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CORROSION RESISTANT COATING

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This invention relates to the formation of corrosion resistant coating on a metal composition, and more particularly to a corrosion resistant coating for a metal composition wherein the coating is an alloy whose constituents comprise the metal and boron. Still more particularly, this invention is concerned with the formation of a boride coating on a metal composition wherein the boride coating comprises an alloy of boron and the metal, and to the novel compositions obtained thereby.

The usual process for the preparation of a boride coating on a metal comprises exposing the metal article to the vapors of a boron halide at a temperature sufficient to cause the halide to decompose and deposit a coating of boron on the metal. The metal is then heated to a still higher temperature to cause the boron to diffuse into and alloy with the metal. In the absence of a reducing gas, a displacement reaction occurs in which some of the metal replaces the boron in the boron halide. In the presence of hydrogen, the boron halide is reduced to boron and hydrogen halide. In order to obtain satisfactory deposition rates, temperatures in the order of 1200-1400° C. are required. The deposition rate must be carefully controlled since rapid deposition results in the formation of a boride undercoating with a fused boron coating as the outermost layer. In order to obtain adherent coatings, it is usually required to deposit a very thin coating followed by a hydrogen soak to diffuse the coating into the metal. Additional coatings are made in the same manner to produce the desired thickness. This method is completely unsatisfactory for the production of high precision machined parts which must be accurately machined to very close tolerances before they are borided. The parts warp causing the dimensions to exceed tolerance limits because of the distortion caused by the high temperatures and phase transitions to which the article is subjected in heating and cooling, especially when repeated steps are required to produce the desired thickness of coating. The rate of deposition of the boron is very dependent on the velocity of the boron halide over the surface and the temperature of the article being coated. Since these conditions are difficult to control, especially for large or irregular shaped articles, the coatings are usually not uniform over the entire surface.

Boride coatings have been made on iron by electrolyzing a fused bath of a boron compound such as boron oxide, boric acid, borax, etc., using the iron object as the cathode and graphite as the anode. Voltages of 4-40 volts and a current density of 50-100 amperes per square decimeter are required. Lower current densities permit the iron to be dissolved in the bath at a rate faster than the boron is deposited on the iron, so that there is a net weight loss. This effect is very noticeable with the boron compounds which are acidic such as boric acid or boron compounds containing boric acid as an impurity.

Unexpectedly, I have discovered that uniform, adherent, tough, corrosion resistant boride coatings can be formed without an overlying layer of boron on specific metals by immersing the selected metal and boron in a fused bath composed essentially of at least one alkali metal fluoride and from 0.5 to 50 mole percent of at least one alkali metal fluoroborate so that at least a portion of the bath isolates the metal from the boron. The alkali metal fluoroborate may be added as such or formed in situ as explained later. I have found that such a combination is an electric cell in which an electric current is generated

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when an electrical connection, which is external to the fused bath, is made between the metal and the boron. Under such conditions, the boron dissolves in the fused bath and boron ions are discharged at the surface of the metal where they form a deposit of boron which immediately diffuses into and reacts with the metal to form a boride coating. I have discovered that the rate of dissolution and deposition of the boron is self-regulating so that the boron is never deposited at a rate faster than it diffuses and alloys with the metal. If a slower rate is desired, it can be easily controlled by means well known in the art, such as by the amount of resistance in the circuit, surface area exposed to the bath, etc. A limited amount of voltage may be impressed upon the electrical circuit to supply additional direct current if a faster rate is desired.

This invention will be easily understood by those skilled in the art from the following detailed description. The metals which may be borided by my process are those having atomic numbers 23-29 inclusive, 41-47 inclusive, and 73-79 inclusive. This range of atomic numbers includes those metals included in the periodic chart of the elements shown on pages 56 and 57 of Lange's Handbook of Chemistry, 9th edition, Handbook Publishers, Inc., Sandusky, Ohio, 1956, as the group IB metals which are copper, silver, and gold, the group VB metals, which are vanadium, niobium and tantalum, group VIB metals, which are chromium, molybdenum and tungsten, the group VIIB metals, which are manganese, technetium and rhenium, and the group VIII metals which are iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum. Alloys of these metals with each other, or alloys containing these metals as the major constituent, i.e., over 50 mole percent but usually over 75 mole percent and preferably at least 90 mole percent, alloyed with other metals as a minor constituent, i.e., less than 50 mole percent but usually less than 25 mole percent and preferably less than 10 mole percent, can also be borided by my process, providing the melting point of the resulting alloy is not less than 600° C. The fact that other metals may be the minor constituents of an alloy with the metals with which this invention is concerned does not prevent the formation of the desired boride coating on the object. These minor constituents may be any of the other metals of the periodic system, i.e., the metals of groups IA, IIA, IIB, IIIA, IIIB, IVA, IVB, VA and VIA. These metals have atomic numbers 3-4 inclusive, 11-13 inclusive, 19-22 inclusive, 30-32 inclusive, 37-40 inclusive, 48-51 inclusive, 55-72 inclusive, 80-84 inclusive and 87-98 inclusive. In the specification and claims I use the term "boride" to designate any solid solution or alloy of boron and metal regardless of whether the metal does or does not form an intermetallic compound with boron in definite stoichiometric proportions which can be represented by a chemical formula.

The alkali metal fluorides and fluoborates for making the fused bath include the fluorides and fluoborates of lithium, sodium, potassium, rubidium, and cesium. Since it is desirable to use as low a temperature as practicable to avoid damaging or distorting the article to be borided, mixtures of one or more of the fluorides with one or more of the fluoborates may be used to provide salt baths having lower fusion temperatures than the individual components.

In order to produce a reasonably fast plating rate and to insure the fusion of the boron into the metal to form the boride, I have found it desirable to operate my process at a temperature no lower than about 600° C., even though the bath has a much lower melting temperature. Although lower temperatures may be used, there is some likelihood that the boron will plate out onto

the surface of the metal without diffusing into the metal. I usually prefer to operate at temperatures no greater than about 800° C. This is because the alkali metal fluoborate is in equilibrium with boron trifluoride and the alkali metal fluoride, and at temperatures exceeding 800° C., the vapor pressure of the boron trifluoride becomes sufficiently high that it is volatilized from the fused salt bath. Because of this equilibrium reaction, it is also possible to form desired alkali metal fluoborate directly in the fused salt bath by dissolving boron trifluoride in the fused bath of the alkali metal fluoride. The actual amount of alkali metal fluoborate required in the bath should normally be at least 0.5% and can be as high as 50% based on molar concentration. Usually, I use a concentration of 1-5% on a molar basis. Amounts less than 0.5% can be used but seriously affect the quality and rate of boride formation. Amounts greater than 5% offer no disadvantage but represent an uneconomical amount since the higher concentration does not speed the formation of the boride coating but does increase the partial pressure of boron trifluoride and, therefore, its loss by volatilization.

The chemical composition of the fused salt bath appears to be critical. The starting salts should be as anhydrous and as free of all impurities as possible, or should be easily dried or purified by simply heating during the fusion step. The role of impurities has not been definitely established, but it appears that many things can interfere with the electrode reactions and make for poor boriding. Because oxygen interferes, the process must be carried out in the substantial absence of oxygen, for example, in an inert gas atmosphere or in a vacuum. Sulfates appear to interfere most drastically, probably to give sulfur which diffuses into the metal and makes it impossible or extremely difficult to obtain good boriding. Other metal compounds can also cause the formation of poor quality boride coatings. Best results are obtained by starting with reagent grade salts and by carrying out the process under vacuum. I have sometimes found that even commercially available reagent grade salts must be purified further in order to operate satisfactorily in my process. This can easily be done by utilizing scrap articles, preferably of the same metal to be used later, to carry out initial boriding runs, with or without an additional applied voltage, thereby plating out and removing from the bath those impurities which interfere with the formation of a high quality boride coating. Carrying out the process in a vacuum also aids the process by volatilizing impurities and interfering substances, such as water. It is also desirable to thoroughly clean the metal surface before introduction into the fused salt, such as by pickling with or without an abrading treatment.

Also, I have found that to obtain a uniform boride coating over large areas, it is highly desirable to use a porous conducting container which is inert under process conditions, for example, a graphite basket with holes, to contain the boron as small pieces, rather than to use a single solid piece of boron. This is apparently due to the fact that boron is not a good conductor of electricity, and therefore the boron dissolves chiefly from the area at the interface formed where the boron enters the bath, due to the voltage drop over the length of the boron. This results in a greater deposition rate of boron on the article being borided in that area which is nearest to this interface, and the lower deposition rate on the area farthest from this interface even though both areas may be equidistant from the solid piece of boron. By using the conductive container, the boron dissolves uniformly from the entire surface and produces uniform coatings on small articles providing the boron electrode is at least 0.25 inch but preferably 1 to 2 inches from the article being borided. In boriding extremely large articles, for example, a sheet, in which one side may be shielded from a single boron electrode, it may be desirable to use two or more boron electrodes, which are judiciously spaced around the article

to produce a uniform coating. Solid boron is very sensitive to thermal shock and may shatter under operating conditions. The porous basket electrode prevents loss of these pieces.

When an electrical circuit is formed external to the fused salt bath by joining the boron to the metal to be borided with a conductor, electric current will flow through the circuit without any applied E.M.F. Apparently, the boron acts as an anode by dissolving in the fused bath to produce electrons and boron ions. The electrons flow through the external circuit formed by the conductor and the boron ions, probably as fluoborate ions, migrate through the fused salt bath to the metal to be borided where the electrons discharge the boron ions as a boron coating. Because of the combined effect of the temperature of the bath and the fluxing action of the fused salts I use, the boron immediately diffuses into the metal and forms a boride as a very smooth, adherent, tough, corrosion resistant coating. The amount of current can be measured with an ammeter which enables one to readily calculate the amount of boron being deposited on the article and converted to the boride layer. Knowing the area of the article being plated, it is possible to calculate the thickness of the boride coating deposited, thereby permitting accurate control of the process to obtain any desired thickness of the boride layer.

Although my process operates very satisfactorily without the impressing of an additional E.M.F. on the electrical circuit, I have found that it is possible to apply a small voltage when it is desired to increase the deposition rate of the boron without exceeding the diffusion rate of boron into the article to form the boride layer. The impressed E.M.F. should not exceed 0.5 volt and usually falls between 0.1 and 0.3 volt. Voltages higher than this indicate one or more of the following conditions: (1) high resistance somewhere in the external circuit, (2) impurities in the bath which interfere with the desired chemical reactions at the electrode, (3) too fast deposition rates, (4) loose or corroded electrical connections, etc. Although my process will operate satisfactorily when such conditions exist, it is desirable that they be corrected for more efficient operation. For example, when the anode is a solid rod of boron, the voltage may sometimes exceed these limits due to the resistance in the circuit due to the poor conductivity of the boron. This may be eliminated, for example, by use of a porous graphite basket containing pieces of boron or by providing the boron with a core of a good conductor.

When operating as a cell, without any impressed E.M.F., the initial current density is between 0.1 and 1.0 ampere per square decimeter at 700°-800° C. As the boride layer increases on the article, the current density drops until, by the time the coating is approximately one mil thick, it is usually one-third to one-tenth the initial value.

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 3 amperes per square decimeter. In preparing thick boride coatings, the current density preferably should not exceed 1 ampere per square decimeter after the boride layer is 1 mil thick. Current densities in excess of these ranges lead to some formation of elemental boron in either the form of non-adherent deposits or as granular or large crystalline deposits which give a rough, undesirable coating which tends to spall on further electrolysis or cooling to room temperature. Such results are desirable for the electro-winning of boron from its compounds but are completely unsatisfactory for the production of smooth, adherent boride coatings on metals.

If an applied E.M.F. is used the source, e.g., 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 borided and the positive terminal is con-

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nected to the external circuit terminating at the boron electrode. 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, and so forth, may be included in the external circuit to aid in the control of the process.

The following examples are given by way of illustration and not by way of limitation. It is readily apparent that variations from the specific reaction conditions and reactants given may be readily used without departing from the scope of my invention.

EXAMPLE 1

Into a stainless steel vessel (11" deep x 4 $\frac{3}{4}$ " I.D.) fitted with a monel liner (10 $\frac{3}{4}$ " deep x 4 $\frac{1}{2}$ " I.D.) was placed 2610 g. (45 moles) of reagent grade anhydrous KF, 1170 g. (45 moles) of reagent grade LiF, and 420 g. (10 moles) of reagent grade NaF. The vessel was covered with a glass dome which contained two ports for electrodes and one port for a thermocouple well, and for connection to a vacuum source. A boron rod ($\frac{1}{4}$ " x $\frac{1}{4}$ " x 3") anode bound by nickel wire to a $\frac{1}{4}$ " nickel rod was sealed in one electrode port with rubber tubing. A similar arrangement was used for an iron strip (2 cm. x 10 cm. x .05 cm.) cathode in the other electrode port.

The vessel was placed in a Nichrome wound, alumina tube, electric furnace, evacuated and brought to a temperature of 600° C. where the salt mixture was a water clear melt. The melt was cooled to room temperature, one mole of KBF₄ added and the salt remelted in vacuum. The vapor pressure of BF₃ above the melt at 700° C. was less than .5 mm. All reactions given below as examples of boriding were run at pressures of .1 to 3.0 mm. Equally successful reactions have been made in inert atmospheres but I prefer vacuum operation as the most consistent method for obtaining excellent results. The boron anode and the iron cathode were lowered into the melt up to $\frac{1}{4}$ to $\frac{1}{2}$ inch of their points of attachment to the nickel rods and the electrolysis carried out by impressing a moderate E.M.F. on the external electrical circuit connecting the anode and cathode. An ammeter and voltmeter were connected in the normal way in the external circuit. The pertinent data was:

Time (min.)	Temp., ° C.	Current density, amp./dm. ²
0	700	1.0
2	700	1.0
11	700	0.75
15	700	0.75
25	700	0.75
31	700	0.75
228 (end)	700	0.50

The electrodes were lifted from the salt and the melt cooled to room temperature before opening the cell. The iron cathode had gained 40 mg. of a theoretical 70-75 mg. gain in weight, and had a hard, smooth, adherent boride layer which proved by metallographic examination to be 1 mil thick, and by X-ray examination to be a mixture of Fe₂B (inner portion of coating) and FeB (outer portion of coating). The boron electrode had broken off just below the surface of the melt. Subsequent breakages indicated that boron rods could not be heated and cooled without shattering, so metal and carbon baskets containing boron granules were substituted for boron rods in all subsequent examples except Example 8.

E.M.F. the current density during boriding of the steel E.M. f. the current density during boriding of the steel was 0.1 ampere per square decimeter.

EXAMPLE 2

For a cathode, a piece of S.A.E. 4140 steel (12 cm. x 4 cm. x .5 cm) was suspended from a $\frac{1}{4}$ " nickel rod with a

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piece of tantalum wire and was completely immersed in the molten salt described in Example 1. A perforated tantalum basket (3" length x $\frac{1}{2}$ " diameter) holding 15 g. of boron granules (6-14 mesh) was used as an anode. The anode and cathode were connected as in Example 1, again using a moderate applied E.M.F.

Time (min.)	Temp., ° C.	Current density, amp./dm. ²
0	700	0.10
5	700	.10
13	700	.10
22	700	.10
45	700	.10
65	700	.085
	700	.085

The tantalum basket lost 17 mg. in weight of a possible 143 mg. if no boron had dissolved, showing that 88% of the anodic attack had occurred on the boron crystals in the basket and only 12% of the anodic attack had occurred on the tantalum. In a series of ten runs which followed the above example, the tantalum basket sustained only 3% of the anodic attack and the boron granules 97%, indicating possible formation of a protective tantalum boride coating due to a partially short-circuited cell action since it is possible to boride tantalum when the latter is present as the cathode.

The cathode piece of S.A.E. 4140 steel gained 101 mg. of a theoretical 143 mg. No dimensional changes could be detected in the steel and the borided surface had the same high polish as the initial surface. The coating (approximately 1.5 mils thick by metallographic determination) was smooth and hard (1700 Vickers hardness number, compared to 300-400 for untreated 4140 steel) and could be dented with a blow from a ball peen hammer without cracking or spalling.

EXAMPLE 3

An iron strip (2 cm. x 12 cm. x .05 cm.) was borided according to the general procedure of Example 2 except that a carbon basket ($\frac{7}{8}$ " O.D. x $\frac{5}{8}$ " I.D. x 7") filled with boron granules (6-14 mesh) was used as the anode and E.M.F. was applied initially to the external circuit, as noted below.

Time (min.)	Temp., ° C.	Current density, amp./dm. ²	Operation
0	680	.32	No applied E.M.F.
13	710	.38	Do.
21	730	.43	Do.
35	750	.50	Do.
55	750	1.0	Applied E.M.F.
140	750	1.0	Do.
170 (end)	750	1.0	Do.

The iron strip gained the theoretical weight calculated for the weight of boron (152 mg.) which would be deposited by the amount of current passing between the electrodes. The strip had a hard, smooth, uniform boride coating. Metallographic analysis showed a 1.5 mil thick coating, although the original thickness had changed less than 0.1 mil.

EXAMPLE 4

A nickel strip (10 cm. x 3 cm. x .075 cm.) was borided using the general procedure of Example 2.

Time (min.)	Temp., ° C.	Current density, amp./dm. ²
0	738	.63
2	740	.31
3	740	.33
60	750	.33
240	750	.33

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The nickel strip gained 111 mg., the theoretical weight for boron, and had a hard, smooth, uniform coat that was 1.5 mils thick, and contained Ni₃B. The nickel strip increased 0.2 to 0.3 mil in thickness. The coating could be flexed and deformed without spalling and cracking, but not to the same extent as with the coating on iron.

EXAMPLE 5

A cobalt strip (2.2 cm. x 11.5 cm. x .028 cm.) was borided in the same general procedure as Example 2.

Time (min.)	Temp., ° C.	Current density, amp./dm. ²	Operation
0	745	.25	No applied E.M.F.
4	745	.20	Do.
20	745	.14	Do.
21	745	.20	Applied E.M.F.
192	745	.20	Do.
247	745	.20	Do.

The cobalt strip gained the theoretical amount of boron, 53 mg., and had a hard, externally smooth, adherent coat that was 0.5 to 1.25 mils thick. The variation in thickness was due to fingers that penetrated into the cobalt ahead of the main body of the coating and seemed to act as roots for the coating. The strip could be bent in a 1/4" radius without cracking or spalling of the coat on the inside curvature and a 1/8" radius without cracking or spalling of the coat on the outside curvature. Deformation from impacting with a ball peen hammer on a steel block, reducing the thickness of the strip from 11 to approximately 5 mils caused no loosening or cracking of the coat. The boride coating had also imparted considerable elasticity to the strip so that the piece of cobalt, which had resembled a piece of annealed copper before boriding, was now like a piece of spring steel.

The edge of the strip readily scratched Pyrex glass when drawn across the surface.

EXAMPLE 6

A chromium disc (.735" dia. x .100" thick) was borided in the same general procedure as Example 2. Since a preliminary test had indicated that chromium borided very slowly the current density was held at a low value for a long time by applying only a very low E.M.F. to the external circuit.

Time (min.)	Temp., ° C.	Current density, amp./dm. ²
0	750	.23
275	750	.23
276	750	.15
926	750	.15

The chromium gained 7.2 mg. of a theoretical weight gain of 22.1 mg. Microscopic examination showed a smooth coating 0.4 mil thick, although the overall gain in thickness of the disc was only approximately 0.1 mil. The coating was extremely hard, could readily wear carbony and was very difficult to polish with emery. The coating was approximately the same color as the untreated metal and could be deformed approximately the same as the base metal.

EXAMPLE 7

A niobium wire loop (20 cm. x .10 cm.) was borided according to the general procedure used in Example 2.

Time (min.)	Temp., ° C.	Current density, amp./dm. ²
0	700	.8
70	700	.8
195	700	.8

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The wire gained 2.8 mg. of a theoretical 21.5 mg. and had a hard, smooth, light grey coating which on microscopic examination was found to be 0.1 to 0.2 mil thick. The wire had increased in diameter approximately 0.1 mil. The coating was quite flexible.

EXAMPLE 8

A molybdenum strip (10 cm. x 1.5 cm. x .050 cm.) was borided according to the general method of Example 1 using a solid boron rod.

Time (min.)	Temp., ° C.	Current density, amp./dm. ²
0	710	1.0
20	720	1.0
110	720	.73
165	720	1.0

The molybdenum strip gained 29 mg. of a theoretical 100 mg. and gained approximately .1 mil in thickness. Microscopic examination of the coating showed it to be .3 to .4 mil thick and in two layers, an outer coat which was quite brittle, very hard and crystalline in appearance, and a lower coat which was much less brittle, very hard and smooth.

EXAMPLE 9

A piece of tungsten rod (.20 cm. x 12 cm.) was borided using the procedure of Example 3.

Time (min.)	Temp., ° C.	Current density, amp./dm. ²
0	800	.7
130	800	.7
131	800	.3
700	800	.3

The tungsten rod gained 12 mg. of a theoretical weight gain of 34 mg. Microscopic examination of a cross-section of the rod showed a coating which was approximately .3 mil thick. The surface was extremely hard, scratching glass and carbony and was polished very slowly with emery paper.

EXAMPLE 10

A rhenium strip (7.5 cm. x .6 cm. x .012 cm.) was borided using the same general procedure as Example 3.

Time (min.)	Temp., ° C.	Current density, amp./dm. ²
0	740	.1
43	740	.2
133	740	.2
223 (end)	740	.2

The rhenium strip gained 5.2 mg. of a theoretical weight increase of 8.6 mg. The boride coating .2 mil thick, was light brown, smooth, uniform, strongly adherent, flexible and extremely hard, scratching silicon carbide and sapphire.

Table I contains other metals and alloys that have been borided by the use of the apparatus and general procedure described in Example 3. The boridings which were run as a cell (no E.M.F. impressed on external circuit) are so indicated in the table. In these cases, the range of current density indicates the initial and final value. All the alloys formed extremely hard coatings ranging from 1200 to above 2000 in Knoop hardness numbers at 100 g. loads. Test on these surfaces definitely showed increased resistance to corrosion and increased resistance to galling over the untreated alloys.

Table I

Ex.	Metal	Temp., °C.	Current density, amp./dm. ²	Percent efficiency	Description of coating
11	Copper	700	.15	30	.3 mil coat, brown, outer surface harder than file, brittle.
12	Tantalum	745	.1	15	.1 mil coat, grey, hard, brittle.
13	Platinum	800	3 to .3 (cell)	100	Coat was hard, shiny and moderately flexible.
Alloys					
14	High carbon iron (3.5% C, 2.5% Si, .75% Mn).	750	0.6 to .2 (cell)	100	3 mil coating, grey, harder than carboloy, slightly flexible.
15	A.I.S.I. 410 steel	750	.4	100	2 mil coat, light grey, very hard, flexible.
16	A.I.S.I. 304 stainless steel	800	.7 to .1 (cell)	100	1.5 mil coat, shiny, hard, flexible.
17	Inconel X (70% Ni, 15% Cr, 7% Fe, 2.5% Ti, 1% Ta & Nb, .7% Mn, .7% Al, .5% Si, .37% C)	750	1.2 to .4 (cell)	100	2 mil coat, shiny, hard, moderately flexible (1200 Knoop Hardness).
18	Hastelloy X (45% Ni, 22% Cr, 23% Fe, 9% Mo)	750	1.3 to .3 (cell)	100	1.5 mil coat, shiny, hard, flexible.
19	Hastelloy B (28% Mo, 5% Fe, 65% Ni, 1% Cr)	800	1.0 to .3 (cell)	100	2 mil coat, shiny, hard, flexible.
20	A 286 (26% Ni, 2% Co, 15% Cr, 1.25% Mo, 1.5% Mn, 2% Ti, 0.35% Al, balance Fe).	750	.4	70	1 mil coat, blue grey, hard, moderately flexible.

EXAMPLE 21

In order to demonstrate the effect of boride surfaces on frictional properties, six standard V-blocks made of S.A.E. 2320 steel and three standard pins made of S.A.E. 3151 steel for use in the Falex Test Machine (D. F. Fuller, "Theory and Practice of Lubrication Engineers," John Wiley & Sons, New York, 1956, pages 363-66) were borided using the general procedure of Example 2.

Time (min.)	Temp., °C.	Current density, amp./dm. ²
0	710	0.30
10	710	0.30
15	710	0.30
50	710	0.27
180	715	0.23

Each of the blocks weighing an average of 9.2336 g. gained an average of 8.6 mg. and each of the pins weighing an average of 7.4302 g. gained an average of 8.2 mg. These pieces were tested under the standard test conditions and compared to the values obtained on the same steels without the borided surface with the following results:

Specimen	Seizure load (lb.)	Load for 1 mil wear (lb.)
Untreated	1,500	750
Borided	4,300	2,500

The above examples have illustrated the preferred embodiments of my invention. However, it will be readily apparent to those skilled in the art that other modifications can be made without departing from the scope of the present invention. For example, the boride coating can be formed on a metal which is itself a coating on the surface of another metal, for example, an electroplate on a metal base, e.g., chromium on iron.

Because the tough, adherent, corrosion resistant properties of the boride coatings are uniform over the entire treated area, the boride 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 fabricate moderators for nuclear reactors, to make turbine blades for both gas and steam driven turbines to resist the corrosive and erosive effects of the gaseous driving fluid, to make gears, bearings, and other articles requiring hard, wear resistant surfaces. 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. It is therefore to be understood that changes may be made in the

particular embodiments of the invention described which are within the full intended scope of the invention as defined by the appended claims.

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

1. A method of forming a boride coating on a metal composition having a melting point of at least 600° C., at least 50 mol percent of said metal composition being at least one of the metals selected from the group of metals whose atomic numbers are 23-29, 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 boron anode and a fused salt electrolyte composed essentially of at least one alkali metal fluoride and from 0.5 to 50 mol percent of at least one alkali metal fluoroborate, said electrolyte being maintained at a temperature of about 600-800° 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 at the cathode does not exceed 3 amperes per square decimeter during the formation of the boride coating, and (3) interrupting the flow of electrical current after the desired thickness of boride coating is formed on the metal composition.

2. The boride coated product obtained by the method of claim 1.

3. The process of claim 1 wherein the absence of oxygen is obtained by use of a vacuum.

4. The process of claim 1 wherein all of the electrical energy for the process is self-generated in the electric cell.

5. The process of claim 1 wherein part of the direct current is supplied by an external E.M.F. impressed upon the electrical circuit.

6. A method of forming a boride coating on a metal composition having a melting point of at least 600° C., at least 90 mol percent of said metal composition being at least one of the metals selected from the group of metals whose atomic numbers are 23-29, 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 boron anode and a fused salt electrolyte composed essentially of at least one alkali metal fluoride and from 0.5 to 50 mol percent of at least one alkali metal fluoroborate, said electrolyte being maintained at a temperature of about 600-800° 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 at the cathode does not exceed 3 amperes per square decimeter during the formation of the boride coating, (3) interrupting the flow of electrical current after the desired thickness of boride coating is

formed on the metal composition, and (4) removing the metal composition with the integrant boride coating from the fused salt electrolyte.

7. The method of claim 6 wherein the metal composition is at least 90 mol percent iron.

8. The method of forming a boride coating on an iron-chromium-nickel alloy which comprises (1) forming an electric cell containing said alloy as the cathode joined through an external electrical circuit to a boron anode and a fused salt electrolyte composed essentially of at least one alkali metal fluoride and from 0.5 to 50 mol percent of at least one alkali metal fluoroborate, said electrolyte being maintained at a temperature of about 600–800° C. 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 3 amperes per square decimeter during the formation of the boride coating, (3) interrupting the flow of electrical current after the desired thickness of boride coating is formed on the alloy, and (4) removing the alloy with its integrant boride coating from the fused salt electrolyte.

9. The method of forming a boride coating on molybdenum which comprises (1) forming an electric cell containing molybdenum as the cathode joined through an external electrical circuit to a boron anode and a fused salt electrolyte composed essentially of at least one alkali metal fluoride and from 0.5 to 50 mol percent of at least one alkali metal fluoroborate, said electrolyte being maintained at a temperature of about 600–800° C. 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 3 amperes per square decimeter during the formation of the boride coating, (3) interrupting the flow of electrical current after the desired thickness of boride coating is formed on the molybdenum, and (4) removing the molybdenum with its integrant boride coating from the fused salt electrolyte.

10. The method of forming a boride coating on cobalt which comprises (1) forming an electric cell containing cobalt as the cathode joined through an external electrical circuit to a boron anode and a fused salt electrolyte composed essentially of at least one alkali metal fluoride and from 0.5 to 50 mol percent of at least one alkali metal fluoroborate, said electrolyte being main-

tained at a temperature of about 600–800° C. 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 3 amperes per square decimeter during the formation of the boride coating, (3) interrupting the flow of electrical current after the desired thickness of boride coating is formed on the cobalt, and (4) removing the cobalt with its integrant boride coating from the fused salt electrolyte.

11. The method of forming a boride coating on niobium which comprises (1) forming an electric cell containing niobium as the cathode joined through an external electrical circuit to a boron anode and a fused salt electrolyte composed essentially of at least one alkali metal fluoride and from 0.5 to 50 mol percent of at least one alkali metal fluoroborate, said electrolyte being maintained at a temperature of about 600–800° C. in the substantial absence of oxygen, (2) controlling the current flowing in the said electric cell so that the current density of the cathode does not exceed 3 amperes per square decimeter during the formation of the boride coating, (3) interrupting the flow of electrical current after the desired thickness of boride coating is formed on the niobium, and (4) removing the niobium with its integrant boride coating from the fused salt electrolyte.

12. The method of forming a boride coating on rhenium which comprises (1) forming an electric cell containing rhenium as the cathode joined through an external electrical circuit to a boron anode and a fused salt electrolyte composed essentially of at least one alkali metal fluoride and from 0.5 to 50 mol percent of at least one alkali metal fluoroborate, said electrolyte being maintained at a temperature of about 600–800° C. 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 3 amperes per square decimeter during the formation of the boride coating, (3) interrupting the flow of electrical current after the desired thickness of boride coating is formed on the rhenium, and (4) removing the rhenium with its integrant boride coating from the fused salt electrolyte.

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