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(54) **LIGHT ALLOY-BASED COMPOSITE PROTECTIVE MULTIFUNCTION COATING**

MULTIFUNKTIONELLE KOMPOSIT-SCHUTZBESCHICHTUNG AUF LEICHTMETALLBASIS

REVETEMENT DE PROTECTION COMPOSITE MULTIFONCTIONS A BASE D'ALLIAGES LEGERS

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(73) Proprietor: **Isle Coat Limited  
Douglas,  
Isle of Man, IM1 2PT (GB)**

(72) Inventor: **SHATROV, Alexandr Sergeevich  
Moscow, 119619 (RU)**

(74) Representative: **Harrison Goddard Foote  
Belgrave Hall  
Belgrave Street  
Leeds  
LS2 8DD (GB)**

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**EP 1 231 299 B1**

**Description****Field of Technology**

**[0001]** The invention can be used in various branches of engineering, electronics, medicine and other fields in which non-ferrous metals and their alloys are used. The invention relates to a technology for applying protective coatings to such metals and alloys and also to components and articles made from them.

**Prior Art**

**[0002]** The use of non-ferrous alloy components with a hardening ceramic coating instead of components of traditional materials (ceramic, high-alloy steels and cast irons) makes possible an considerable increase in the durability and reliability of highly-loaded and rapidly wearing components, a reduction in weight and an improvement in the dynamic characteristics of units.

**[0003]** At the present time, a considerable quantity of hard ceramic coatings has been created, but these have very significant deficiencies which used in extreme conditions with insufficient lubrication or no lubrication at all. Such thin wear-resistant coatings as TiN, TiCN, due to inadequate wettability, often destroy the lubricant film, which leads to a higher degree of wear. The relatively thick ceramic coatings are close to sintered ceramic in the nature of their friction wear. Their main faults are a high friction coefficient, heating of the friction interface where there is insufficient lubricant, intensive wear of the counter-body as a result of the micro-cutting effect, the breakaway and micro-chipping of ceramic particles and their participation in the acceleration of abrasive wear. Extensive surface finishing operations to a roughness of Ra 0.04-0.06  $\mu\text{m}$  only partly solve this problem.

**[0004]** There have been increasingly frequent attempts recently to create universal protective coatings for non-ferrous alloy components, capable of operating in harsh extreme conditions and still possessing a low friction coefficient, high resistance to wear and good resistance to aggressive media.

**[0005]** One way of creating such coatings is the formation on the protected component of a porous ceramic coating, into the pores of which various fillers are introduced.

**[0006]** Thus, there is a known process (US Patent 5,487,826A) of forming a composite layer on alloys of Al, Mg and Ti, consisting of a porous protective oxide layer, with the introduction of particles of fluoropolymers into its pores.

**[0007]** There is a known process (WO 97/05302) for forming a porous oxide film on alloys of Al, Mg and Ti, with the introduction of particles of  $\text{SiO}_2$  into its pores using sol-gel technology.

**[0008]** There is also a known process (RU 2073752) for the introduction of a silicon-organic oligomer into an oxide layer formed on aluminium alloy components, with subsequent heat treatment at 300-500°C.

**[0009]** A fault common to all the above processes is the limitation of their application at high temperatures arising in operating in extreme conditions of use of the components, and low ratings for the thermal and electrical conductivity of the coatings.

**[0010]** Factors of triboelectrisation and heat emission significantly influence the nature of wear and the formation of the products of wear in friction pairs. Therefore an increase in the thermal and electrical conductivity of composite coatings can be achieved by using metallic or metal-like components in them.

**[0011]** There is a known process (US Patent 5,645,896A) for the surface treatment of the rotor of a screw pump involving the application to its surface by the gas-thermal dusting-on process initially of a layer of coarse-grain tungsten carbide to a thickness of 50-125  $\mu\text{m}$ , and then a nickel-chrome layer of thickness 75-150  $\mu\text{m}$  until the carbide layer is completely covered. Final polishing reduces the rotor to its required dimensions and reveals the protecting apexes of the carbide layer, which takes the main load when the rotor is in use.

**[0012]** In the process described, the rotor is made of steel. But the gas-thermal dusting-on process can be used to apply coatings of virtually any compositions to any backings. However, it is difficult to form uniform coatings on components of complex shape by this process. Furthermore, coatings applied by gas-thermal dusting-on do not bond firmly enough to the base. This fault is worse if non-ferrous alloys form the base, since they rapidly dissipate heat and intensively form thin oxide films under the effect of the plasma jet. Also, non-ferrous alloys react critically to the high temperature of the dusting-on process, since the surfaces of aluminium and magnesium alloys can be melted, and the overheating of titanium alloys leads to a reduction in their fatigue resistance.

**[0013]** There is a known process (US Patent 5,364,522A) of applying multifunctional composite coatings consisting of ceramic films enriched with borides, carbides, nitrides, oxynitrides and silicides. In the first stage of the process, a hydroxide ceramic layer is applied to the backing electrochemically; in the second stage, enrichment (infiltration) of the ceramic layer with refractory compounds takes place in a flow of gas or steam at temperature 450-800°C.

**[0014]** The coatings produced by this process are strong, wear-resistant and resistant to corrosion at high temperatures. However, the use of high temperatures in this technology makes it impossible to apply such coatings to components made of non-ferrous alloys.

**[0015]** There is a known process (WO 91/13625) for the application of wear-resistant anti-friction coatings to aluminium and aluminium alloys. The aluminium backing is first anodised in a 15% solution of sulfuric acid. A layer of a soft metal, namely indium, tin, gallium or a combination of these is then applied to the porous anode-oxide surface. The thickness of the anode-oxide coating comprises 1-500  $\mu\text{m}$  and the thickness of the metal layer, 10-100  $\mu\text{m}$ . In the course of this process, at least 80% of the pores of the anode layer should be filled with metal.

**[0016]** The main problem with the process described is the low mechanical strength and instability of the basic anode-oxide coating.

**[0017]** Anode coatings of a thickness of more than 10  $\mu\text{m}$  have a large number of pores, which are hydrated to a considerable degree (water content in the coating exceeds 10%), and their composition also includes 10-20% of electrolyte anions built into the structure of the coating. When heated to more than 120°C, the electrolyte components and water depart from the structure of the coating, which leads to breaks and crumbling in the anode-oxide layer and is detrimental to its protective properties. Furthermore, the anode-oxide layers consist mainly of amorphous phases of oxides, and consequently their strength and micro-hardness are not high.

## Substance of the Invention

**[0018]** One task of the present invention is to develop a composite coating for non-ferrous alloy components, possessing good wear resistance and a low friction coefficient throughout the working life of the component, resistance to aggressive media and ability to withstand dynamic contact loads and vibrations.

**[0019]** A second task of this invention is to develop a composite coating for non-ferrous alloy components, possessing high wear resistance and scratch resistance, resistance to erosion wear and to the action of abrasive media at high temperatures, and also resistance to corrosion.

**[0020]** A third task of this invention is to develop an ecologically safe and comparatively inexpensive technology for the application of composite coatings to non-ferrous alloys, which can be used in series production.

**[0021]** These and certain other tasks are solved by the present invention due to the creation of a coating which takes the form of a porous oxide-ceramic coating formed by the oxidation of the surface layer of the material being protected by the plasma-electrolytic oxidation method, into the pores of which are introduced metals such as Ni, Cu, Co, Fe, Cr, Mo, Ti, Al, Sb, Ag, Zn, Cd, Pb, Sn, Bi, In, Ga and mixtures of them or the carbides, oxides, nitrides, borides and silicides of metals in Groups IVB-VIB of the Mendeleev periodic system, and mixtures of them.

**[0022]** The formation of porous oxide-ceramic coatings on non-ferrous alloys by the plasma-electrolytic oxidation method was proposed by the author of this invention in the earlier international application PCT/RU97/00408 (publication WO 99/31303).

**[0023]** The adhesion of these coatings to the base is 5-10 times as strong as the adhesion of gas-thermal dusted-on coatings, and their strength and micro-hardness are 2-5 times as great, higher than for anode-oxide layers.

**[0024]** Oxidation takes place in ecologically harmless weakly alkaline aqueous electrolytes at a temperature of 15-55°C. Pulse voltage of 100-1000 V (amplitude value) is supplied to the components.

**[0025]** The frequency of succession of the pulses is 50-3000 Hz. Current density is 2-200 A/dm<sup>2</sup>.

**[0026]** A fine crystalline oxide layer of micro-hardness 300-2000 Hv, depending on the composition of the alloy base, is created on the surfaces of the non-ferrous alloy components under the effect of plasm-chemical reactions. The thickness of the layer may be from 1 to 600  $\mu\text{m}$ .

**[0027]** By changing the electrolysis regimes and the composition of the electrolyte, significant changes may be made to the physico-mechanical characteristics of the oxide-ceramic coatings, and particularly to the magnitude of their open porosity, which can be varied between 5 and 35%.

**[0028]** As a result of studies, it has been discovered that if the above-listed metals or carbides, oxides, nitrides, borides, and silicides of metals of groups IVB-VIB of the periodic system and mixtures of them are introduced into the pores of such a coating, the coating acquires unique properties such as strength and hardness in combination with plasticity, high resistance to wear and scratches, high corrosion resistance and resistance to mechanical contact loads and vibrations.

**[0029]** The size of the pores varies from several tens of nanometres to several microns in diameter. Pores of size larger than one micron comprise more than 90% of the volume of all the pores. It is into these pores that the main mass of the functional compounds is introduced.

**[0030]** The porous structure of the oxide-ceramic layer serves as a matrix for the creation of the multifunctional composite coating. Note that the porosity of the coating varies through the depth of the coating. It is at its maximum at the surface, but is less by a factor of 2-6 as it approaches the basic metal. The concentration of functional compounds introduced into the pores conforms to these characteristics - it is at its maximum in the layer next to the surface and decreases exponentially as the depth of coating increases. Oxide-ceramic coatings with open porosity of 10-20% form an ideal matrix for the creation of composite coatings by filling this matrix with compounds possessing specific properties and fulfilling specific functions (anti-friction, thermal conductivity, anti-corrosion etc.).

**[0031]** The micro-hardness of an oxide-ceramic coating, on the other hand, has maximum values close to the basic metal and steadily decreases towards the outer surface of the coating (by 20-30%).

**[0032]** The strongly developed surface of the porous structure of the matrix layer provides excellent adhesion of the functional compounds to the oxide coating. This gives the composite coating its high cohesion strength..

**[0033]** The first group of functional compounds introduced into the pores of the oxide layer consists of the soft metals Ni, Cu, Co, Fe, Cr, Mo, Ti, Al, Sb, Ag, Zn, Cd, Pb, Sn, Bi, In, Ga and mixtures of these.

**[0034]** The metal exerts a plasticising influence on the composite coating. The specific nature of this coating is due to its deformation behaviour under thermo-mechanical load. The two-phase ceramic-metal structure provides a fivefold increase in shock viscosity as compared with pure ceramic.

**[0035]** Such coatings can also be used as anti-friction coatings. After finishing treatment, sectors of the oxide-ceramic layer are laid bare. These stronger sectors on the friction surface take the main load and thus raise the bearing capacity of the surface.

**[0036]** Furthermore, the softer sectors of the surface, as they wear, form micro-recesses and grooves, which serve as reservoirs for lubricant, and the presence of which alters the friction regime in the friction contact, facilitates the removal of the products of wear and thus improves the working capabilities of the surface.

**[0037]** Taking into account the friction regime in the unit, the presence of lubricant and the state of the contacting surfaces, composite coatings can be formed which optimally correspond to the specific conditions of use with optimal porosity and optimal composition of the functional compounds in the pores of the composite coating.

**[0038]** The second group of functional compounds introduced into the pores of the oxide layer consists of refractory compounds of metals of groups IVB-VIB in Mendeleyev's periodic system of elements: carbides, oxides, nitrides, borides and silicides.

**[0039]** The use of these compounds separately or together with metals as functional materials introduced into the ceramic matrix of the coating imparts to the composite coating such properties as high hardness and strength, resistance to high temperatures and exceptionally high wear resistance. Such compounds, located in the pores, harden the composite coating and alter its thermo-physical and mechanical properties.

**[0040]** All the above-listed functional compounds are applied to the porous ceramic matrix layer by known methods of electrolytic or chemical precipitation from aqueous or organic solutions, including the use of ultra-disperse powders, chemical or physical precipitation from gas or vapour phases or the friction-mechanical method (rubbing on) using powders, bars, brushes etc.

**[0041]** Using these methods, the functional compounds are introduced into the pores of the oxide-ceramic matrix coating to a depth of 1-150  $\mu\text{m}$ , depending on the depth of the oxide coating itself and the volume of the pores in it.

**[0042]** The working surface is subjected to machine finishing (polishing, lapping, fine grinding, honing, superfinish) until the components are at the required dimensions and roughness of the surfaces, or until the apexes of the oxide-ceramic coating are revealed (bared). This machine treatment makes it possible to remove excess layers of functional compounds and to distribute the remaining part uniformly over the surface. Machine treatment also means that there is no need for the friction surfaces to be run in.

### Brief Description of the Drawings

**[0043]** The attached drawings show:

On Fig. 1, a cross section through a specimen with composite coating applied to it, where 1 = binding functional material; 2 = pores in the oxide matrix coating; 3 = oxide-ceramic matrix coating; 4 = transitional layer between the basic metal and the oxide coating; 5 = the basic metal.

On Fig. 2, a cross section of a specimen after finishing treatment (polishing) of the composite coating. 1 = binding functional material; 2 = pores in the oxide matrix coating; 3 = oxide-ceramic matrix coating; 4 = transitional layer between the basic metal and the oxide coating; 5 = the basic metal; 6 = projections of the oxide coating on the working surface.

### Examples of the Implementation of the Invention

**[0044]** The following examples are given as specific illustrations of the claimed invention. However, it should be taken into account that the invention is not limited to those specific components which are considered in the examples given.

#### Example 1 (for comparison)

**[0045]** A specimen of alloy D16 ( $\text{AlCu}_4\text{Mg}_2$ ) is in the form of a ring of dimensions  $D = 40 \text{ mm}$ ,  $d = 16 \text{ mm}$  and  $h = 12 \text{ mm}$ . The external cylindrical surface is subjected to plasma electrolytic oxidation over a period of 120 min in a phosphate-

silicate electrolyte (pH 11) at a temperature of 30°C. The regime is anode-cathode; current density 20 A/dm<sup>2</sup>; magnitude (amplitude) of final voltage; anode 600 V, cathode 190 V. The depth of the oxide-ceramic coating is 120 μm, micro-hardness 1800 Hv, open porosity 20%.

## Example 2

[0046] A specimen of alloy D16 (AlCu<sub>4</sub>Mg<sub>2</sub>) is subjected to the same treatment as that in Example 1, and possesses the following characteristics: depth of oxide coating 120 μm, micro-hardness 1800 Hv, open porosity 20%.

[0047] The specimen was subjected to chemical nickel-plating and then polishing. The depth of penetration of the nickel after polishing is about 10 μm. The concentration of nickel is at its maximum in the layer next to the surface and decreases exponentially as the depth of coating increases.

## Example 3

[0048] A specimen of alloy AK4-2 (AlCu<sub>2</sub>, Mg<sub>2</sub> Fe Ni) is subjected to plasma electrolytic oxidation for a period of 90 minutes in a phosphate-silicate electrolyte (pH 11) at a temperature of 30°C. The regime is anode-cathode; current density 15 A/dm<sup>2</sup>; magnitude of final voltage: anode 550 V, cathode 120 V. Depth of oxide-ceramic coating 70 μm, micro-hardness 1550 Hv, open porosity 16%.

[0049] A composite layer consisting of 20% Cr and 80% Cr<sub>3</sub>C<sub>2</sub> is applied to the specimen by the chemical precipitation method from the gaseous phase. In the course of precipitation, the specimen was heated to 300°C. After this, the specimen was polished. The depth of penetration of the functional compound Cr-Cr<sub>3</sub>C<sub>2</sub> into the porous structure was about 7 μm.

## Example 4

[0050] A specimen of alloy VT6 (TiAl<sub>6</sub>V<sub>4</sub>) was oxidised in an aluminate-sulfate electrolyte (pH 9) for 20 minutes at a temperature of 20°C. Regime: anode; current density 50 A/dm<sup>2</sup>; magnitude of final anode voltage 300 V. Depth of oxide coating 15 μm, micro-hardness 690 Hv, open porosity 12%.

[0051] A layer of nickel was applied to the specimen by the method of chemical precipitation from the gaseous phase. In the course of precipitation, the specimen was heated to 200°C. After this, the cylindrical surface of the specimen was polished. The depth of penetration of the nickel compound into the porous structure was 3 μm.

## Example 5

[0052] A specimen of alloy VMD12 (MgZn<sub>6</sub>MnCu) was oxidised in an aluminate-fluoride electrolyte (pH 12) for 40 minutes at a temperature of 20°C. Regime: anode-cathode; current density 8 A/dm<sup>2</sup>; magnitude of final voltage: anode 350 V, cathode 130 V. Depth of oxide-ceramic coating 30 μm, micro-hardness 750 Hv, open porosity 25%.

[0053] A composite layer of nickel was applied to the specimen by the method of chemical precipitation from the gaseous phase. During precipitation, the specimen was heated to 200°C. After this, the cylindrical surface of the specimen was polished. The depth of penetration of the nickel compound into the porous structure of the layer was 10 μm.

## Example 6

[0054] A specimen of alloy ABM-3 (AlBe<sub>60</sub>Mg<sub>2</sub>) - of the "localloy" type - was oxidised in a phosphate-silicate electrolyte (pH 11) for 120 minutes at a temperature of 30°C. Regime anode-cathode; current density 15 A/dm<sup>2</sup>; magnitude of final voltage: anode 480 V, cathode 110 V. Depth of oxide-ceramic coating 100 μm, micro-hardness 790 Hv, open porosity 18%.

[0055] A composite layer of nickel was applied to the specimen by the method of chemical precipitation from the gaseous phase. In the course of precipitation, the specimen was heated to 200°C. After this, the cylindrical surface of the specimen was polished. Depth of penetration of the nickel compound into the porous structure of the oxide layer: 8 μm.

[0056] Tests of friction pairs formed from components with different types of coating and counter-specimens of hardened steel were conducted on a universal friction machine.

[0057] A ring-cylinder arrangement with intersecting axes for point contact was selected. A fixed specimen of steel ShKh15, hardness HRC<sub>3</sub> 58-60 was pressed to the moving specimen (ring) to which the coating under study had been applied.

[0058] The tests were conducted in boundary friction regime, in which several droplets of spindle oil are applied to the coated specimen before the test. The slip rate was 2 m/sec, normal load in the contact of the specimens - 75 N. The test took 60 seconds. Ten identical tests were conducted on each ring. The mean values for the characteristics were calculated from the results of these tests.

[0059] The studies also served for the evaluation of such friction characteristics as wear resistance, friction coefficient and load capacity. Wear resistance was assessed from wear in weight and dimensions by comparing the dimensions of spots on the steel specimen and the loss of mass of the coated specimen.

[0060] The results of the technical friction tests are given in Table 1.

Table 1

| No. of specimen tested (No. of example) | Wear of specimen with coating, mg | Area of wear spot of steel counter-body, mm <sup>2</sup> | Friction coefficient |
|-----------------------------------------|-----------------------------------|----------------------------------------------------------|----------------------|
| 1                                       | 1.96                              | 2.83                                                     | 0.439                |
| 2                                       | 0.25                              | 1.18                                                     | 0.202                |
| 3                                       | 0.16                              | 1.46                                                     | 0.232                |
| 4                                       | 0.63                              | 0.74                                                     | 0.185                |
| 5                                       | 0.75                              | 0.55                                                     | 0.171                |
| 6                                       | 0.19                              | 1.23                                                     | 0.225                |

[0061] The test results demonstrate the efficiency of using composite coatings on various backings as compared with the usual oxide-ceramic coating on aluminium alloy. Thus, the friction coefficient is little more than half, counter-body wear is reduced by a factor of 2-5 and wear of the ring coating itself by a factor of up to 10.

### Industrial Applicability

[0062] Since the proposed composite coating has such unique properties as high strength and hardness in combination with a certain plasticity, exceptional resistance to wear and scratching, and high resistance to corrosion and vibrations, we have the opportunity to widen considerably the application of non-ferrous metal components.

[0063] The durability and reliability of components operating in extreme conditions under the simultaneous effect of different forms of wear (abrasive wear at high temperatures and in aggressive media, dynamic contact loads and vibration) are also increased.

[0064] The wide range of metals and refractory compounds used as functional materials introduced into the porous ceramic matrix makes it possible to select the optimal characteristics of composite coatings for actual conditions of use.

[0065] The proposed process for producing protective coatings is distinguished by being ecologically harmless and by its low costs, and is suitable for use on an industrial scale.

### Claims

1. Protective composite coating, applied onto non-ferrous metals, their alloys and intermetallic compounds (5), and also onto components therefrom, wherein the composite coating takes the form of a first porous oxide-ceramic matrix coating (3), formed by plasma electrolytic oxidation of a surface layer (4) of a material (5) to be protected, and a second coating (1) formed by introducing at least one functional component selected from the group comprising: Ni, Cu, Co, Fe, Cr, Mo, Ti, Al, Sb, Ag, Zn, Cd, Pb, Sn, Bi, In, Ga and mixtures thereof, carbides, oxides, nitride, borides, silicides and refractory compounds of the metals of groups IVB-VIB of Mendeleyev's periodic system of elements, and mixtures thereof; into the pores (2) of the first matrix coating (3); **characterised in that** surface portions (6) of the first matrix coating (3) protrude beyond the second coating (1).
2. Composite coating in accordance with claim 1, **characterised in that** it is applied to the non-ferrous metals Al, Mg, Ti, Nb and their alloys, and also the compounds Al-Ti, Ti-Nb and Al-Be.
3. Composite coating in accordance with claim 1 or 2, **characterised in that** the oxide-ceramic matrix coating (3) has an open porosity of 5-35%, with porosity decreasing through the thickness of the coating (3) in the direction inward from the outer layer, the micro-hardness of the oxide-ceramic coating (3) is 300-2000 HV and increases through the thickness inward from the outer layer, and the total thickness of the oxide-ceramic layer (3) comprises 1-600  $\mu\text{m}$ , preferably 3-150  $\mu\text{m}$ .
4. Composite coating in accordance with claim 3, **characterised in that** the oxide-ceramic matrix coating (3) has an

open porosity of 10-12%.

5. Composite coating in accordance with claim 1, 2, 3 or 4, **characterised in that** the functional components are introduced into the pores of the oxide-ceramic matrix coating (3) to a depth of 1-150 µm, preferably 2-100 µm.

6. Process for the application of a protective composite coating to non-ferrous metals, their alloys and intermetallic compounds (5), and also to components made therefrom, **characterised in that** it includes the following stages:

(a) plasma electrolytic oxidation of a surface layer (4) of the material (5) being protected, with a process voltage and current density being controlled so as to produce a first oxide-ceramic matrix coating (3) with predetermined porosity;

(b) introduction into the pores (2) of the first oxide-ceramic matrix coating (3) formed in stage (a) of at least one functional component selected from the group comprising: Ni, Cu, Co, Fe, Cr, Mo, Ti, Al, Sb, Ag, Zn, Cd, Pb, Sn, Bi, In, Ga and mixtures thereof, carbides, oxides, nitride, borides, silicides and refractory compounds of the metals of groups IVB-VIB of Mendeleyev's periodic system of elements, and mixtures thereof; so as to form a second coating (1); and

(c) finishing of the surface of the composite coating so as to cause surface portions (6) of the first matrix coating (3) to protrude beyond the second coating (1).

7. Process in accordance with claim 6, **characterised in that** the plasma electrolytic oxidation takes place at a voltage of 100-1000 V and a current density of 2-200 A/dm<sup>2</sup>.

8. Process in accordance with claim 6 or 7, **characterised in that** the plasma electrolytic oxidation takes place at a temperature of 10-55°C.

9. Process in accordance with claim 6, 7 or 8, **characterised in that** the introduction of the functional components into the pores (2) of the first matrix coating (3) is done by electrochemical precipitation from aqueous or organic solutions, including the use of ultra-disperse powders.

10. Process in accordance with claim 6, 7 or 8, **characterised in that** the introduction of the functional components into the pores (2) of the first matrix coating (3) is done by chemical precipitation from aqueous or organic solutions.

11. Process in accordance with claim 6, 7 or 8, **characterised in that** the introduction of the functional components into the pores (2) of the first matrix coating (3) is done by chemical precipitation from the gaseous phase.

12. Process in accordance with claim 6, 7 or 8, **characterised in that** the introduction of the functional components into the pores (2) of the first matrix coating (3) is done with the aid of physical precipitation methods.

13. Process in accordance with claim 6, 7 or 8, **characterised in that** the introduction of the functional components into the pores (2) of the first matrix coating (3) is done with the aid of friction-mechanical rubbing on, using powders, bars or brushes.

14. Process in accordance with any of claims 6 to 13, **characterised in that** the finishing treatment of the composite coating is selected from the following operations: polishing, fine grinding, lapping, honing and superfinishing.

## Patentansprüche

1. Schützende Komposit-Beschichtung, die auf Nichteisenmetall, deren Legierungen und intermetallischen Verbindungen (5) aufgetragen wird, und ferner auf Komponenten daraus, wobei die Komposit-Beschichtung die Form einer ersten porösen oxidkeramischen Matrixbeschichtung (3) annimmt, gebildet durch plasmaelektrolytische Oxidation einer Oberflächenschicht (4) aus einem zu schützenden Material (5), und einer zweiten Beschichtung (1), die gebildet wird durch Einführen mindestens einer funktionalen Komponente, die aus der Gruppe ausgewählt wird, die folgendes umfasst: Ni, Cu, Co, Fe, Cr, Mo, Ti, Al, Sb, Ag, Zn, Cd, Pb, Sn, Bi, In, Ga und Mischungen dieser, Karbide, Oxide, Nitride, Boride, Silicide und feuerfeste Verbindungen aus Metallen der Gruppen IVB-VIB des Mendeleyew'schen Periodensystems der Elemente und Mischungen dieser, in die Poren (2) der ersten Matrixbeschichtung (3); **dadurch gekennzeichnet, dass** Oberflächenabschnitte (6) der ersten Matrixbeschichtung (3) über die zweite Beschichtung (1) vorstehen.

2. Komposit-Beschichtung nach Anspruch 1, **dadurch gekennzeichnet, dass** diese auf die Nichteisenmetalle Al, Mg, Ti, Nb und deren Legierungen sowie die Verbindungen Al-Ti, Ti-Nb und Al-Be aufgetragen wird.
- 5 3. Komposit-Beschichtung nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die oxidkeramische Matrixbeschichtung (3) eine offene Porosität von 5 bis 35 % aufweist, wobei die Porosität durch die Dicke der Beschichtung (3) in die Einwärtsrichtung von der äußeren Schicht abnimmt, wobei die Mikrohärtigkeit der oxidkeramischen Beschichtung (3) zwischen 300 und 2000 HV liegt und durch die Dicke von der äußeren Schicht einwärts zunimmt, und wobei die Gesamtdicke der oxidkeramischen Schicht (3) 1 bis 600 µm umfasst, vorzugsweise 3 bis 150 µm.
- 10 4. Komposit-Beschichtung nach Anspruch 3, **dadurch gekennzeichnet, dass** die oxidkeramische Beschichtung (3) eine offene Porosität von 10 bis 12 % aufweist.
- 15 5. Komposit-Beschichtung nach Anspruch 1, 2, 3 oder 4, **dadurch gekennzeichnet, dass** die funktionalen Komponenten in die Poren der oxidkeramischen Beschichtung (3) bis auf eine Tiefe von 1 bis 150 µm, vorzugsweise von 2 bis 100 µm eingeführt werden.
- 20 6. Verfahren zum Auftragen einer schützenden Komposit-Beschichtung auf Nichteisenmetalle, deren Legierungen und intermetallischen Verbindungen (5), und ferner auf Komponenten daraus, **dadurch gekennzeichnet, dass** das Verfahren die folgenden Schritte aufweist:
  - (a) plasmalektrolytische Oxidation einer Oberflächenschicht (4) des geschützten Materials (5), mit einer geordneten Verfahrensspannung und Stromdichte, so dass eine erste oxidkeramische Matrixbeschichtung (3) mit vorbestimmter Porosität erzeugt wird;
  - 25 (b) das Einführen in die Poren (2) der ersten oxidkeramischen Matrixbeschichtung (3), die in Schritt (a) gebildet wird, mindestens einer funktionalen Komponente, die aus der Gruppe ausgewählt wird, die folgendes umfasst: Ni, Cu, Co, Fe, Cr, Mo, Ti, Al, Sb, Ag, Zn, Cd, Pb, Sn, Bi, In, Ga und Mischungen dieser, Karbide, Oxide, Nitride, Boride, Silicide und feuerfeste Verbindungen aus Metallen der Gruppen IVB-VIB des Mendelejewschen Periodensystems der Elemente und Mischungen dieser, so dass eine zweite Beschichtung (1) gebildet wird; und
  - 30 (c) Endbearbeitung der Oberfläche der Komposit-Beschichtung, so dass es bewirkt wird, dass Oberflächenabschnitte (6) der ersten Matrixbeschichtung (3) über die zweite Beschichtung (1) vorstehen.
7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet, dass** die plasmalektrolytische Oxidation auf einer Spannung von 100 bis 1000 V und einer Stromdichte von 2 bis 200 A/dm<sup>2</sup> erfolgt.
- 35 8. Verfahren nach Anspruch 6 oder 7, **dadurch gekennzeichnet, dass** die plasmalektrolytische Oxidation auf einer Temperatur von 10 bis 55 °C erfolgt.
- 40 9. Verfahren nach Anspruch 6, 7 oder 8, **dadurch gekennzeichnet, dass** das Einführen der funktionalen Komponenten in die Poren (2) der ersten Matrixbeschichtung (3) durch elektrochemische Ablagerung aus wässrigen oder organischen Lösungen erfolgt, einschließlich der Verwendung von ultradispersen Pulvern.
- 45 10. Verfahren nach Anspruch 6, 7 oder 8, **dadurch gekennzeichnet, dass** das Einführen der funktionalen Komponenten in die Poren (2) der ersten Matrixbeschichtung (3) durch chemische Ablagerung aus wässrigen oder organischen Lösungen erfolgt.
- 50 11. Verfahren nach Anspruch 6, 7 oder 8, **dadurch gekennzeichnet, dass** das Einführen der funktionalen Komponenten in die Poren (2) der ersten Matrixbeschichtung (3) durch chemische Ablagerung aus der gasförmigen Phase erfolgt.
12. Verfahren nach Anspruch 6, 7 oder 8, **dadurch gekennzeichnet, dass** das Einführen der funktionalen Komponenten in die Poren (2) der ersten Matrixbeschichtung (3) mit Unterstützung physikalischer Ablagerungsmethoden erfolgt.
- 55 13. Verfahren nach Anspruch 6, 7 oder 8, **dadurch gekennzeichnet, dass** das Einführen der funktionalen Komponenten in die Poren (2) der ersten Matrixbeschichtung (3) mit Unterstützung durch reibungsmechanisches Reiben unter Verwendung von Pulvern an Stäben oder Bürsten erfolgt.
14. Verfahren nach einem der Ansprüche 6 bis 13, **dadurch gekennzeichnet, dass** die Endbearbeitungsbehandlung der Komposit-Beschichtung aus den folgenden Operationen ausgewählt wird: Polieren, Feinzerkleinerung, Läppen, Honen und Supfinieren.

## Revendications

1. Revêtement composite protecteur appliqué sur des métaux non ferreux, leurs alliages et composés intermétalliques (5), ainsi que sur des composants provenant de ceux-ci, dans lequel le revêtement composite prend la forme d'un premier revêtement à matrice d'oxyde poreux-céramique (3) formé par oxydation électrolytique de plasma d'une couche superficielle (4) d'un matériau (5) devant être protégé, et d'un second revêtement (1) formé par introduction d'au moins un composant fonctionnel sélectionné parmi le groupe comprenant : Ni, Cu, Co, Fe, Cr, Mo, Ti, Al, Sb, Ag, Zn, Cd, Pb, Sn, Bi, In, Ga et des mélanges de ceux-ci, carbures, oxydes, nitrure, borures, siliciures et composés réfractaires des métaux des groupes IVB-VIB de la classification périodique des éléments de Mendeleïev, et des mélanges de ceux-ci ; dans les pores (2) du premier revêtement à matrice (3) ; **caractérisé en ce que** des portions superficielles (6) du premier revêtement à matrice (3) font saillie au-delà du second revêtement (1).
2. Revêtement composite selon la revendication 1, **caractérisé en ce qu'il** est appliqué aux métaux non ferreux Al, Mg, Ti, Nb et leurs alliages, ainsi qu'aux composés Al-Ti, Ti-Nb et Al-Be.
3. Revêtement composite selon la revendication 1 ou 2, **caractérisé en ce que** le revêtement à matrice d'oxyde-céramique (3) possède une porosité ouverte de 5 à 35 %, avec la porosité qui diminue à travers l'épaisseur du revêtement (3) dans la direction vers l'intérieur depuis la couche externe, la microdureté du revêtement d'oxyde-céramique (3) est de 300 à 2000 HV et augmente à travers l'épaisseur vers l'intérieur depuis la couche externe, et l'épaisseur totale de la couche d'oxyde-céramique (3) comprend 1 à 600  $\mu\text{m}$ , de préférence 3 à 150  $\mu\text{m}$ .
4. Revêtement composite selon la revendication 3, **caractérisé en ce que** le revêtement à matrice d'oxyde-céramique (3) possède une porosité ouverte de 10 à 12 %.
5. Revêtement composite selon la revendication 1, 2, 3 ou 4, **caractérisé en ce que** les composants fonctionnels sont introduits dans les pores du revêtement à matrice d'oxyde-céramique (3) à une profondeur de 1 à 150  $\mu\text{m}$ , de préférence 2 à 100  $\mu\text{m}$ .
6. Procédé pour l'application d'un revêtement composite protecteur à des métaux non ferreux, leurs alliages et composés intermétalliques (5), ainsi qu'à des composants fabriqués à partir de ceux-ci, **caractérisé en ce qu'il** inclut les étapes suivantes :
  - (a) oxydation électrolytique de plasma d'une couche superficielle (4) du matériau (5) qui est protégé, avec une tension opératoire et une densité du courant qui sont commandées de manière à produire un premier revêtement à matrice d'oxyde-céramique (3) de porosité prédéterminée ;
  - (b) introduction dans les pores (2) du premier revêtement à matrice d'oxyde-céramique (3) formé à l'étape (a) d'au moins un composant fonctionnel sélectionné parmi le groupe comprenant : Ni, Cu, Co, Fe, Cr, Mo, Ti, Al, Sb, Ag, Zn, Cd, Pb, Sn, Bi, In, Ga et des mélanges de ceux-ci, carbures, oxydes, nitrure, borures, siliciures et composés réfractaires des métaux des groupes IVB-VIB de la classification périodique des éléments de Mendeleïev, et des mélanges de ceux-ci ; de manière à former un second revêtement (1) ; et
  - (c) finition de la surface du revêtement composite de manière à provoquer la saillie de portions superficielles (6) du premier revêtement à matrice (3) au-delà du second revêtement (1).
7. Procédé selon la revendication 6, **caractérisé en ce que** l'oxydation électrolytique de plasma a lieu à une tension de 100 à 1000 V et une densité de courant de 2 à 200 A/dm<sup>2</sup>.
8. Procédé selon la revendication 6 ou 7, **caractérisé en ce que** l'oxydation électrolytique de plasma a lieu à une température de 10 à 55°C.
9. Procédé selon la revendication 6, 7 ou 8, **caractérisé en ce que** l'introduction des composants fonctionnels dans les pores (2) du premier revêtement à matrice (3) est réalisée par précipitation électrochimique à partir de solutions aqueuses ou organiques, incluant l'utilisation de poudres ultradispersibles.
10. Procédé selon la revendication 6, 7 ou 8, **caractérisé en ce que** l'introduction des composants fonctionnels dans les pores (2) du premier revêtement à matrice (3) est réalisée par précipitation chimique à partir de solutions aqueuses ou organiques.
11. Procédé selon la revendication 6, 7 ou 8, **caractérisé en ce que** l'introduction des composants fonctionnels dans

## EP 1 231 299 B1

les pores (2) du premier revêtement à matrice (3) est réalisée par précipitation chimique à partir de la phase gazeuse.

12. Procédé selon la revendication 6, 7 ou 8, **caractérisé en ce que** l'introduction des composants fonctionnels dans les pores (2) du premier revêtement à matrice (3) est réalisée à l'aide de procédés de précipitation physique.

13. Procédé selon la revendication 6, 7 ou 8, **caractérisé en ce que** l'introduction des composants fonctionnels dans les pores (2) du premier revêtement à matrice (3) est réalisée à l'aide de friction-frottement mécanique utilisant des poudres, barres ou brosses.

14. Procédé selon l'une quelconque des revendications 6 à 13, **caractérisé en ce que** le traitement de finition du revêtement composite est sélectionné parmi les opérations suivantes : polissage, broyage fin, rodage, rodage au liquide et micropolissage.

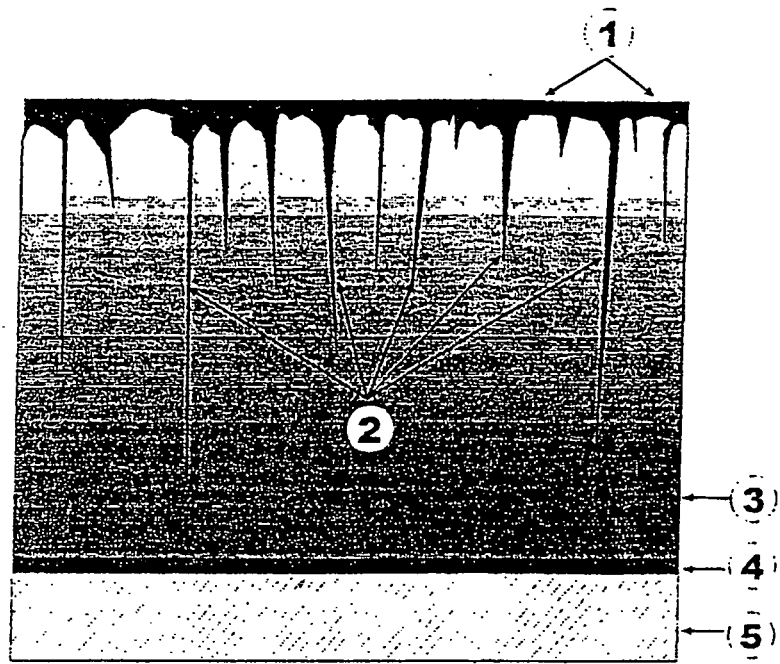


Fig. 1.

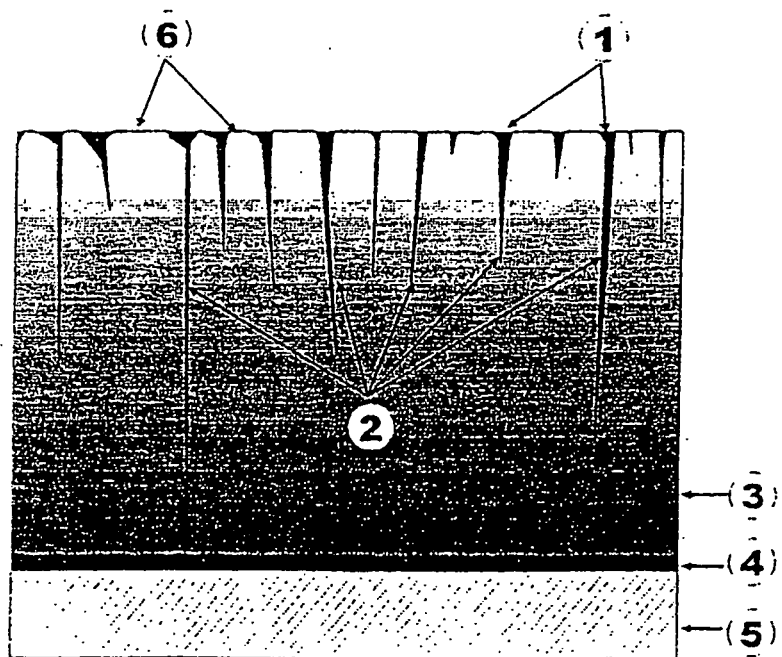


Fig. 2.

**REFERENCES CITED IN THE DESCRIPTION**

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