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(54) **PLASMA-CHEMICAL METHOD FOR PRODUCTION OF BLACK OXIDE-CERAMIC LAYERS AND CORRESPONDINGLY COATED OBJECT**

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(57) **ABSTRACT**

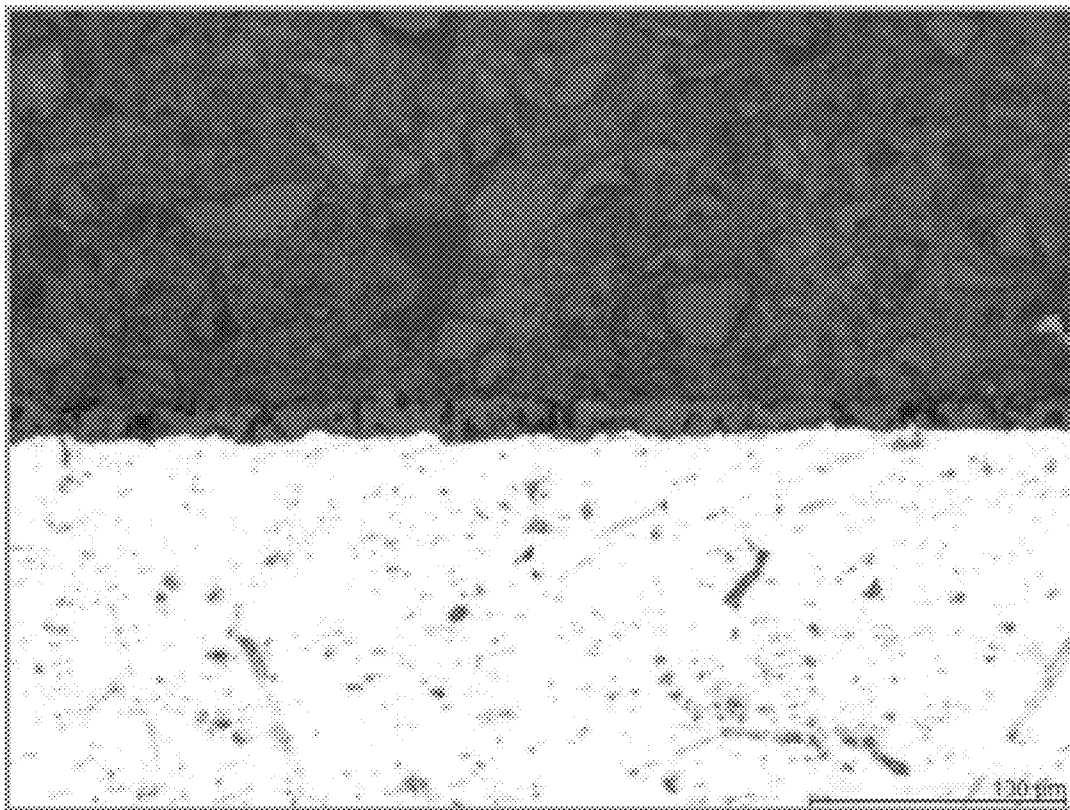
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Plasma-chemical method for production of black oxide ceramic layers on aluminium, magnesium, titanium or alloys thereof and special materials containing these substances according to the process of anodic oxidation in aqueous electrolytes, wherein an electrolyte is used which contains iron and vanadium.

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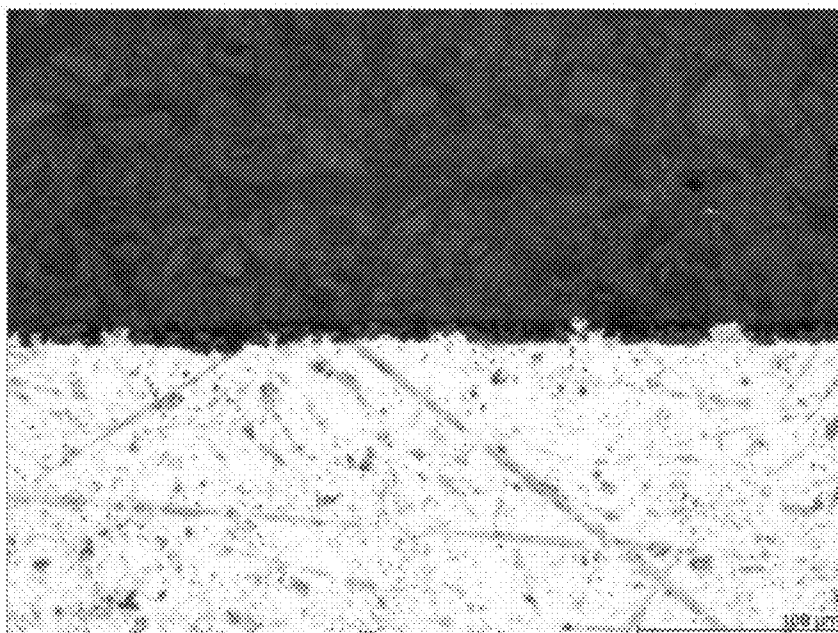


Figure 1

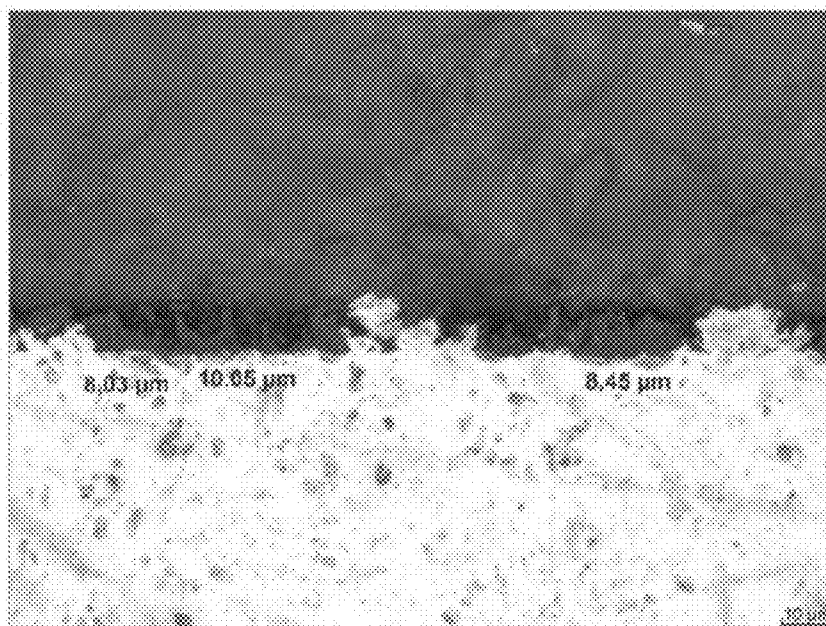


Figure 2

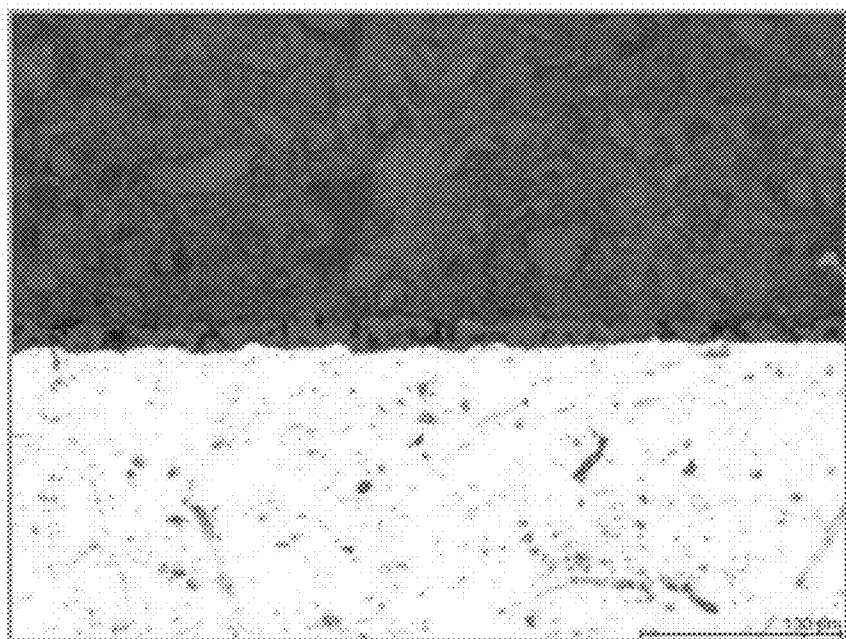


Figure 3

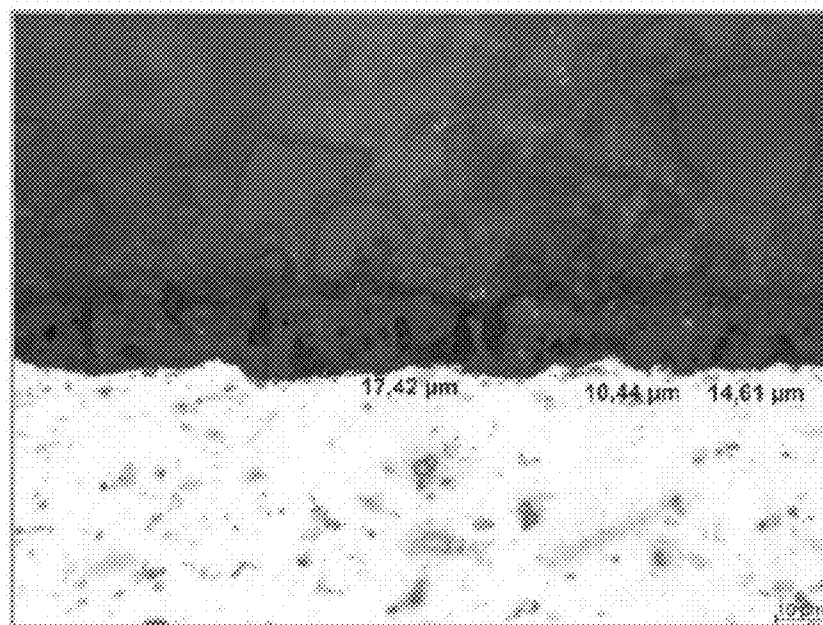


Figure 4

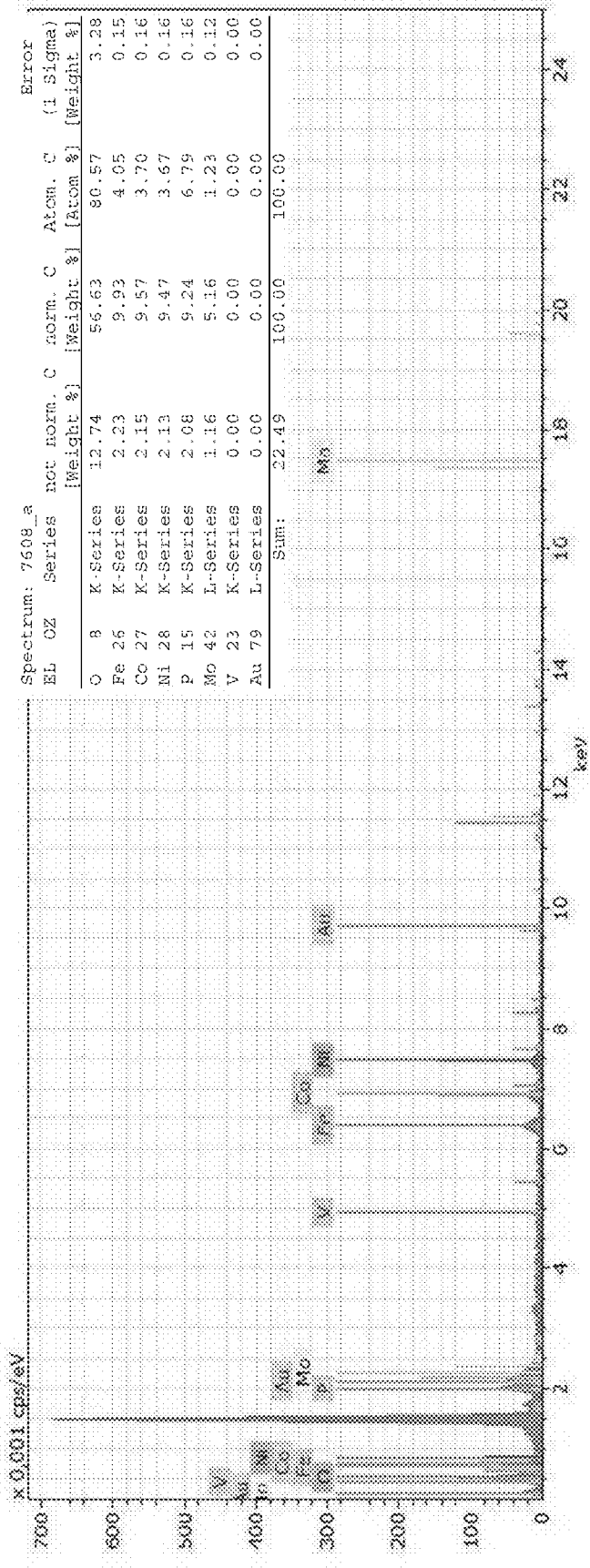


Figure 5

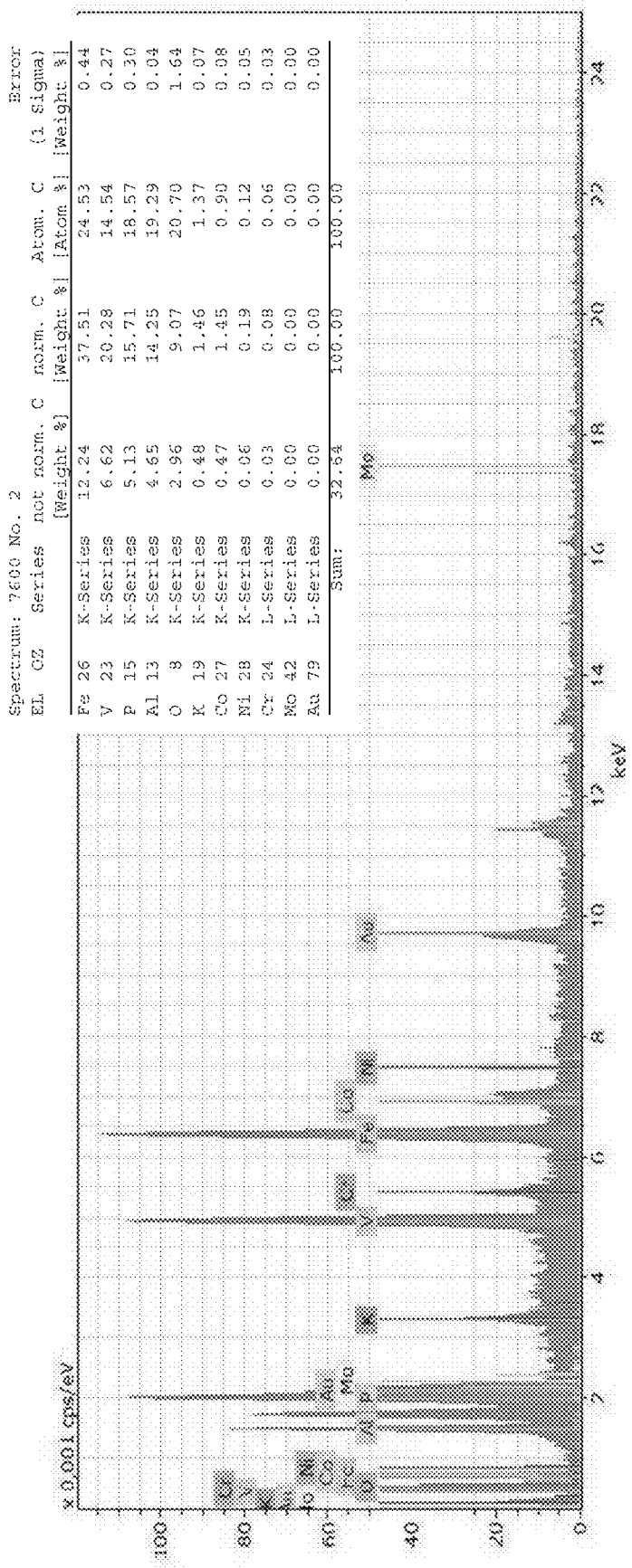


Figure 6

**PLASMA-CHEMICAL METHOD FOR
PRODUCTION OF BLACK OXIDE-CERAMIC
LAYERS AND CORRESPONDINGLY COATED
OBJECT**

CROSS-REFERENCE TO RELATED
APPLICATION

[0001] This application claims the benefit and priority of German Patent Application No. 102013110660.9 filed Sep. 26, 2013. The entire disclosure of the above application is incorporated herein by reference.

FIELD

[0002] The invention relates to a plasma-chemical method for production of black oxide-ceramic layers on light metals, in particular aluminium, titanium, magnesium or alloys thereof according to the process of anodic spark oxidation in aqueous electrolytes.

BACKGROUND

[0003] The production of oxide-ceramic layers on light metals by plasma-chemical processes in aqueous electrolytes is known. These processes are known in the literature inter alia under the following terms: anodic spark oxidation (ASO), plasma-chemical oxidation (PCO), plasma electrolytic oxidation (PEO), anodic spark deposition (ASD) and micro arc oxidation (MAO).

[0004] As is known from EP 0 545 230 A1, this anodic oxidation in aqueous electrolytes is a gas-solid-reaction under plasma conditions, in which the high input of energy at the foot of the discharge column produces liquid metal on the anode, which metal forms a briefly molten oxide with the activated oxygen. The layer formation is effected via partial anodes. A shaping region is disposed upstream of the spark discharge (P. Kurze; Dechema-Monographien vol. 121—VCH Verlagsgesellschaft 1990, page 167-180 with further literature references). The electrolytes have been combined in such a way that their positive properties are united and high-quality anodically produced oxide-ceramic layers are produced on aluminium. By combining different salts it is possible to achieve higher salt concentrations in the electrolyte bath and therefore higher viscosities. Such highly viscous electrolytes have a high heat capacity, stabilise the formed oxygen film on the anode and therefore guarantee uniform oxide layer formation (DD-WP 142 360).

[0005] The course of the current density potential curves (CDPC) for the anodic spark discharge allows three distinctive ranges to be differentiated, the Faraday, spark discharge and arc discharge range (see P. Kurze loc.cit). A barrier layer is naturally found on the metal or the metal alloy. By increasing the voltage of the anodically polled metal, the barrier layer grows. Then, at the metal/gas/electrolyte phase boundary an oxygen plasma is partially produced by which the oxide ceramic layer is formed. The metal ion in the oxide ceramic layer results from the metal, the oxygen from the anodic reaction in the aqueous electrolyte used. The oxide ceramic is liquid at the detected plasma temperatures of about 7.000 Kelvin. As far as the metal is concerned there is sufficient time for the melt of the oxide ceramic to be able to contract well and it thus forms a low-pore oxide ceramic layer sintered thereon. As far as the electrolyte is concerned, the melt of the oxide ceramic is rapidly cooled by the electrolyte and the still migrating gasses, in particular oxygen and water vapour,

leave behind an oxide ceramic layer with a capillary system which is linked to form a wide mesh. Examinations using a scanning electron microscope have shown pore diameters of 0.1 μm to 30 μm (CERAMIC COATINGS BY ANODIC SPARK DEPOSITION G. P. Wirtz et al, MATERIALS & MANUFACTURING PROCESSES 6 (1), 87-115 (1991), in particular FIG. 12).

[0006] Components provided with such resistant coatings are used inter alia in the automobile, aviation and aerospace industries as well as the optical industry and also medical technology.

[0007] DD 299 595 and DD 299 596 describe the production of black conversion layers on light metal using electrolytes which contain chromate.

[0008] DD 221 762 A1 and DD 257 275 A1 disclose e.g. the addition of metal salts such as iron hexacyanoferrate, nickel salts, cobalt salts, or chromium salts to the electrolyte in order to produce dark coloured oxide layers.

[0009] U.S. Pat. No. 4,659,440 discloses the use of electrolytes which, in addition to hydrofluoric acid and peroxides, can also contain vanadium compounds to impart colour.

[0010] On the one hand, in the known methods substances which according to our current knowledge are considered to be hazardous are used in the electrolytes, in particular carcinogenic chromium salts or metal salts which are on the ECHA List (<http://echa.europa.eu>) since they are classified as harmful to the environment or occupational safety.

[0011] Thus from DE 10 2011 055 644 B4 the use of electrolytes which contain cobalt salts and nickel salts is known.

[0012] On the other hand, there is still a desire for black oxide ceramic layers with chemical stability and wear-resistance.

[0013] Thus in the future, electrolytes which contain molybdenum ions, cobalt ions, chromium ions or nickel ions or cyanide ions or other substances which give cause for concern should no longer be used since they can pose problems for occupational safety and the environment.

SUMMARY

[0014] The object of the invention is thus to provide a method for production of black oxide ceramic layers on aluminium, magnesium, titanium or alloys thereof and special materials containing these substances according to the process of anodic spark oxidation (ASO), in which electrolytes are used which are low in harmful substances and are easy to handle. In particular, the electrolytes should not contain any molybdenum ions, cobalt ions, chromium ions or nickel ions or cyanide ions or borates.

[0015] This object is achieved by the method set out in claim 1.

[0016] In accordance with the invention, it has been recognised that through the use of an iron and vanadium-containing electrolyte, black oxide ceramic layers can be produced on aluminium, magnesium, titanium or alloys thereof and special materials containing these substances according to the anodic oxidation process. The electrolyte is thus free of molybdenum, cobalt, chromium or nickel.

[0017] By means of the invention, black and stable oxide ceramic layers can be produced, the layer thickness of which can be varied over a wide range.

[0018] In terms of the invention, all layers which according to the CIEL*a*b* system have values of L* less than or equal to 30 are understood to be jet black.

[0019] Aluminium and alloys thereof can include pure aluminium and alloys with aluminium as the main component, such as forgeable aluminium alloys of the series: EN-AW 1000, 2000, 3000, 4000, 5000, 6000, 7000, or cast aluminium alloys of the series: EN-AC 21000, 21100, 42000, 43000, 43200, 43400, 44300, 46000, 46200, 47000, 47100, 48000, 51000, 51100.

[0020] Magnesium and alloys thereof can include pure magnesium and the cast magnesium alloys of the ASTM designations: AS41, AM60, AZ61, AZ63, AZ81, AZ91, AZ92, HK31, QE22, ZE41, ZH62, ZK51, ZK61, EZ33, HZ32 and the forgeable alloys AZ31, AZ61, AZ80, M1, ZK60, ZK40.

[0021] Furthermore, pure titanium or even titanium alloys such as TiAl6V4; TiAl5Fe2,5 etc can be used.

[0022] Intermetallic compounds or phases, for example, such as titanium aluminides can be used as special materials with aluminium, magnesium, titanium or alloys thereof.

[0023] Most particularly preferred is the use of aluminium and alloys thereof.

[0024] Within the scope of the invention it has proved particularly advantageous if the electrolyte has a pH value of 5.4 to 10.0 during anodic oxidation.

[0025] The electrolyte can also contain inorganic or organic anions. It preferably contains 0.2 to 0.9 Mol/L of a phosphate of an alkali metal, preferably a dihydrogen phosphate or pyrophosphate, in particular potassium dihydrogen phosphate or potassium pyrophosphate, and/or 0.15 to 0.5 Mol/L citric acid or salts thereof. Citrates are particularly preferred since they support a controlled sparking process. Phosphates permit improved layer growth.

[0026] It is also useful if the electrolyte contains 0.8 to 2.9 Mol/L, preferably 0.8 to 2.1 Mol/L of a stabiliser, in particular hexamethylene tetramine.

[0027] Within the scope of the invention, iron salts and vanadium salts are added to the electrolyte in order to obtain the desired black colour for the oxide ceramic layer. In particular, by the combination in accordance with the invention of iron and vanadium, thick, jet black layers (up to 100 µm) are obtained. The production thereof necessarily requires the presence of both metal salts. As shown by the comparative tests (see below), with only one of the two metal salts no jet black layers in terms of the invention are obtained.

[0028] It is particularly preferred if for this purpose an iron(II) and a vanadium(V) salt are used. Preferably 0.04 to 0.09 Mol/L of an iron(III) salt and 0.035 to 0.090 Mol/L of a vanadium(V) salt are used. Most particularly preferred is the use of ammonium iron(III) citrate and ammonium (mono) vanadate as a source for the metal ions. Thus, 0.04 to 0.09 mol/L ammonium iron(III) citrate and 0.035 to 0.09 mol/L ammonium (mono)vanadate are preferably used.

[0029] An electrolyte temperature of 15 to 60, preferably up to 40 degrees Celsius has proved particularly suitable.

[0030] The current density used is preferably between 0.02 and 0.10 Acm⁻², preferably 0.04 to 0.08 Acm⁻², without the quality and layer thickness of the oxide ceramic layers having to be compromised.

[0031] The current density is advantageously kept constant until a final voltage below 1000 V, preferably 300 to 650 V is achieved.

[0032] The oxide ceramic layers obtained by means of the invention can comprise a layer thickness of 5 µm to 100 µm and consist of oxides, in particular spinels, of aluminium, iron and vanadium.

[0033] With the electrolyte combinations in accordance with the invention, it is possible for the first time to produce jet black (of L* less than or equal to 30, cf. above) and also strongly adhesive layer thicknesses of greater than 50 µm. In particular, the electrolyte combination in accordance with the invention permits the production of thinner or thicker strongly adhesive, jet black layers of up to 100 µm.

[0034] It is also particularly preferred if the electrolyte is low in harmful substances and is easy to handle, i.e. contains no molybdenum ions, cobalt ions, chromium ions or nickel ions and cyanide ions or borate ions.

[0035] Further features and details of the invention will become clear from the following description of examples.

[0036] Material and Measurement Devices Used in the Tests

[0037] sample material: a) EN-AW 6082 (EN-AW AlSi1MgMn, heat treatment state T6 and T4); b) EN-AC 46000 (GD-AlSi9Cu3(Fe)),

[0038] rectifier: from the company RGB, type WER 21.877 (30 A/380V),

[0039] frame material: aluminium (isolated),

[0040] colour measuring device: from the company BYK-Gardner spectro-guide (serial no. 1020746), lighting type/observer D65/10°, measuring geometry 45°/0°,

[0041] layer thickness measuring device: from the company Helmut Fischer GmbH & Co.KG, DUALSCOPE® MP40E, probe ETA 3.3 H

[0042] Implementation of the Test

[0043] The electrolyte solutions were freshly prepared and placed into standard devices for anodic oxidation. Prior to oxidation, all sample plates were degreased with a commercially available cleaner and then immersed in the electrolyte baths and contacted. The voltage was applied with a rectifier from RGB (30 A/380V). After about 10 min. the voltages were in the range of 230 to 290 Volt.

[0044] After the set duration, the sample plates were removed, cleaned and examined according to standard methods.

[0045] Layer thickness measurements and cross-hatch adhesion tests according to DIN 2499 were carried out on the samples to characterise the layer according to the CIE L*a*b* system as per DIN EN ISO 11664-4.

[0046] In order to characterise individual layers, cross-section polishing was effected and these polished areas were examined using solid-state analysis techniques by means of SEM (scanning electron microscopy) or EDX (energy dispersive X-ray spectroscopy) and were documented.

DRAWINGS

[0047] FIGS. 1 and 2 show cross-section polishing tests of the prior art according to DD 221 762 A1.

[0048] FIGS. 3 and 4 show cross-section polishing tests according to the Exemplified embodiment No. 1.

[0049] FIGS. 5 and 6 show EDX spectra of the prior art (FIG. 5) and of the Exemplified embodiment No. 1 (FIG. 6).

DETAILED DESCRIPTION

[0050] The invention will be described by way of example with reference to the following examples.

Exemplified Embodiment 1

[0051] An alkali-degreased aluminium plate of the forgeable alloy EN-AW 6082/AlSi1MgMn is immersed in an

aqueous electrolyte with 0.4 Mol/L citric acid; 1.5 Mol/L hexamethylene tetramine; 0.7 Mol/L potassium dihydrogen phosphate; 0.05 Mol/L ammonium iron(III) citrate; 0.075 Mol/L ammonium (mono)vanadate with a pH value of 6.1 and contacted as an anode and coated at a current density of 0.035 Acm⁻², at 25° C. for a run time of 15 min. by means of spark discharge. A jet black, strongly adhering coating was obtained with a layer thickness of 20 μm and a colour characteristic of L* 28.68; a* -0.01; b* -0.33.

Exemplified Embodiment 2

[0052] An alkali-degreased aluminium plate of the forgeable alloy EN-AW 6082/AlSi1 MgMn is contacted as an anode in an aqueous electrolyte comprising 0.4 Mol/L citric acid; 1.5 Mol/L hexamethylene tetramine; 0.7 Mol/L potassium dihydrogen phosphate; 0.05 Mol/L ammonium iron(III) citrate; 0.075 Mol/L ammonium (mono)vanadate with a pH value of 6.1 and coated at a current density of 0.035 Acm⁻², at 25° C. for a run time of 60 min. by means of spark discharge.

[0053] A jet black, strongly adhering coating was obtained with a layer thickness of 80 μm and a colour characteristic of L* 26.38; a* -0.15; b* -0.76.

Exemplified Embodiment 3

[0054] An alkali-degreased aluminium plate of the cast alloy EN-AC 46000/GD-AlSi9Cu3(Fe) is contacted as an anode in an aqueous electrolyte comprising 0.4 Mol/L citric acid; 1.5 Mol/L hexamethylene tetramine; 0.7 Mol/L potassium dihydrogen phosphate; 0.05 mol/L ammonium iron(III) citrate; 0.075 Mol/L ammonium (mono)vanadate with a pH value of 6.1 and coated at a current density of 0.05 Acm⁻², at 30° C. for a run time of 40 min. by means of spark discharge.

[0055] A jet black, strongly adhering coating was obtained with a layer thickness of 22 μm and a colour characteristic of L* 25.97; a* 0.40; b* 0.20.

Exemplified Embodiment 4

[0056] An alkali-degreased aluminium plate of the forgeable alloy EN-AW 6082/AlSi1 MgMn is contacted as an anode in an aqueous electrolyte comprising 1.3 Mol/L hexamethylene tetramine; 0.35 Mol/L potassium pyrophosphate; 0.05 mol/L ammonium iron(III) citrate; 0.075 Mol/L ammonium (mono)vanadate with a pH value of 9.6 and coated at a current density of 0.032 Acm⁻², at 40° C. for a run time of 30 min. by means of spark discharge. A jet black, strongly adhering coating was obtained with a layer thickness of 22 μm and a colour characteristic of L* 26.60; a* 0.00; b* -0.60.

Exemplified Embodiment 5

[0057] An alkali-degreased and acid-etched pure titanium plate (grade 2) is immersed and contacted as an anode in an aqueous electrolyte with the composition: 0.4 mol/L citric acid; 1.5 mol/L hexamethylene tetramine; 0.7 mol/L potassium dihydrogen phosphate; 0.05 ammonium iron(III) citrate; 0.075 mol/L ammonium (mono)vanadate with a pH value of 6.1 and coated at a current density of 0.03 Acm⁻², at 20° C. for a run time of 15 min. by means of spark discharge.

[0058] A jet black, strongly adhering coating was obtained with a layer thickness of 26.5 μm and a colour characteristic of L* 29.67; a* 3.91; b* 4.01.

Exemplified Embodiment 6

[0059] An alkali-degreased aluminium plate of the forgeable alloy EN-AW 6082/AlSi1 MgMn is immersed and contacted as an anode in an aqueous electrolyte comprising 0.35 Mol/L citric acid, 2.85 Mol/L hexamethylene tetramine, 0.5 Mol/L potassium dihydrogen phosphate, 0.05 Mol/L ammonium iron(III) citrate and 0.07 Mol/L ammonium (mono)vanadate with a pH value of 6.6 and coated at a current density of 0.035 Acm⁻², at 25° C. for a run time of 15 min. by means of spark discharge.

[0060] A jet black, strongly adhering coating was obtained with a layer thickness of 12.3 μm and a colour characteristic of L* 27.91; a* 0.34; b* -0.16.

[0061] The colour measurements were effected using the stated colour measuring device from BYK-Gardner GmbH (see above). For each sample plate a colour measurement was carried out according to the CIE L*a*b* system.

[0062] The layer thickness measurements were effected with the stated measuring device from Helmut Fischer GmbH & Co.KG (see above). For each sample plate 10 measurements of the layer thickness were carried out and the average given.

[0063] Polishing Tests

[0064] Cross-section polishing tests show that in the case of the comparative variation according to DD 221 762 A1 on EN-AW 6082 AlSi1 MgMn there are considerable variations in layer thickness, the oxide layer is not closed in parts (FIGS. 1 and 2). The layer thickness of Exemplified embodiment 1 (FIGS. 3 and 4) is clearly greater and acts in a more homogeneous manner than that of the comparative variation.

[0065] EDX

[0066] Comparison of the EDX spectra (FIGS. 5 and 6) show that in the comparative variation (FIG. 5) cobalt, nickel and molybdenum are contained in the layer. In contrast, in the layer according to the invention (Exemplified embodiment 1, FIG. 6) only the iron and vanadate atoms can be detected (FIG. 6). The traces of nickel and chromium are material-dependent.

[0067] Comparative Tests

[0068] a) A comparison between the invention and the prior art uses values of coatings according to DD 221 762 A1 which were also measured analogously. Although black coatings according to DD 221 762 A1 show colour values according to the CIE L*a*b* system where L* is less than or equal to 30 such layers have layer thicknesses of ca. 12 μm when the tests are carried out in an analogous manner. Although greater layer thicknesses would be possible in this case they are then not homogeneous in colour and layer thickness.

[0069] b) If, in the case of the electrolyte of Exemplified embodiment 1, the vanadium concentration is changed, i.e. the electrolyte contains NO vanadium (i.e. 0 g/L) in addition to iron then L* values of 51.44 are achieved.

[0070] When increasing the proportion of vanadium in the same electrolyte to 3 g/L, brown layers with L*=32.8; a*=1.87; b*=3.87 are also obtained.

[0071] c) If, in the case of the electrolyte of Exemplified embodiment 1, the iron concentration is changed, i.e. only a vanadium compound and NO iron (i.e. 0 g/L Fe) is present as a metal salt in the electrolyte, only brown layers with L*=37.23; a*=1.99; b*=7.24 are also obtained.

[0072] If the iron concentration is increased while keeping the vanadium concentration constant at 4 g/L Fe, brown layers with L*=33.45; a*=1.48; b*=4.0 are also obtained.

1. Plasma-chemical method for production of black oxide ceramic layers on aluminium, magnesium, titanium or alloys thereof and special materials containing these substances according to the process of anodic oxidation in aqueous electrolytes, characterised in that an electrolyte is used which contains iron and vanadium.

2. Method as claimed in claim 1, characterised in that the electrolyte has a pH value of 5.4 to 10.0.

3. Method as claimed in claim 1, characterised in that the electrolyte contains 0.15 to 0.5 Mol/L citric acid or salts thereof.

4. Method as claimed in claim 1, characterised in that the electrolyte contains 0.8 to 2.9 Mol/L of a stabiliser, in particular hexamethylene tetramine.

5. Method as claimed in claim 1, characterised in that the electrolyte contains 0.2 to 0.9 Mol/L of a phosphate of an alkali metal, preferably a dihydrogen phosphate or pyrophosphate, in particular potassium dihydrogen phosphate or potassium pyrophosphate.

6. Method as claimed in claim 1, characterised in that the electrolyte contains 0.04 to 0.09 Mol/L of an iron(III) salt, in particular ammonium iron(III) citrate.

7. Method as claimed in claim 1, characterised in that the electrolyte contains 0.035 to 0.090 Mol/L of a vanadium(V) salt, in particular ammonium (mono)vanadate.

8. Method as claimed in claim 1, characterised in that the electrolyte bath is at a temperature of 15 to 60 degrees Celsius.

9. Method as claimed in claim 1, characterised in that the current density used is from 0.02 to 0.10 Acm⁻², preferably 0.04 to 0.08 Acm⁻².

10. Method as claimed in claim 9, characterised in that a final voltage below 1000 V, preferably 300 to 650 V, is achieved.

11. Method as claimed in claim 1, characterised in that the oxide ceramic layers have a layer thickness in the range of 5 µm to 100 µm.

12. Method as claimed in claim 1, characterised in that the oxide ceramic layers produced consist of oxides, in particular spinels, of aluminium, iron and vanadium.

13. Method as claimed in claim 1, characterised in that jet black oxide ceramic layers with a colour characteristic of L* being less than or equal to 30 are produced.

14. Object with an oxide ceramic layer, in particular an oxide layer of aluminium, iron and vanadium, which can be obtained by a method as claimed in claim 1.

15. Object with an oxide ceramic layer, in particular an oxide layer of aluminium, iron and vanadium, which can be obtained by a method as claimed in claim 2.

16. Object with an oxide ceramic layer, in particular an oxide layer of aluminium, iron and vanadium, which can be obtained by a method as claimed in claim 3.

17. Object with an oxide ceramic layer, in particular an oxide layer of aluminium, iron and vanadium, which can be obtained by a method as claimed in claim 4.

18. Object with an oxide ceramic layer, in particular an oxide layer of aluminium, iron and vanadium, which can be obtained by a method as claimed in claim 6.

19. Object with an oxide ceramic layer, in particular an oxide layer of aluminium, iron and vanadium, which can be obtained by a method as claimed in claim 7.

20. Object with an oxide ceramic layer, in particular an oxide layer of aluminium, iron and vanadium, which can be obtained by a method as claimed in claim 10.

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