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PROCESS FOR METALLIDING ALUMINUM SURFACES

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ABSTRACT OF THE DISCLOSURE

Hard, adherent, tough, corrosion-resistant coatings are formed on aluminum by electrolytically depositing certain metals onto the aluminum surface employing certain fused salt mixtures as the electrolyte and at temperatures below the melting point of aluminum. These materials are useful to make gears, bearings and other articles requiring hard wear and corrosion-resistant surfaces.

This invention relates to a method for forming diffusion coatings on aluminum and aluminum alloy surfaces. More particularly this invention is concerned with an electrolytic process for alloying the surface of aluminum in molten salt baths.

It is known that diffusion coatings can be formed on metal surfaces by several high temperature processes—evaporative, gaseous, pack cementation, immersion in molten metals and electrolysis in molten salts. These methods, however, have been used almost exclusively to coat metals that melt above 1000° C. in which operating temperatures were usually above 800° C. and frequently at 1000–1200° C. The low melting point of aluminum (660° C.) and the high temperatures generally required for operating most of the coating processes had made it appear unlikely that diffusion coatings could be formed on aluminum and aluminum alloys.

It has been discovered, however, that hard, adherent, tough, corrosion resistant coatings can be formed on aluminum and aluminum alloys by electrolytically depositing certain metals onto the aluminum surface from fused halide salt mixtures operating at temperatures below the melting point of aluminum and using anodes of the material being deposited, current densities which match the diffusion rates, and atmospheres that are inert to the coating system.

In accordance with the process of this invention, a metalliding metal is employed as the anode and is immersed in a fused mixed halide bath composed essentially of a mixture of the chlorides, bromides, with or without the fluorides of members from the alkali, alkaline earth metals and from 0.01 to 100 mole percent of a halide of the metalliding metal. The cathode employed is aluminum or an aluminum alloy upon which deposit is to be made. It has been 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 aluminum cathode and the metalliding anode. Under such conditions, the metalliding metal dissolves in the fused salt bath and metalliding ions are discharged at the surface of the aluminum cathode where they form a deposit of the metalliding metal which immediately diffuses into and reacts with the aluminum to form a metallide coating.

In the specification and claims the term "metallide" is

employed to designate any solid solution or alloy of the metalliding metal and the aluminum metal substrate regardless of whether the aluminum does or does not form an intermetallic compound with the metalliding reagents in definite stoichiometric proportions which can be represented by a chemical formula.

The rate of dissolution and deposition of the metalliding agent is self-regulating in that the rate of deposition is equal to the rate of diffusion of the metalliding metal into the aluminum 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 molten salts that can be employed in the process of this invention are the mixtures of chlorides, and/or bromides, with or without the fluorides, of Group I–A, II–A metals and/or the halides of the metalliding metal being employed, that melt below the melting point of aluminum or the aluminum alloy coating being formed thereon, and which mixtures do not contain metal ions that interfere with the desired coating process. More specifically, the metal halide mixture, which can be employed in the process of this invention, includes the alkali and alkaline earth metal chlorides; mixtures of the above chlorides with the alkali and alkaline earth metal fluorides; mixtures of the alkali and alkaline earth metal bromides and chlorides; and mixtures of these bromides and fluorides providing the salt mixtures melt below the melting point of aluminum and the alloy coating being formed thereon. When a mixture containing substantial concentrations of fluoride is employed, it is preferred to avoid the use of the fluorides of potassium, rubidium and cesium because of the displacement of these metals by aluminum and the volatilization of these metals with obvious disadvantages. It is also advantageous, at times, to avoid the use of lithium salts in the melts because lithium sometimes diffuses into aluminum causing undesirable properties in the alloyed surface. In some instances it is possible to conduct the process of this invention employing a fused salt bath consisting essentially of the chloride or bromide of the metalliding metal and mixtures thereof or mixtures of the chloride or bromide with the fluoride.

Because of the low melting point of aluminum and some of the alloy surfaces formed on it, the temperature at which the process of this invention is operated is critical but can readily be determined by one skilled in the art from such melting points. The particular halide mixtures employed in the process of this invention must melt below the melting point of aluminum or the alloy coating. There are many chloride systems or mixed chloride-fluoride systems which melt low enough to permit their use. Many of these halide eutectic systems can be found in and in "Phase Diagrams for Ceramists" by Levin, Robbins, and McMurdie published by American Ceramic Society (1964) and in "Phase Diagrams for Nuclear Reactor Materials" by R. E. Thoma of Oak Ridge National Laboratory, ONRL–2548.

In order to produce diffusion coatings rapidly, it is preferred to operate the process of this invention at temperatures as high as possible; e.g., 500° C. to about 650° C. Inasmuch as the diffusion coatings of some metals form compounds that lower the melting point of aluminum, the process in those instances has to be run considerably below the melting point of aluminum; e.g., at 400 to 500° C. for magnesiding, etc. Other diffusion coatings form compounds that have very high melting points—

that is, the rare earth aluminides—and in such instances it is preferable to operate as close as possible to the melting point of aluminum; i.e., 600–650° C. It has been found that the density of the salts, about 2 to 3, will give sufficient bouyancy to the light weight aluminum that it is possible to operate very near to the melting point of aluminum without causing distortion of the parts being coated.

The metalliding reagents which can be diffused into aluminum in accordance with the process of this invention include the metals lithium, magnesium, scandium, yttrium, lanthanum and the natural rare earths of the lanthanide series, actinium and the natural rare earths of the actinide series, hafnium and zirconium. Combinations of these metalliding reagents can also be diffused into the aluminum surface—simultaneously, when proper adjustments of molar concentrations of the metalliding ions are made in the salt, and/or sequentially, by selecting the correct sequence as dictated by reactivities of the metalliding agents. The amount of metalliding halide in the fused salt bath can be from 0.01 to 100 mole percent. It is preferred in most instances for ecenomy that the amount of metalliding halide in the fused salt bath be maintained at about 0.1 to 50 mole percent, and even more preferred from 0.1 to 5 mole percent.

The chemical composition of the fused salt bath is critical if good metallide coatings on aluminum 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 most of the metalliding reagents which can be diffused into aluminum react with oxygen, nitrogen and hydrogen, the process must be carried out in an inert atmosphere and especially in the substantial absence of oxygen. Thus, for example, the process can be carried out in an argon gas atmosphere. 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 in an inert gas atmosphere, for example, in an atmosphere of argon, helium, neon, krypton or xenon, and in the case of magnesiding, in an atmosphere of nitrogen or forming gas (10% H_2, 90% N_2).

It has been found that even commercially available reagent grade salts must be purified further in order to operate satisfactorily in the process of this invention. The 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 metal impurities which interfere with the formation of high quality metallide coatings on aluminum.

When an electrical circuit is formed external to the fused salt bath by joining the metalliding anode to the aluminum 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 metalliding ions. The electrons flow through the external circuit formed by the conductor and the metal ions migrate through the fused salt bath to the aluminum metal cathode to be metallided, where the electrons discharge the metalliding ions and form a metallide coating on the aluminum. The amount of current can be measured with an ammeter which enables one to readily calculate the amount of metal being deposited on the aluminum 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, it has been found that it is possible to apply a small voltage to obtain constant current densities during the reaction, and to increase the deposition rate of the metalliding agent being deposited. The additional E.M.F. should be adjusted so that the diffusion rate of the metalliding reagent into the aluminum cathode is not exceeded. The additional E.M.F. (when external resistance is negligible) should not exceed 1.0 volt and preferably should fall between 0.1 and 0.5 volt.

Since the diffusion rate of the metalliding reagent into the aluminum varies from one reagent 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 will generally not exceed 10 amperes per dm.^{2}. Higher current densities can sometimes be used to form coatings 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 metallide coatings on aluminum fall between 0.1 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 aluminum cathode 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.

Because the tough adherent corrosion resistant properties of the metallide coatings are uniform over the entire treated area, the metallided aluminum compositions prepared by the process of this invention 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 this invention. All parts are by weight unless otherwise stated.

EXAMPLE 1

A mixture of barium chloride (1070 g., 5.2 moles), potassium chloride (555 g., 7.4 moles) and sodium chloride (342 g., 5.9 moles) was charged into a Monel pot (3¼" I.D. x 3½" O.D. x 12" deep, with a top flange 6½" x ½" thick) which was then sealed with a water-cooled nickel plated steel cover plate (6½" diam. x 1" thick) fitted with two glass electrode towers (1½" diameter), a bubbler for introducing inert gas beneath the salt and a thermocouple well for measuring and controlling the temperature of the molten salt. The cell was alternately evacuated to 0.5 mm. Hg and refilled with argon three times and then the salt was melted (M.P. 542° C.) and the temperature adjusted to 590° C. Anhydrous cerium chloride (2.3 g., .009 mole; 0.05 mol percent $CeCl_3$ in solution) was then added to the salt and a cerium metal anode (2" x ⅜" rod) was immersed ½ inch into the salt through one of the glass electrode towers. After positioning a cathode of nickel screen (5" x 1") in the salt through the other glass electrode tower, a cleanup electrolysis was run for sixteen minutes at 5 amperes in an argon atmosphere. A copper strip (5" x 1") was then immersed in the salt and cerided overnight at 590° C. to clean up the fused salt.

An aluminum strip (8 x 1.2 x 0.1 cm.) was then immersed in the salt for five minutes and found to have neither lost or gained weight and to have retained its smooth surface, demonstrating that aluminum was stable in the salt bath.

Cerium chloride (37.1 g., 0.15 mole) was added to bring total molar concentration of $CeCl_3$ in the fused salt to ∼0.9% and after one-half hour of electrolytic cleanup at 0.1 ampere against a nickel screen, an aluminum strip (8 x 1.2 x 0.1) was cerided at 600° C. as follows:

Time, Minutes	Volts, Anode Polarity	Amperes	Remarks
0	−0.85	0	
1	−0.41	0.2	Current on.
15	−0.45	0.2	Current off.
15:10	−0.60	0	
16	−0.62	0	Sample out.

The surface of the aluminum had developed a mat finish and the sample had gained 0.091 g. (theoretical=0.087 g.) of cerium. The presence of cerium was verified by X-ray emission. Another sample of aluminum treated in the same bath and at one ampere for thirty minutes gained 0.869 g. (theoretical=0.871 g.) of cerium, developed a silvery gray coating three mils thick which was aluminum ceride and had a Knoop Hardness Number (KHN) of about 450, which was much harder than aluminum, KHN about 30. The sample could be bent in a two inch radius before cracking on the compression side and in a one inch radius before cracking on the tension side. The surface of the sample was readily polished by emery paper into a smooth shiny surface that has retained its luster for three months in air; also the surface of the coating is resistant to both concentrated and dilute nitric acid. Pure cerium is very reactive with nitric acid and tarnishes rapidly in air.

More $CeCl_3$ (103 g., 0.42 mole—bringing total molar concentration of $CeCl_3$ in salt to 3.1 mole percent) was added to the salt and another coating made on an aluminum strip (8 x 1.2 x 0.1 cm.) at 580° C. as follows:

Time, Minutes	Volts, Anode Polarity	Amperes	Remarks
0	−0.56	0	
1	−0.24	0.5	Current on.
67	+0.30	0.5	Current off.
67:10	−0.15	0	
68	−0.47	0	Sample out.

The aluminum strip gained 1.050 g. (theoretical=.950 g.) and developed a five mil coating similar to the one previously described.

EXAMPLE 2

A mixture of barium chloride (1456 g., 7 moles) and lithium chloride (555 g., 9 moles) was melted in a cell identical to the one described in Example 1. An yttrium metal anode (∼½" square x 5" long) was immersed approximately one-half inch in the salt, and after 107 minutes of cleanup electrolysis in an argon atmosphere against a nickel screen cathode (5" x 1") at one ampere and 0.7 to 0.8 volt, 7.5 g. (.05 mole, 0.3 mole percent concentration in salt) of anhydrous YF_3 was added to the salt. An aluminum strip (8 x 1.2 x 0.1 cm.) was then immersed in the salt and yttrided at 580° C. as follows:

Time, Minutes	Volts, Anode Polarity	Amperes	Remarks
0	−0.55	0	
2	−0.40	0.1	Current on.
26	−0.43	0.1	Current off.
26:10	−0.54	0	
27	−0.54	0	Sample out.

The aluminum sample was washed free of salt and found to have gained 0.050 g. of yttrium (theoretical=0.044 g.) and developed a thin (0.3 mil), hard, light grey, smooth coating. X-ray examination proved the presence of yttrium and also trace amounts of barium.

After adding more YF_3 (25 g., 0.17 mole, increasing total concentration in salt to 1.4 mole percent) several samples of aluminum were yttrided and the barium content of the coatings decreased to very low traces or disappeared. After adding an additional 50 g. of YF_3 (0.34 mole, increasing total concentration in salt to 3.5 mole percent) no more barium was detected in any of the coatings, formed at either high or low current densities. A series of yttriding runs on aluminum at 560° C. in the yttriding cell containing 3.3 mole percent YF_3 are listed in Table I.

TABLE I.—YTTRIDED ALUMINUM

Run	Time, Min.	Volts, Anode Polarity	C.D.[1], Amp/$dm.^2$	Wt. Gain, Grams	Theor. Wt. Gain	Coating Thickness, Mils	Coating Description
1	1	−.6 to −.1	2	0.016	0.0147	∼.1	Bright mat finish, mod. hard.
2	1	−.6 to +.1	4	0.028	0.029	∼.2	Do.
3	1	−.6 to +.7	7	0.060	0.052	∼.3	Bright shiny finish, mod. hard.
4	1	−.6 to +1.0	10	0.060	0.073	∼.3	Dull brown finish, dendritic, mod. hard
5	30	−.6 to +.1	0.6	0.126	0.133	.8	Bright, smooth golden tint, mod. hard.
6	56	−.6 to +.1	0.5	0.193	0.205	1.5	Do.
7	120	−.6 to +.1	0.25	0.218	0.221	1.6	Do.
8	240	−.6 to +.02	0.15	0.266	0.266	2.0	Do.
9	900	−.6 to −.36	∼.035	0.588	∼0.600	3.0	Do.

[1] C.D. is Current Density.

EXAMPLE 3

A mixture of magnesium chloride (652 g., 7.7 moles) and potassium chloride (1035 g., 13.8 moles) was melted in a cell and in a manner identical to that described in Example 1.

Using argon as a cover gas, and a magnesium rod (½" diam. x 4" long) as an anode, 2.2 ampere hours of electrolytic cleanup of the salt was made with nickel strips and screen as cathodes (∼40 $cm.^2$ area) at 460–500° C. and at 0.1 to 1.5 volts).

An aluminum strip (8 x 1.2 x 0.1 cm.) was then immersed in the salt and magnesided at 500° as follows:

Time, Minutes	Volts, Anode Polarity	Amperes	Remarks
0	−0.15	0	
1	−0.034	0.1	Current on.
53	±0.000	0.1	
60	−0.004	0.1	Current off.
60:10	−0.046	0	
61	−0.046	0	Sample out.

The sample gained 0.044 g. (theoretical=0.045 g.) and developed a smooth shiny coating that was approximately one mil thick and considerably harder (∼200 KHN) than aluminum (∼30 KHN). The coating was very flexible, maintained its bright finish for several months exposure in air and X-ray examination showed it to be an alloy of aluminum and magnesium.

Several other magnesiding runs were made against aluminum strips in the cell described above with the results listed in Table II.

TABLE II.—MAGNESIDED ALUMINUM

Run	Time	Temp., ° C.	Volts, Anode Polarity	C.D.,[1] Amp./dm.^{2}	Wt. Gain, Grams	Theor. Wt. Gain, Grams	Coating Thickness, Mils	Coating Description
1	30 min	500	−.14 to +.01	0.25	0.043	0.045	1	Shiny, smooth, trace of melting.
2	4 Hrs	500	−.15 to +.03	0.5	0.145	0.180		Shiny, melted and ran to bottom.
3	30 min.	450	−.29 to +.15	1.0	0.075	0.091	2	Shiny coating, partial melting. KHN-170-250.
4	80 min	440	−.26 to +.04	0.25	0.043	0.060	1	Shiny, smooth, no melting.
5	30 min	440	−.26 to +.19	1.0	0.078	0.091	2	Dendritic, no melting.
6	3 Hrs	500	−.1 to −.005	0.125	0.076	0.070	2	Shiny, smooth, no melting.
7	4⅓ Hrs	440	−.06 to +.08	0.25	0.449	0.275	5	Do.

[1] C.D. is Current Density.

[2] At 440° C. thick, smooth, shiny coatings can be formed below 0.5 amp./dm.^{2}; above 0.5 ampere dendritic deposits occur; at 450° and above melting begins to occur unless current density is kept below 1 amp/dm.^{2}.

[3] At 500° C. good coatings up to several mils in thickness can be made if current densities are very low (~.125) so that coatings dilute in magnesium can be formed.

The results in Table II show that in the diffusion of magnesium into aluminum:

(1) At 440° C. shiny smooth coatings up to several mils in thickness can be formed at current densities below 0.5 amp/dm.^{2}, and above 0.5 ampere dendritic deposits are formed;

(2) At 450° C. and above, melting of the coating begins to occur unless the current density is kept below 1 amp/dm.^{2};

(3) At 500° C. good coatings greater than a mil in thickness can be made if the current densities are low (~0.125 amp/dm.^{2}) so that magnesium concentration in the coating remains low.

EXAMPLE 4

A mixture of barium chloride (1070 g., 5.1 moles), potassium chloride (550 gm., 7.4 moles), and sodium chloride (342 g., 6.0 moles) was charged into a cell identical with that used in Example 1 and the salt melted down in a similar manner. Uranium tetrachloride (7.1 g., 0.018 mole) was added to the salt and using argon as a cover gas and a uranium rod (1" x 5") as an anode 2.3 ampere hours of electrolysis was run against nickel screens. After the cleanup runs an aluminum coupon (8 x 1.2 x 0.1 cm.) was uranided at 590° C. as follows:

Time, Minutes	Volts, Anode Polarity	C.D., Amperes	Remarks
0	−.36	0	
1	−.17	0.15	Current on.
11	−.28	0.15	Current off.
11:10	−.37	0	
12	−.37	0	Sample out.

The aluminum coupon gained 0.093 g. of a theoretical gain of 0.083 g. for reducing U^{+3} ions. The coating formed had a bright mat finish, was approximately 0.2 mil thick, considerably harder than aluminum, and by X-ray emission analysis was a uranide coating with no other elements present other than uranium and aluminum.

Other uranide coatings made in the same cell are described in Table III.

TABLE III

Run	Time, Min.	Temp. ° C.	Volts, Anode Polarity	C.D.[1], Amp/dm.^{2}	Wt. Gain, Grams	Theor. Wt. Gain, Grams	Coating Thickness, Mils	Coating Description
1	37	610	−.34 to −.26	0.5	0.565	0.370	1.8	Grainy, mat finish, pinholes present.
2	69	600	−.35 to −.30	0.25	0.770	0.340	2.5	Do.
3	130	600	−.35 to −.32	0.125	1.113	0.320	4	Do.
4	32	600	−.34 to −.08	2.5	1.700	1.555	6	Do.
5	15	600	0	0	.121	0	0.3	Do.

[1] C.D. is Current Density.

The greater than 100% efficiency data for reducing U^{+3} to uranium, followed by the diffusion of uranium into the aluminum surface, indicates that aluminum metal

in the coupon is probably exchanging with uranium ions in the salt, and thereby picking up excess weight. Furthermore, run 5 in Table III shows that no electrolysis is necessary to obtain a generation of uranium and diffusion of it into the aluminum surface. The good efficiency of run A and run 4 in Table III, however, shows that a high measure of coulombic control can be obtained in uraniding aluminum in the molten chlorides and that some unique and not yet understood characteristics of the aluminum-uranium system cause a deviation from the normal behavior.

What is claimed is:

1. A method for forming metallide coatings on aluminum and aluminum alloys with a metalliding metal selected from the group consisting of lithium, magnesium, scandium, yttrium, lanthanum and the natural rare earth metals of the lanthanide series, actinium and the natural rare earth metals of the actinide series, hafnium and zirconium, said method comprising (1) forming an electric cell containing an aluminum metal composition as the cathode, joined through an external electrical circuit to one of the said metalliding metals and an anhydrous fused salt electrolyte whose composition is so chosen that (a) it is liquid at the operating temperature, (b) contains from 0.1 to 50 mol percent of the halide of the metalliding metal and (c) consists essentially of at least one of the salts selected from the group consisting of the chlorides, and bromides of sodium, potassium, rubidium, cesium, calcium, strontium, barium, and metalliding metals, said electrolyte being maintained at a temperature of at least 350° C., but below the melting points of the aluminum composition and the alloy coating being formed thereon, in the substantial absence of oxygen, (2) controlling the current flow in said electrical cell so that the current density of the cathode does not exceed approximately 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 metallide coating is formed on the aluminum object.

2. The method of claim **1** wherein all of the salts are chlorides.

3. The method of claim **1** wherein the salt composition is a mixture of chlorides and bromides.

4. The method of claim **1** wherein the fused salt consists essentially of barium chloride, potassium, sodium chloride and cerium chloride.

5. The method of claim **1** wherein the fused salt is composed essentially of barium chloride, lithium chloride and yttrium chloride.

6. The method of claim **1** wherein the fused salt consists essentially of magnesium chloride and potassium chloride.

7. The method of claim **1** wherein the fused salt consists essentially of barium chloride, potassium chloride, sodium chloride and uranium chloride.

8. The method of claim **1** wherein the absence of oxygen is obtained by use of a vacuum.

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

10. Metal products produced in accordance with the process of claim **1**.

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