lutetium on a base metal selected from the group consisting of (a) metal compositions having a melting point greater than 900° C., at least 50 mole percent of which is at least one metal selected from the group of metals whose atomic numbers are 4, 21, 22, 25 to 29, 40, 43 to 47, 72 and 75 to 79 and (b) a member of the class consisting of beryllided, borided, and silicided, vanadium, chromium, niobium, molybdenum, tantalum and tungsten, which comprises (1) forming an electric cell containing said base metal as the cathode, a carbon anode or said coating metal as an anode and a fused salt electrolyte consisting esentially of a member of the class consisting of lithium fluoride, sodium fluoride, mixtures thereof and mixtures of the said fluorides with barium fluoride or strontium fluoride, and containing from 0.01 to 40 mole percent of a fluoride of the coating metal, 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) passing a current between said anode and said cathode sufficient to establish a cathode current density of from 0.01 to 30 amperes per square decimeter and a cell voltage below 3.0 volts, (3) interrupting the flow of electrical current after the desired thickness of the metallide coating is formed and (4) immediately removing the metallided base metal composition from the fused salt electrolyte.

2. The method of claim 1 wherein the carbon anode is shielded with a tightly woven metal screen, such as niobium, molybdenum, tantalum, tungstun and iron.

3. A method of forming a yttride or rare earthide coating on a base metal selected from the class consisting of (a) metal compositions 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 4, 21, 22, 25 to 29, 40, 43 to 47, 72 and, 75 to 79, and (b) a member of the class consisting of beryllided, borided and silicided vanadium, chromium, niobium, molybdenum, tantalum and tungsten, said method comprising (1) forming an electric cell containing said base metal as the cathode, joined through an external electrical circuit to a yttrium or rare earth metal 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 0.1–40 mole percent of yttrium fluoride or a rare earth 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 aof the cathode does not exceed 10 amperes/dm.^{2} during the formation of the metallide coating, and (3) interrupting the flow of electrical current after the desired thickness of the yttride or rare earthide coating is formed on the metal composition.

4. The method of claim 3 wherein the fused salt electrolyte consists essentially of lithium fluoride and the fluoride of the metal being deposited to form the metallided coating.

5. The method of claim 3 which is also conducted in the substantial absence of carbon.

6. The method of claim 3 wherein the absence of oxygen is obtained by use of an inert gas in the cell.

7. The method of claim 3 wherein the metal composition is nickel.

8. The method of claim 3 wherein the metal composition is cobalt.

9. The method of claim 3 wherein the metal composition is titanium.

10. The method of claim 3 wherein the metal composition is zirconium.

11. The product produced by the process of claim 1.

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