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3,489,537

ALUMINIDING

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ABSTRACT OF THE DISCLOSURE

Aluminide coatings are formed on specified metal compositions by forming an electric cell containing said metal composition as the cathode joined through an external electrical circuit to an aluminum anode using a specified fused salt electrolyte maintained at a temperature of at least 600° C., but below melting point of said metal composition. This cell generates electricity, but if desired an E.M.F. may be impressed on the circuit providing the density of the cathode does not exceed 10 amperes/dm.². The aluminum diffuses into the base metal to form a coating on the substrate composed of aluminum and the substrate metal. This process is useful in making such coatings on the substrate metals.

This invention relates to a method for metallizing a base metal composition. More particularly, this invention is concerned with a process for aluminiding a base metal composition in a fused salt bath.

Aluminiding has been a valuable commercial process for many years and is usually accomplished by the immersion of base metals in molten aluminum. This method of aluminiding has the disadvantages in that the amount and degree of aluminiding cannot be accurately controlled, and it is difficult to avoid having free aluminum on the surface and some metals dissolved in the aluminum.

I have discovered a method whereby I can aluminide base metals without the above disadvantages.

I have discovered that a uniform tough, adherent aluminide coating can be formed on a specific group of metals employing low current densities, that is, current densities in the range of 0.05–10 amperes/dm.².

In accordance with the process of this invention, the aluminum 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 with a member of the class consisting of calcium, strontium and barium fluorides and containing from 0.01–5 mole percent of aluminum 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 aluminum anode. Under such conditions, the aluminum dissolves in the fused salt bath and aluminum ions are discharged at the surface of the base metal cathode where they form a deposit of aluminum which immediately diffuses into and reacts with the base metal to form an aluminide coating. In the specification and claims I use the term "aluminide" to designate any solid solution or alloy of alu-

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minum and the base metal regardless of whether the base metal does not form an intermetallic compound with aluminum in definite stoichiometric proportions which can be represented by a chemical formula.

The rate of dissolution and deposition of the aluminum is self regulating in that the rate of deposition is equal to the rate of diffusion of the aluminum 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 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. 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 aluminum 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 calcium fluoride, strontium fluoride and/or barium fluoride can also be employed as a fused salt in the process of this invention.

The amount of aluminum fluoride in the fused salt bath can be from 0.01 to 5 mole percent. Preferably the amount of aluminum fluoride is maintained at about 0.1 to 0.5 mole percent.

The chemical composition of the fused salt bath is critical if good aluminide 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. Because oxygen interferes, the process must be carried out in the substantial absence of oxygen. 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 forming gas (10% H₂, 90% N₂), nitrogen, 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 aluminiding runs with or without an additional applied voltage, thereby plating out and removing from the bath those metal impurities which interfere with the formation of high quality aluminide coatings.

The base metals which can be aluminided in accordance with the process of this invention included the metals having atomic numbers of from 23 to 29, 41 to 47, and 73 to 79 inclusive. These metals are, for example, vanadium, chromium, manganese, iron, cobalt, nickel, copper, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, tantalum, tungsten, 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 aluminided 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.

I have also found that when the metal to be aluminided is vanadium, niobium, tantalum, chromium, molybdenum or tungsten, it is advantageous to conduct the aluminiding process in the absence of carbon, because carbon forms a very stable metal carbide on the surface of such base metals thereby rendering it difficult to further aluminide 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 metals such as vanadium or niobium, until the carbide coating is no longer formed on the surface of the metal.

Inasmuch as titanium, zirconium and hafnium are more electropositive than aluminum, it is not possible to aluminide these metals while operating the cell as a battery. I have found, however, that titanium, zirconium or hafnium can be aluminided if a negative potential is applied to the titanium, zirconium or hafnium cathode. By the term "electropositive" is meant that titanium, zirconium and hafnium more readily give up their electrons and become positive ions than does aluminum. Thus, for example, if titanium is put in contact with a fused salt bath containing aluminum ions, the titanium loses its electrons to the aluminum and displaces the aluminum ions from the fused salt bath.

I have found that when a negative potential of at least 0.1 volt is applied to the titanium, zirconium or hafnium cathode, that these metals can be aluminided. Otherwise, the aluminiding is not readily controllable inasmuch as such cathodes, when placed in contact with the bath, immediately begin to displace the aluminum ions with resultant loss of the base metal from the cathode. I have discovered that the loss of the base metal of the cathode can be prevented by placing a negative potential on the cathode before it is immersed in the fused salt bath to complete the electrical circuit and start the aluminiding, immediately upon contact of the cathode sample with the fused salt.

I have also found that the displacement reaction will still take place after the titanium, zirconium or hafnium cathode has been aluminided, if the circuit is broken prior to removing the cathode from the bath. It is therefore essential if a controlled aluminiding is to take place, that a negative potential be maintained on the cathode at all times when the cathode is in contact with the fused salt electrolyte.

The amount of the negative potential necessary to be applied to the titanium, zirconium or hafnium must be at least 0.1 volt and can be from 0.1 to 5.0 volts, and is preferably from 0.5 to 2.0. After the cathode has been inserted in the bath, it is, of course, necessary to see that the current density is within the above-defined limits if good aluminide coatings are to be obtained.

The aluminiding of titanium, hafnium or zirconium must, of course, be conducted in the substantial absence of oxygen and carbon as set forth above.

Inasmuch as aluminum has a melting point of 660° C. and the cell is operated at temperatures above 660° C., it is necessary to employ as the anode an alloy of aluminum and nickel if a rod-type electrode is to be used. I have also found that aluminum can be employed in liquid form if it is placed in a graphite basket which has been shielded by means of a tightly woven monel screen to prevent carbon from contaminating the fused salt bath. I have also found that a nickel strip which has been

previously aluminided in accordance with the process of this invention can be employed as the anode.

In order to produce a reasonably fast plating rate and to insure the diffusion of the metal into the base metal to form an aluminide, I have found it desirable to operate my process at a temperature no lower than about 600° C. It is usually preferred to operate at temperatures of from 900°–1200° C. and even more preferably, 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 700° C. are desired, an eutectic of 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 aluminum 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 aluminum 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 metallized, where the electrons discharge the aluminum ions as the aluminide 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 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 aluminum being deposited without exceeding the diffusion rate of the aluminum 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.

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 aluminum deposition rate exceeds the diffusion rate and the base metal cathode becomes coated with a plate of pure aluminum.

Since the diffusion rate of aluminum into the cathode articles 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 aluminiding is 10 amperes per dm.², when operating within the preferred temperature ranges of this disclosure. Higher current densities can sometimes be used to form coatings with aluminum 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 aluminide coatings

fall between 0.5 and 5 amperes/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 metallized 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.

Because the tough adherent corrosion resistant properties of the aluminide coatings are uniform over the entire treated area, the aluminum coated metal compositions prepared by my process have a wide variety of uses. They can be used to fabricate vessels for chemical reactions, to make gears, bearings and other articles requiring hard, wear and corrosion resistant surfaces, and other articles where close tolerances are needed. 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.

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

EXAMPLE 1

Lithium fluoride (9988 grams) was charged into a Monel liner (6" diameter x 17¼" deep x 1/16" thick) and fitted into a mild steel pot (6½" diameter x 18" deep x 1/4" thick) with top flange (11" diameter x 5/8" thick). A cover plate (11" diameter x 1" thick) with a water cooling channel and holes for two electrode ports, a bubbler and a thermocouple well, was then attached with a gasket to the flange of the cell. The cell was evacuated to 0.1 mm. pressure and the lithium fluoride melted (M.P. 846° C.). Argon was allowed to flow into the cell to break the vacuum and then with a flow of argon to prevent air from diffusing into the cell, high purity aluminum fluoride (150 grams) was added to the lithium fluoride. A carbon anode (3/8" diameter) completely surrounded by a Monel cloth screen (from which it was electrically insulated) was then introduced into the salt to a depth of 6" and the cell was run employing the cathodes shown in Table I to remove oxygen and other impurities from the fluoride salt.

TABLE I

Run	Time	Temp., ° C.	Volts, anode polarity	Current Density, amps/dm. ²	Weight gained	Percent coulombic efficiency
(1) (Ni)-----	30 min.-----	980	+1.7-2.2	1.2	0.060	36
(2) (Ni)-----	60 min.-----	1,000	+1.6-2.3	1.2	0.200	60
(3) (Ni)-----	14 hrs.-----	1,000	+1.2-1.6	0.2	1.54	60
(4) (Fe)-----	28 hrs.-----	1,000	+2.3-2.65	0.4	1.5	16

Coulombic efficiencies are based on the cathode reaction $Al^{+3} + 3e \rightarrow Al^0$

EXAMPLE 2

The carbon anode with the surrounding Monel screen employed in the cell in Example 1 was then removed and replaced by a graphite crucible (3" x 1") holding 60 grams of aluminum. The graphite cup was tightly fitted into a 1" Monel screen to prevent carbon particles from getting into the fused salt bath.

A piece of cold rolled steel 3" by 2" by 0.032" was placed in a fused salt bath as a cathode and the aluminid-

ing conducted at 1000° C. in accordance with the details given in the following table.

TABLE II

Time (min.)	Volts, anode polarity	Amps
0-----	-0.398	0
1-----	-0.400	0
2-----	+0.086	1.0 Current on.
3-----	+0.092	1.0
4-----	+0.112	1.0 Current off.
5-----	+0.025	0
7-----	+0.007	0
8-----	-0.002	0
16-----	-0.210	0
17-----	+0.040	0.5 Current on.
33-----	+0.086	0.5 Current off.
34-----	+0.051	0
45-----	+0.012	0
50-----	-0.005	0

Very little salt adhered to the steel sample on removal and was easily scraped off. The sample gained 0.059 gram which was exactly theoretical. The coating was shiny, smooth and had a thickness of 0.3 mil. The coating was much harder than the initial steel surface and resisted the action of nitric acid much better than the uncoated steel. X-ray emissions spectra showed the surface to be high in both aluminum and iron and to be substantially free of any other metal.

EXAMPLE 3

Employing the procedure described in Example 2, after inserting the aluminum-filled graphite crucible, a nickel cathode (6" x 1" x 0.020") was aluminided at 1000° C. in accordance with the conditions set forth in the following table.

TABLE III

Time (min.)	Volts, anode polarity	Amps
0-----	-9.255	0
1-----	-0.060	1.0 Current on.
2-----	-0.040	1.0
3-----	+0.030	1.0
5-----	+0.040	1.0 Current off.
5:10-----	-0.020	0
6-----	-0.030	0
7-----	-0.035	0

The sample was shiny and had almost no salt adhering to it when lifted from the fused salt bath. It had gained 0.030 gram as compared to a theoretical gain of 0.028 gram. The coating showed improved resistance to the action of nitric acid as compared to the action of nitric acid on pure nickel.

EXAMPLE 4

Following the procedure described in Example 2, the following metals are aluminided at 1000° C. in accordance with the conditions set forth in the following table.

TABLE IV

Run No.	Metal	Time	Current density amps/dm ²	Weight gain, grams	Percent coulombic efficiency	Description of clothing
1.....	C.R. Steel (1015).....	15 hrs.....	0.2	0.896	100	6 mil. coat, light grey, smooth, hard, flexible, resistant to HNO ₃ and oxidation at high temperature.
2.....	Nickel.....	3 hrs.....	0.6	4.486	100	2 mil. coat, grey, smooth, hard, brittle, very resistant to HNO ₃ .
3.....	Cobalt.....	5 hrs.....	0.3	0.127	85	1 mil. coat, shiny, smooth, hard, brittle, very resistant to HNO ₃ .
4.....	Vanadium.....	104 min.....	0.4	0.035	100	0.5 mil. coat, shiny, smooth, fair flexibility, very hard, very resistant to HNO ₃ , improved high temperature, oxidation resistance.
5.....	Chromium.....	117 min.....	1.2	0.036	100	1 mil. coat, dark grey, smooth, brittle.
6.....	Molybdenum.....	12 hrs.....	0.18	0.317	80	1.5 mil. coat, light grey, smooth, hard, very flexible, resistant to HNO ₃ and elevated temperature oxidation.
7.....	Niobium.....	20 min.....	0.3	0.103	100	0.3 mil. coat, greyish brown, smooth, fairly hard, very flexible, marked improvement in air oxidation resistance.
8.....	Platinum.....	10 min.....	5	0.028	100	0.5 mil. coat, shiny, smooth very flexible, hard.
9.....	Palladium.....	10 min.....	5	0.026	92	0.3 mil. coat, shiny, smooth, very flexible, hard.
10.....	Copper.....	63 min.....	1.0	0.378	100	3 mil. coat, shiny, golden colored, smooth, very flexible, slightly harder than base copper.
11.....	Chromium (18%) Iron (82%).....	390 min.....	0.4	0.415	99	2.5 mil. coat, shiny, smooth, hard, flexible.
12.....	Kovar.....	110 min.....	1.2	0.113	98	1.2 mil. coat, shiny, smooth, very hard, flexible.
13.....	Monel.....	12 hrs.....	0.25	0.700	100	4 mil. coat, shiny, smooth, hard, flexible, very resistant to HNO ₃ .
14.....	Stainless Steel (304).....	230 min.....	0.3	0.310	100	3 mil. coat, shiny, smooth, hard, very flexible, improved resistance to HNO ₃ .
15.....	Titanided Nickel.*.....	60 min.....	1.0	0.163	97	1 mil. outer coating of Al, Ti and Ni; outer coat hardest and most oxidation resistant.
16.....	Silicided Molybdenum*.....	53 min.....	0.25	0.009	74	0.5 mil. outer coat of Al, Si, and Mo, 0.5 mil. inner layer of Si and Mo; both coatings hard and oxidation resistant.
17.....	4140 Steel.....	153 min.....	0.2	5.02	100	15 mil. coat, shiny, smooth, moderately hard, flexible.

*The nickel sample was titanided in accordance with the process disclosed in application Ser. No. 593,275, filed concurrently herewith and assigned to the same assignee as the present invention and the molybdenum sample was silicided by the process disclosed in the United States Reissue Patent 25,630, which references are made a part of this application by reference.

EXAMPLE 5

The cell described in Example 2 was employed in this example. Inasmuch as titanium, zirconium, and hafnium are all more electropositive than aluminum (i.e., $Ti^0 \rightarrow Ti^{+3} + 3e^- > Al \rightarrow Al^{+3} + 3e^-$), it is necessary to keep a negative electrical force on the cathode at all times in order to prevent the displacement of aluminum ions from the fused salt bath by the titanium, zirconium or hafnium cathode. This is accomplished by connecting a battery or other source of direct current in series with the metal electrodes of the cell before the titanium electrode is allowed to come into contact with the salt. A potential of at least 0.1 volt is necessary to stop the displacement reaction, but a potential of 0.5 volt works better, and it can be considerably higher, i.e., up to 5 volts.

In operating this cell the negative potential was applied to the cathode prior to immersing the cathode in the fused salt electrolyte to complete the electrical circuit. Of course, prior to completion of the circuit, no current was flowing. At the end of each run, the electrical circuit was broken by withdrawing the cathode from the electrolyte prior to disconnecting the source of negative potential.

Table V summarizes the operating conditions and results of several runs wherein titanium, zirconium and hafnium were aluminided.

TABLE V

Run No.	Metal	Volts,* cathode polarity	Time (min.)	Current density, amps/dm ²	Weight gain, grams	Percent coulombic efficiency	Description of coating
18.....	Titanium.....	-1.0	3	3	0.050	96	0.5 mil. coat, grey, smooth, flexible and springy.
19.....	do.....	-5.0	5	10	0.270	96	1 mil. coating, grey, smooth, flexible and springy.
20.....	Beta-Titanium, 13% V, 11% Cr, 3% Al.....	-2.0	8	6	0.035	80	0.3 mil. coating, shiny, smooth flexible.
21.....	Zirconium.....	-2.0	10	5	0.099	89	0.5 mil. coat, grey, smooth, hard, flexible, marked improvement to air oxidation.
22.....	Hafnium.....	-2.0	3	7	0.020	80	0.5 mil. coat, shiny, smooth, flexible, very hard, very oxidation resistant at high temperatures.

*Before immersing cathode sample.

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 an aluminide 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 23 to 29, 41 to 47 and 73 to 79, said method comprising (1) forming an electric cell containing said metal composition as the cathode, joined through an external electrical circuit to an aluminum 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 calcium fluoride, strontium fluoride or barium 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/dm² during the formation of the aluminiding coating, and (3) interrupting the flow of electrical current after the desired thickness of the aluminiding coating is formed on the metal object.

2. The method of claim 1 wherein the fused salt elec-

trolyte consists essentially of lithium fluoride and aluminum fluoride.

3. The method of claim 1 which is also conducted in the substantial absence of carbonaceous materials.

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

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

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

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

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

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

10. The method of claim 1 wherein the metal composition is stainless steel.

11. A method of forming an aluminide coating on a metal composition selected from the class consisting of titanium, zirconium or hafnium and alloys thereof wherein at least 50 mole percent of said alloy is titanium, zirconium or hafnium, said method comprising (1) forming an electric cell containing said metal composition as the cathode, joined through an external electrical circuit to an aluminum 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 calcium fluoride, strontium fluoride or barium fluoride and from 0.01-5 mole percent of aluminum fluoride, said electrolyte being maintained at temperature of at least 900° C., but below the melting point of said metal composition in the substantial absence of oxygen, said cathode having a negative potential of from 0.1 to 5.0 volts, applied thereto prior to immersion of said cathode into said electrolyte to complete the electrical circuit, (2) thereafter 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 aluminide coating, and (3) withdrawing the cathode to interrupt the flow of electrical current after the desired thickness of the aluminide coating is formed on said cathode.

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

References Cited

UNITED STATES PATENTS

Re. 25,630	8/1964	Cook	204—39
3,024,175	3/1962	Cook	204—39
3,232,853	2/1966	Cook	204—39
3,024,176	3/1962	Cook	204—39
2,828,251	3/1958	Sibert et al.	204—39

OTHER REFERENCES

J. Electrochemical Soc., v. 112, No. 3, p. 266.

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U.S. Cl. X.R.

204—39