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(54) ENHANCED CORROSION RESISTANCE PROCESS FOR BULK METALLIC GLASS SUBSTRATES

(57) The invention relates to a process for enhancing corrosion resistance of a metal-based glass substrate, wherein the metal of the metal-based glass is one or more of zirconium, titanium, hafnium, aluminium, magnesium, and gold, and wherein the process comprises a step of exposing the substrate to an electrochemical anodic treatment applying a current density from 0.5 $mA.cm^{-2}$ to 1000 $mA.cm^{-2}$.

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Description

FIELD OF THE INVENTION

[0001] The invention relates to a surface treatment improving the resistance to corrosion of a metal-based glass (or bulk metallic glass) substrate. It involves an electrochemical anodic treatment, and eventually a chemical treatment, of the BMG substrate.

BACKGROUND OF THE INVENTION

[0002] Bulk-metallic-glasses (BMG) are metallic alloys having an amorphous structure. Some BMG can exhibit improved mechanical properties as compared to crystalline metals or crystalline alloys, such as large elastic strains to failure, high tensile strength, high hardness, high fatigue limit and high corrosion resistance.

[0003] The amorphous properties of the BMG result from their manufacturing. Since they are made by rapid solidification from a melted phase (gas or liquid), the atoms are essentially blocked in a disordered matrix. Due to this fast solidification process, the resulting material, i.e. the BMG, has an amorphous structure rather than a periodic and well-defined crystalline structure.

[0004] Another important feature of BMG is their glass formability. It relates to the ability of casting a sample free of crystals or nanocrystals. It is also described as the critical casting thickness of BMG, which is the maximum thickness of amorphous material that can be attained.

[0005] Some BMG have a critical casting thickness of several millimetres, which widens the scope of applications. For instance, zirconium based BMG such as the commercially available Vit105 ($Zr_{52.5}CU_{17.9}Ni_{14.6}Al_{10}Ti_5$, at%) and Vit106a ($Zr_{58.5}Nb_{2.8}Al_{10.3}Ni_{12.8}Cu_{15.6}$, at%) have a critical casting thickness of 18 and 32 mm, respectively. Such a difference may be due to the larger Cu/Zr ratio in Vit105.

[0006] In view of the above properties, BMG can be used in many fields, for instance in the fields of fashion and luxury (watches, jewellery...).

[0007] Typically, BMG are amorphous alloys having the following features:

- multicomponent system,
- the constituting elements have atomic size ratios exceeding 1.12,
- most of the alloying elements have a large and negative mixing enthalpy.

[0008] Other important properties of BMG alloys include their resistance to general corrosion. However, the presence of halides in solution may significantly alter their corrosion resistance and give rise to pitting phenomena: this can be particularly observed in zirconium-based BMG.

[0009] The resistance to corrosion of BMG substrates can be affected by:

- The presence of defects at the surface of the BMG. For instance, nanocrystals or mechanically generated defects can promote the initiation of local corrosion and its propagation within the BMG, that is, formation of pits and crevices.
- The surface finishing of the BMG. Evidences of this have been given by Gebert *et al.* [A. Gebert, P. Gostin and L. Schultz, "Effect of surface finishing of a Zr-based bulk metallic glass on its corrosion behaviour," Corr. Sci., vol. 52, pp. 1711-1720, 2010], where a fine surface polishing of Zr-based BMGs (0.02 μm SiO_2 abrasive solution) resulted in a copper enrichment of the outmost surface with low resistance to pitting corrosion, whereas a rougher polishing (4000 SiC paper) led to a zirconium and aluminium oxides enriched surface, with an improved corrosion resistance.
- The chemical composition of the passivation layer of the BMG.
- The presence of halides and/or oxidising compounds.
- The presence of local composition-inhomogeneity, originated from a not optimised manufacturing process.

[0010] Although BMG alloys exhibit many advantageous properties, they may still suffer from pitting corrosion in the presence of oxidizing agents and halides / depassivating agents, such as chloride, bromide, fluoride and others. It can be significantly improved if the amount of non-passivable metals and halide friendly metals is reduced or eliminated in favour of passivable elements. Examples of non-passivable elements are copper, nickel, iron and silver.

[0011] In order to improve the resistance to corrosion of BMG alloy, such as Vit105, passivation treatments have been tested. Such treatments are commonly, and successfully, used for improving the resistance to corrosion of aluminium, titanium or stainless steel substrates. However, when carrying out conventional anodisation on Vit105, the formation of a typical passivation layer is not usually achieved.

[0012] Indeed, when passivating titanium or zirconium, the current density significantly decreases during the process, due to the formation of thick and insulating TiO_2 and ZrO_2 layers. Conversely, on Vit105 this particular current density

decrease is not observed due to the low content of passivation elements (Zr, Ti and Al) and, certainly, to the significant content of non-passivable elements (Cu and Ni), within the oxide layer of ZrO_2, TiO_2 and Al_2O_3 and, that weaken its whole stability. As a result, the skilled person in the art could not find any motivation to apply such an anodisation treatment on a BMG alloy in order to form a passivation layer.

[0013] However, despite this, the Applicant has find out that, when anodising Vit105, the selective dissolution of non-passivable elements and the simultaneous surface enrichment of ZrO_2, TiO_2 and Al_2O_3 occur and lead to an enhancement of the pitting-corrosion resistance.

[0014] The Applicant has developed a process that allows improving the resistance of BMG alloys to corrosion (general and pitting corrosion). This process involves an electrochemical anodisation and is applicable to all sorts of BMG alloys, even those having non-passivable elements.

SUMMARY OF THE INVENTION

[0015] The Applicant has developed a process for improving the resistance to corrosion of BMG alloys thanks to specific passivation conditions.

[0016] Unlike traditional anodisation processes, the invention involves the selective extraction of non-passivable elements such as copper or nickel from the external portion of the matrix i.e. from the surface of the treated substrate. Consequently, the outmost substrate layer has a composition enriched in passivable elements, such as zirconium, titanium or aluminium, which significantly differs from the bulk alloy composition and confers to the BMG an enhanced resistance to corrosion, particularly to pitting corrosion.

[0017] More specifically, the invention relates to a process for enhancing corrosion resistance of a metal-based glass (BMG) substrate, wherein the metal of the metal-based glass is any one of zirconium, titanium, hafnium, aluminium, magnesium, gold or a mixture thereof, and wherein the process comprises a step of exposing the substrate to an electrochemical anodic treatment applying a current density of from 0.2 $mA.cm^{-2}$ to 500 $mA.cm^{-2}$.

[0018] These conditions allow the above mentioned selective extraction of non-passivable elements and also preserve the aesthetic of the substrate. It can therefore be applied on a substrate after a surface finishing treatment, for instance on a substrate (preferably a luxury component or luxury goods) that is ready to be commercialized.

Pre-treatment

[0019] According to a preferred embodiment, the BMG substrate has a smooth surface. It has a surface roughness Ra of preferably less than 1 μm, more preferably less than 0.2 μm.

[0020] As a result, a surface finishing treatment may be carried out on the BMG substrate prior to the electrochemical anodic treatment (EAT). The process may comprise a step of surface finishing, such as at least one of polishing, brushing, staining and sandblasting polishing, the metal-based glass substrate prior to the electrochemical anodic treatment.

[0021] This optional surface finishing step may be carried out with any abrasive, for instance with abrasive paper grade 800, followed by grades 2000 and 4000, and final polishing with alumina suspension.

[0022] Prior to the EAT, but after the optional surface finishing step, the BMG substrate may be degreased. Any conventional degreasing mean may be used, for instance an alcohol such as isopropanol.

[0023] Degreasing the BMG is preferably completed at room temperature, for instance at a temperature of between 16 and 30°C.

[0024] Prior to the EAT, and preferably after each of the surface finishing step and degreasing steps, the BMG substrate may be rinsed with deionized water. Rinsing is preferably carried out at room temperature, for instance at a temperature of between 16 and 30°C.

[0025] The pre-treatment may include a chemical passivation step of the BMG substrate, preferably in an acidic solution (Brønsted acid), for instance in an aqueous solution having a pH of less than 7.

[0026] The acidic solution is preferably an aqueous solution comprising one or more of the following acids: nitric acid, sulfuric acid, oxalic acid, and citric acid, preferably citric acid.

[0027] The acid (Brønsted acid) concentration of the passivation solution preferably ranges from 10^{-3} M to 2 M ($mol.L^{-1}$).

[0028] The chemical passivation is preferably performed at a temperature of from 5°C to 60°C, more preferably from 20°C to 40°C, for instance at 25°C.

[0029] The duration of the chemical passivation is not crucial since contacting the BMG substrate with the passivation solution can be as short as a few seconds, for instance from 1 second to 5 minutes.

[0030] After the chemical passivation, the BMG substrates can be rinsed, preferably with deionized water. It can also be dried prior to the EAT.

[0031] This chemical passivation allows concentrating passivating elements at the surface of the BMG substrate.

[0032] Accordingly, the pre-treatment may include the following sequence:

a) optionally, surface finishing the BMG substrate,
b) optionally rinsing the BMG substrate with deionized water,
c) optionally degreasing the BMG substrate,
d) optionally rinsing the BMG substrate with deionized water,
e) optionally, passivating the BMG substrate,
f) optionally rinsing the BMG substrate with deionized water,
e) optionally, drying the BMG substrate.

EAT: Electrochemical anodic treatment

[0033] The electrochemical anodic treatment involves exposing the BMG substrate to a 0.5 $mA.cm^{-2}$ to 1000 $mA.cm^{-2}$ current density, preferably 10 to 500 mA cm^{-2}, more preferably 50 to 300 $mA.cm^{-2}$.

[0034] This specific treatment enhances the resistance to corrosion of the BMG substrate while conventional anodisation treatments, when performed at higher current densities, lead to the dissolution of the BMG surface layer, thus altering the shape and the aesthetic of the specimen. This phenomenon may be due to the presence of non-passivable elements, for instance any one of Cu, Co, Ni or Fe. Such non-passivable elements are present in BMG since they bring in mechanical properties and improve the critical casting thickness of the alloys.

[0035] These non-passivable elements are responsible of the BMG surface dissolution in conventional anodisation conditions. However, the Applicant has surprisingly found out that applying mild current densities leads to the selective dissolution of non-passivable elements and to the formation of a stable metal oxide layer. The resulting passivation layer is enriched in passivation elements. Passivation elements include, for instance, one or more of zirconium, titanium and aluminium. Figure 3 clearly shows i) how the BMG surface composition changes when the process of the invention is applied, and ii) the formation of a passivation layer (dashed line).

[0036] Figure 3 illustrates this phenomenon for a BMG substrate such as $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (at%). In fact, it shows that an equilibrium is attainted with i) the enrichment of the surface layer in Zr, Ti and Al and ii) the selective dissolution of Cu and Ni. This is due to the specific conditions of the invention.

[0037] Due to the loss of non-passivable elements, the thickness of the treated substrate decreases. In general, if a current densities ranging between 10 and 500 mA cm^{-2} is applied for 60 seconds on a $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (at%) substrate, a size reduction of approximately 1 to 1.5 micrometers is observed, preserving the aesthetic of the substrate. On the other hand, if the current density is too important, the dissolution rate overcomes the passivation rate, and the sample simply physically degrades. As already mentioned, the invention preserves the aesthetic of the BMG substrate including its visual aspect, such as its colour.

[0038] Due to the presence of non passivable elements, BMG substrates do not behave like Ti, Zr or Al substrates, for which, upon applying a high current density, an oxide layer with a thickness ranging from a couple of nanometers to several hundred nanometers, is readily formed and physically protects the underneath Ti, Zr or Al metal.

[0039] The above 0.5-1000 $mA.cm^{-2}$ current density is applied for a duration that preferably ranges from 5 seconds to 300 seconds, more preferably 30 to 90 seconds.

[0040] The EAT is generally carried out in an electrolyte bath, preferably in an aqueous solution.

[0041] The electrolyte bath may be acidic, neutral or alkaline, preferably acidic (pH < 7), more preferably at a pH of between 0 and 6.

[0042] The electrolyte bath is preferably an acidic aqueous solution comprising one or more acid selected from the group consisting of sulfuric acid, phosphoric acid, oxalic acid, citric acid, perchloric acid and nitric acid. It is preferably an aqueous solution of a mixture of sulfuric acid and phosphoric acid.

[0043] The electrolyte bath can have a concentration in acid preferably ranging from 10^{-4} M to 10 M, preferentially from 10^{-3} M to 2 M.

[0044] The EAT is preferably carried out at a temperature preferably ranging from 5°C to 60°C, more preferably from 20°C to 40°C. For instance, it may be carried out at 40°C for 60 seconds.

[0045] The EAT may be carried out in a solution, preferably an aqueous solution, comprising one or more complexing agent selected from the group consisting of ethylenediaminetetraacetic acid, citrate, ethylenediamine, and oxalate.

[0046] When present, the complexing agent can have a concentration preferably ranging from 10^{-4} M to 1 M.

[0047] As already mentioned, the BMG substrate is an amorphous metal-based glass (BMG) substrate, wherein the metal is one or more of zirconium, titanium, hafnium, aluminium, magnesium and gold.

[0048] The BMG substrate is preferably a zirconium based BMG. In other words, it is preferably an alloy whose main element (largest atomic percentage) is zirconium.

[0049] Examples of preferred BMG include $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (at%), $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$.

Post-treatment

[0050] Optionally, the EAT is followed by a chemical passivation of the BMG substrate. Although it may differ from the early chemical passivation of the pre-treatment, the general conditions of this late chemical passivation are identical (passivation solution, temperature and duration).

[0051] Thereafter the BMG substrate can be rinsed, preferably with deionized water. It may also be dried. Any conventional drying may be carried out, for instance by blowing hot air on the substrate or in an oven, preferably at a temperature of between 30 and 50 °C.

[0052] The post-treatment may therefore include the following sequence:

aa) optionally rinsing the BMG substrate, preferably with deionized water,
bb) optionally, passivating the BMG substrate,
cc) optionally rinsing the BMG substrate, preferably with deionized water,
dd) optionally, drying the BMG substrate.

Use of the treated BMG

[0053] The invention also relates to a luxury component or good (horology, jewellery, leather goods, writing accessories, ornaments and fashion) comprising the BMG substrate treated according to the present invention.

[0054] The fields of use of the BMG substrate treated according to the present invention include horology (watch case, dial, watch strap, watch clasp, mechanical part of a watch movement...), jewellery (ring, earring, necklace, bracelet, pendant, etc.), leather goods (belt buckles, handbag clasps...), writing accessories (pens, paper cutters...), ornaments and fashion accessories (cuff links, tie pin, money clip, hairpin, hair clip...).

[0055] The invention and its advantages will become more apparent to one skilled in the art from the following figures and examples.

BRIEF DESCRIPTION OF THE DRAWINGS

[0056]

Figure 1 shows potentiodynamic polarisation curves of BMG substrates that have been treated according to the invention or not.

Figure 2 shows electrochemical impedance spectra of BMG substrates that have been treated according to the invention or not. The Inset shows the Bode plots (phase angle and modulus of the impedance) for these substrates.

Figure 3 illustrates the enhanced corrosion resistance resulting from the process according to the invention.

Figure 4 shows electrochemical impedance spectra of BMG substrates that have not been treated according to the invention, after ageing for 1 to 42 hours in a 3M NaCl solution at pH 3.

Figure 5 is an optical microscope image of a non-treated BMG substrate, after EIS electrochemical monitoring test in a 3M NaCl solution at pH 3.

Figure 6 is a SEM image of a non-treated BMG substrate, after EIS electrochemical monitoring test in a 3M NaCl solution at pH 3.

Figure 7 is an optical microscope image of a BMG substrate treated according to the invention, after EIS electrochemical monitoring test in a 3M NaCl solution at pH 3.

Figure 8 shows electrochemical impedance spectra of BMG substrates that have been treated according to the invention, after ageing for 1 to 67 hours in a 3M NaCl solution at pH 3.

EXAMPLES

[0057] Zr-based BMG substrates (Vit105, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ - 15 mm x 15 mm and thickness of 2 mm) have been treated according to the invention:

1) pre-treatment of the BMG substrates:

- surface finishing with abrasive paper 800, 2500 and 4000 grades followed by 1 μm alumina dispersion slurry mirror-like finishing,
- degreasing of the BMG substrate using isopropanol at room temperature (RT),
- rinsing the BMG substrate with deionized water,

2) anodic treatment of the BMG substrate in a 0.5 M H_2SO_4 + H_3PO_4 (70-30 % ratio - pH 0.2-0.3) electrolytic bath with a continuous current density of 100 mA cm^{-2} for 60 seconds and a temperature of 30° C,
3) rinsing the BMG substrate with deionized water.

[0058] The resulting BMG substrates have been compared to the non-treated BMG substrate i.e. the substrate before step 2.

Electrochemical instruments

[0059] The treatment according to the invention has been carried out in an electrochemical cell having a three electrode configuration: working electrode (BMG), auxiliary electrode (large Pt sheet) and a KCl saturated reference calomel electrode (SCE).
[0060] Tests were carried out at 23 ± 1°C. Unless otherwise stated, all the potential values are referred to SCE. Electrochemical tests, such as EIS measurements (EIS: electrochemical impedance spectroscopy), were carried out in potentiostat such as the Gamry Reference 600.
[0061] Potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) were carried out to characterize the electrochemical behavior. Prior testing, open circuit potential (OCP) was measured for 60 minutes to assess the stability of the BMG.
[0062] PP were performed sweeping the potential from cathodic (-0.2 V vs. OCP) to anodic values at a scan rate of 0.15 mV/s and step potential of 0.15 mV. The used solution for both PP and EIS was an artificial sweat EN1811, made with ultrapure water (conductivity of 18.2 MQ.cm). EIS tests was carried out applying an alternate potential of 5 mV at OCP within a frequency range from 100000 Hz and 0.005 Hz with ten points per decade. The electrode surface was either 0.50 cm^2 or 0.12 cm^2.

Electrochemical monitoring

[0063] Electrochemical monitoring was carried out by exposing (anodically treated or not) Zr-BMG substrates to a 3 M NaCl solution at pH 3 (figures 4 and 8). The monitoring consisted of OCP measurements alternated with EIS measurements.
[0064] EIS were measured after 1 hr, 4 hr, 9 hr, 24 hr, 43 hr and 67 hr and were carried out applying an alternate potential of 5 mV at OCP within a frequency ranging from 100000 Hz to 0.005 Hz, with ten points per decade.

Ageing tests

[0065] Ageing tests were carried out on (anodically treated or not) Zr-BMG substrates. Zr-BMG substrates, produced with different shapes, were subjected to the following ageing tests:

1. Salt-fog-chamber test carried out by exposing the samples to a salt-fog environment (0.9 M NaCl) at 40° C for 4 days, according to the standard NIHS 96-50,
2. Thermal shock test carried out by submerging samples in water at 70° C for 30 minutes followed by submersion in water at 5° C for 5 minutes,
3. Moist-heat test carried out exposing the samples to a 95 % humid environment at 70° C for 7 days, according to the standard NIHS 96-50,
4. Artificial sweat test carried out exposing the samples to an artificial sweat solution at 40° C for 7 days, according to the standard NIHS 96-50.

[0066] At the end of the series of tests, the aged BMG substrates were rinsed with water and corrosion inspected, using an optical microscope (figures 5, 6 and 7).
[0067] At least 10 samples per each surface treatment were considered for statistical analysis.

Results

[0068] Figure 1 shows an overlay of potentiodynamic polarisations carried out in artificial sweat (EN1811) at 0.15 mV/s on the following BMG substrates:

- BMG according to the invention ("invention" curve),
- non-treated BMG ("non-treated" curve).

[0069] As already mentioned, the original BMG is the same for all experiments, 1 μm polished $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$.

[0070] The corrosion current density for the invention substrate was determined significantly lower than that of the other BMG substrates. The determined values were in fact 1 $nA.cm^{-2}$ and 18 $nA.cm^{-2}$, for the invention and the non-treated substrate, respectively.

[0071] As already mentioned, the resistance to pitting corrosion of BMG substrates, in particular Zr-based BMG, significantly decreases in the presence of chloride ions or other depassivating agent in the electrolyte (0.085 M NaCl in the EN1811 solution of the PP and EIS tests).

[0072] Figure 1 shows that localized corrosion is initiated at 0.180 V for the non-treated BMG substrate while potential values up to 1.0 V are attainable for the BMG according to the invention.

[0073] Figure 2 shows the EIS Nyquist plot of the BMG substrate according to the invention and the non-treated BMG substrate, in artificial sweat EN1811 with a potential amplitude of 5 mV, within a frequency range from 100000 Hz and 0.005 Hz.

[0074] The BMG substrate treated according to the invention shows a higher impedance response than the non-treated BMG substrate. It actually shows a nearly vertical trend, which is typical of capacitive response and therefore of the presence of a thin passive layer. On the other hand, the non-treated substrate exhibits a lower impedance and therefore no protective layer or at least a thinner protective layer than that of the BMG substrate according to the invention.

[0075] The higher capacitive response of the anodically treated BMG substrate can be explained in terms of Cu and Ni dissolution from the outmost electrode surface, and its simultaneous enrichment of Zr, Al and Ti elements, present as oxides. From Figure 2 inset it can be appreciated the higher impedance modulus values for the treated sample, and as well as the attainment of a phase angle of 90° at low frequencies, typical of a capacitive behaviour.

[0076] The above mentioned reaction mechanisms, that is, i) enrichment of Zr, Ti and Al and ii) selective dissolution of Cu and Ni, attain an equilibrium as depicted in Figure 3. However, if high anodic current densities are applied, the dissolution rate overcomes the passivation rate, and the sample simply physically degrades.

[0077] Electrochemical monitoring tests were also carried out to assess how the treated samples endured long-lasting aggressive solutions (3M NaCl, pH 3) compared to non-treated samples.

[0078] Figure 4 shows the EIS response (Nyquist plot) carried out over 42 hours of monitoring on a non-treated substrate. The low hand-side Figure 4 inset highlights the OCP, recorded in between the EIS, whereas the top hand-side Figure 4 shows a magnification of the recorded EIS. The stability of the non-treated BMG substrate significantly decreases between 15 and 25 hours, the impedance response changing from a capacitive to a kinetic transfer controlled behaviour (see the top hand side inset of figure 4).

[0079] An optical microscope image of the BMG sample surface after monitoring testing for 42 hours is shown in Figure 5. The sample, in addition to be completely whitish on the external surface (signs of formation of insoluble chlorides, $ZrCl_4$ and CuCl) also exhibited two deep greenish-brownish pits, enriched in copper (ca. 70 at. %) and depleted in Zr and other alloying elements. This dissolution mechanism corresponds to pitting corrosion in chloride solutions of Zr, Al and Ti with the simultaneous accumulation of copper. The scanning-electron microscope image of the pits (Figure 6) shows the corrosion pits after 42 hours of sample exposure to the solution.

[0080] On the other hand, EIS monitoring tests carried out on the BMG substrate, treated according to the invention, shows a rather stable capacitive response during a monitoring time of 72 hours (Figure 8). The substrate does not show any visible signs of corrosion after testing. For instance, Figure 7 shows the absence of whitish surface portions and of greenish-brownish pits.

[0081] Indeed, the impedance response recorded over the time interval was observed to be rather stable and to have a capacitive behaviour up to 67 hours. The recorded OCP starts at values of approximately -0.15 V, decreases down to approximately -0.25 V and then steadily increases attaining values of -0.10 V (inset of Figure 8). No OCP scattering (common sign chemical instability) was observed on treated samples.

[0082] Ageing tests were also performed on treated and non-treated BMG substrates. Corrosion observations and statistical analysis were then carried out on the different samples and results are listed in Table 1. The total counted defects were determine to be 35 and 13 for the non-treated substrates and for the anodically treated substrates (invention), respectively. The average corrosion defects on the non-treated substrates was calculated to be 3.5 ± 1.6 per sample, whereas 1.3 ± 1.1 for the treated substrates, respectively.

Table 1: Corrosion test on treated BMG substrates (invention) and non-treated BMG substrates.

Sample Ref.	Non-Treated / Corrosion defects	Anod. Treated / Corrosion defects
1	3	1
2	4	2
3	4	3
4	2	3
5	6	1
6	6	1
7	3	1
8	3	0
9	3	0
10	1	1
Total	35	13
Average	3.5 ± 1.6	1.3 ± 1.1

1. Salt-fog-chamber test, according to the standard NIHS 96-50,

2. Thermal shock test, according to the standard NIHS 96-50,

3. Moist-heat tests, according to the standard NIHS 96-50,

4. Artificial sweat test, according to the standard NIHS 96-50.

Claims

1. A process for enhancing corrosion resistance of a metal-based glass substrate, wherein the metal of the metal-based glass is one or more of zirconium, titanium, hafnium, aluminium, magnesium, and gold,
wherein the process comprises a step of exposing the substrate to an electrochemical anodic treatment applying a current density from 0.5 $mA.cm^{-2}$ to 1000 $mA.cm^{-2}$.

2. Process according to claim 1, ***characterized*** **in that** the electrochemical anodic treatment is carried out with a current density from 10 to 500 $mA.cm^{-2}$.

3. Process according to claim 1 or 2, ***characterized*** **in that** the current density is applied for 5 and 300 seconds, preferably for 30 to 90 seconds.

4. Process according to any one of claims 1 to 3, ***characterized*** **in that** the electrochemical anodic treatment is carried out in an aqueous solution having a pH ranging from 0 to 6.

5. Process according to any one of claims 1 to 4, ***characterized*** **in that** the electrochemical anodic treatment is carried out in an aqueous solution comprising one or more of sulfuric acid, phosphoric acid, oxalic acid, citric acid, perchloric acid, and nitric acid, preferably a mixture of sulfuric acid and phosphoric acid.

6. Process according to any one of claims 1 to 5, ***characterized*** **in that** the electrochemical anodic treatment is carried out at a temperature preferably ranging from 5° C to 60° C, more preferably from 20° C to 40° C.

7. Process according to any one of claims 1 to 6, ***characterized*** **in that** the electrochemical anodic treatment is carried out in an aqueous solution comprising one or more complexing agent selected from the group consisting of ethylenediaminetetraacetic acid, citrate, ethylenediamine, and oxalate.

8. Process according to any one of claims 1 to 7, ***characterized*** **in that** the metal-based glass substrate is selected from the group consisting of zirconium, titanium, hafnium, aluminium, magnesium, and gold-based alloys.

9. Process according to any one of claims 1 to 8, ***characterized*** **in that** the metal-based glass substrate is zirconium based.

10. Process according to any one of claims 1 to 9, ***characterized*** **in that** the process comprises a step of surface finishing, such as at least one of polishing, brushing, staining and sandblasting polishing, the metal-based glass substrate prior to the electrochemical anodic treatment.

11. Process according to any one of claims 1 to 10, ***characterized*** **in that** the process comprises a step of degreasing the metal-based glass substrate prior to the electrochemical anodic treatment, preferably after a surface finishing step.

12. Process according to any one of claims 1 to 11, ***characterized*** **in that** the process comprises a step of chemically passivating the metal-based glass substrate before and/or after the electrochemical anodic treatment, using nitric acid, sulfuric acid, oxalic acid, and citric acid, preferably citric acid or a mix of them, with concentration ranging from 10^{-3} M to 2 M (mol.L^{-1}) and a temperature from 5°C to 60°C, more preferably from 20°C to 40°C, for instance at 25°C.

13. Process according to any one of claims 1 to 12, ***characterized*** **in that** the process comprises a pre-treatment, carried out before the electrochemical anodic treatment, including the following sequence:

a) surface finishing the metal-based glass substrate,
b) optionally rinsing the metal-based glass substrate with deionized water,
c) degreasing the metal-based glass substrate,
d) optionally rinsing the metal-based glass substrate with deionized water,
e) passivating the metal-based glass substrate,
f) optionally rinsing the metal-based glass substrate with deionized water.

14. Process according to any one of claims 1 to 13, ***characterized*** **in that** the electrochemical anodic treatment is carried out with a current density from 10 to 500 mA.cm^{-2} for 5 and 300 seconds, preferably for 30 to 90 seconds, in an aqueous solution having a pH ranging from 0 to 6, at a temperature preferably ranging from 5° C to 60° C, wherein the metal-based glass is zirconium based.

15. Luxury component or good comprising a metal-based glass substrate obtained according to any one of claims 1 to 14, wherein luxury includes horology, jewellery, leather goods, writing accessories, ornaments and fashion.

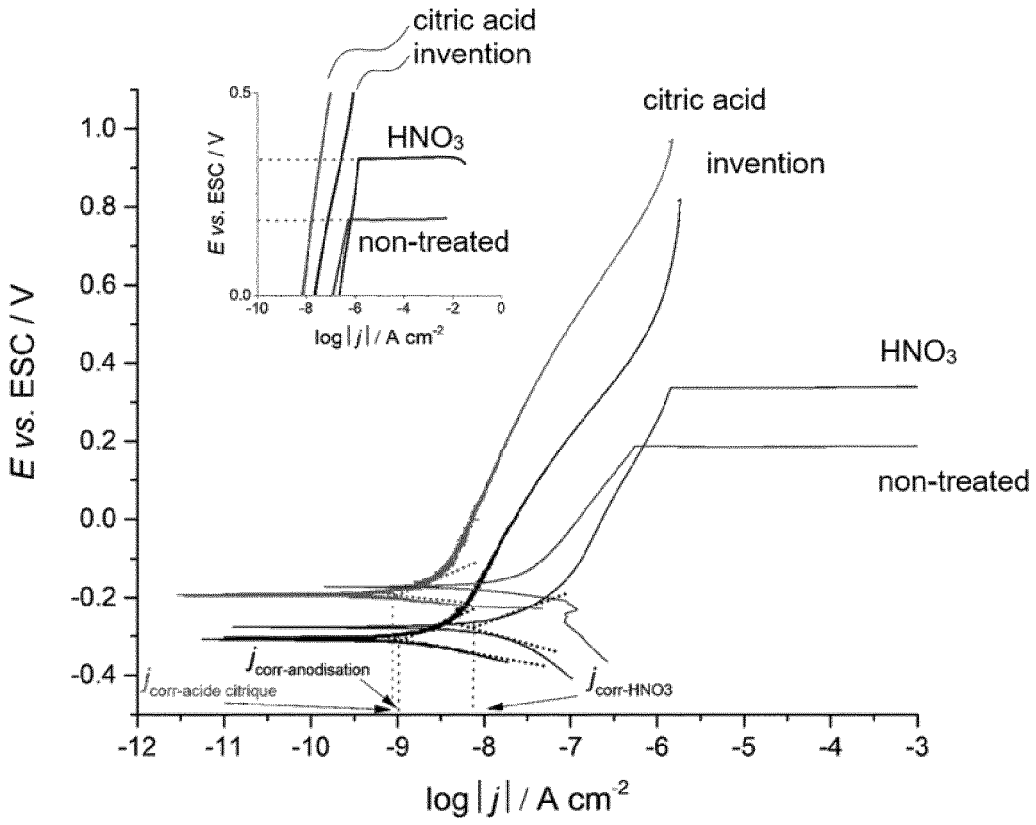
citric acid
invention
HNO3
non-treated
E vs. ESC / V
log | j | / A cm-2
j corr-anodisation
j corr-acide citrique
j corr-HNO3

Fig. 1

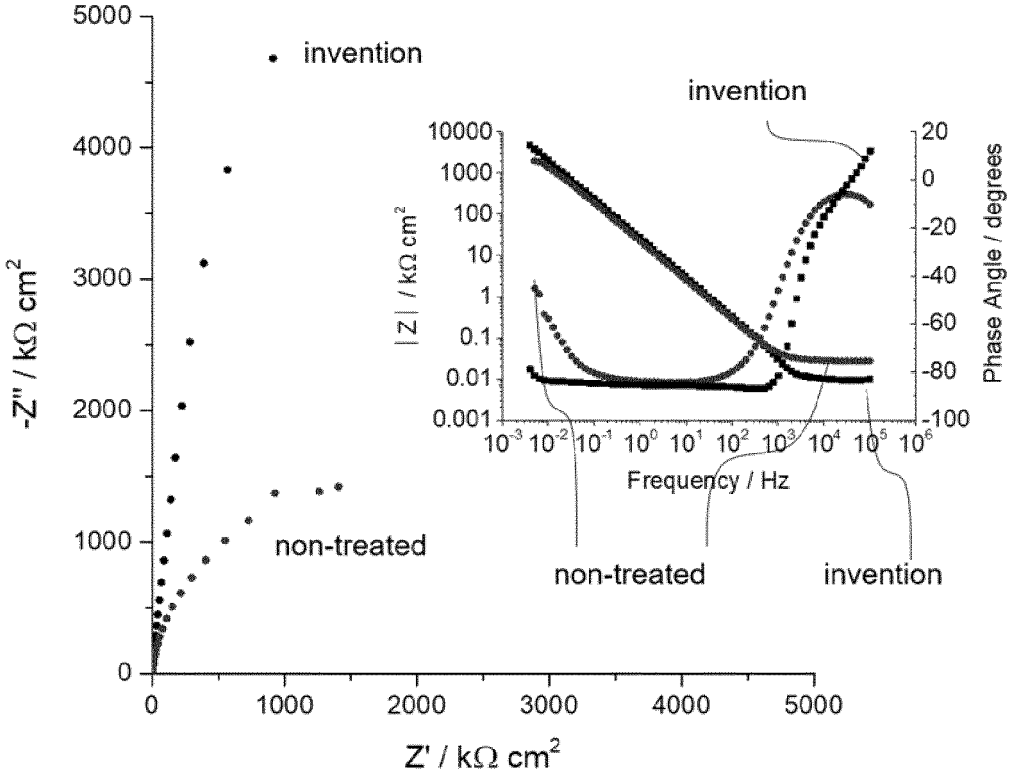
invention
non-treated
-Z'' / kΩ cm2
Z' / kΩ cm2
| Z | / kΩ cm2
Phase Angle / degrees
Frequency / Hz

Fig. 2

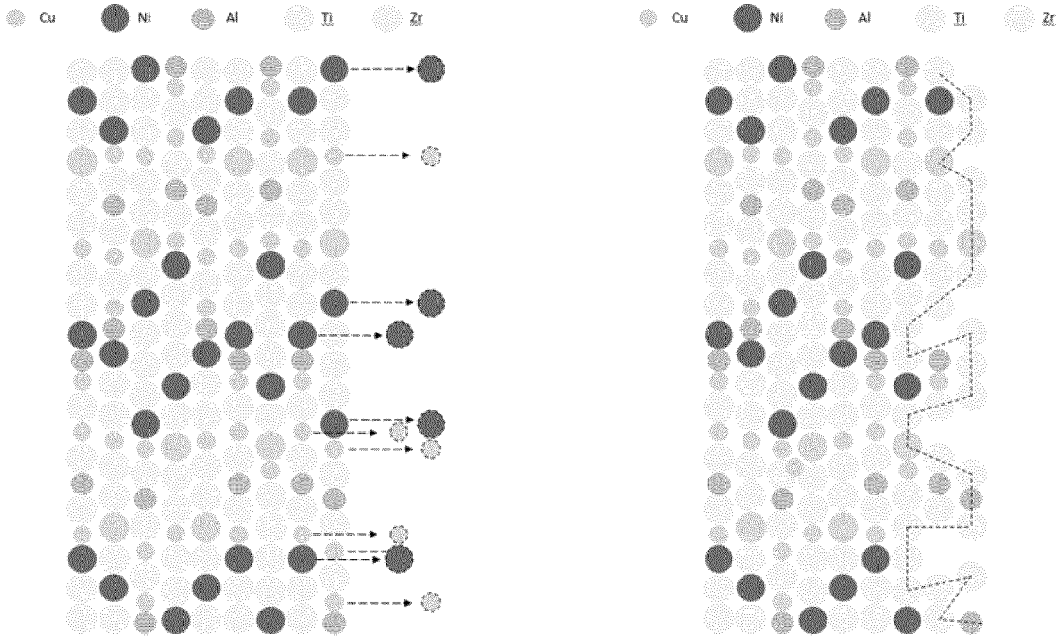
Cu
Ni
Al
Ti
Zr
Cu
Ni
Al
Ti
Zr

Fig. 3

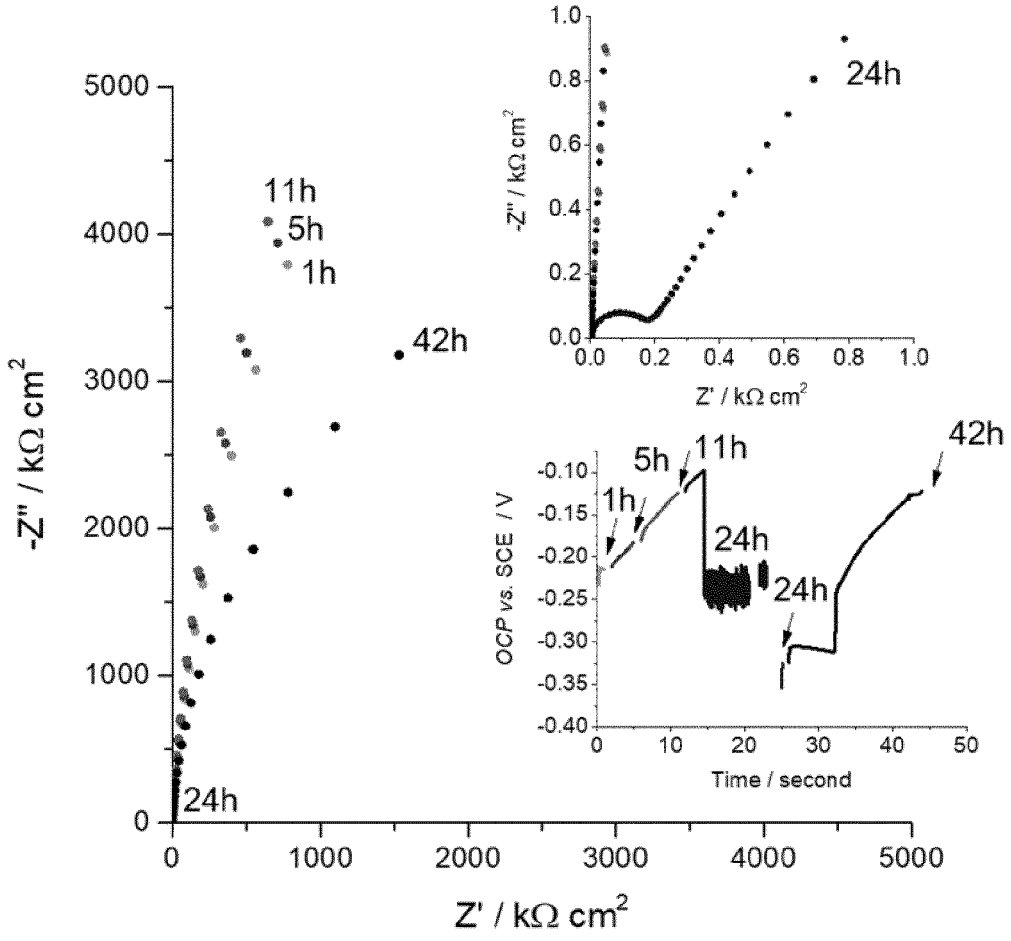
-Z'' / kΩ cm2
Z' / kΩ cm2
11h
5h
1h
42h
24h
-Z'' / kΩ cm2
Z' / kΩ cm2
24h
OCP vs. SCE / V
Time / second
1h
5h
11h
24h
24h
42h

Fig. 4

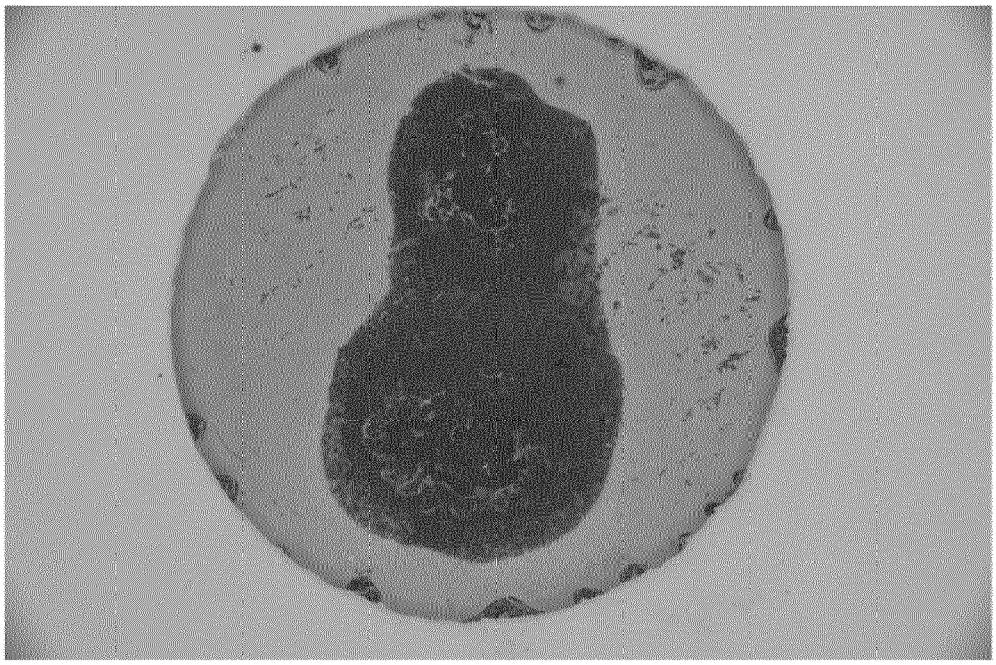

Fig. 5

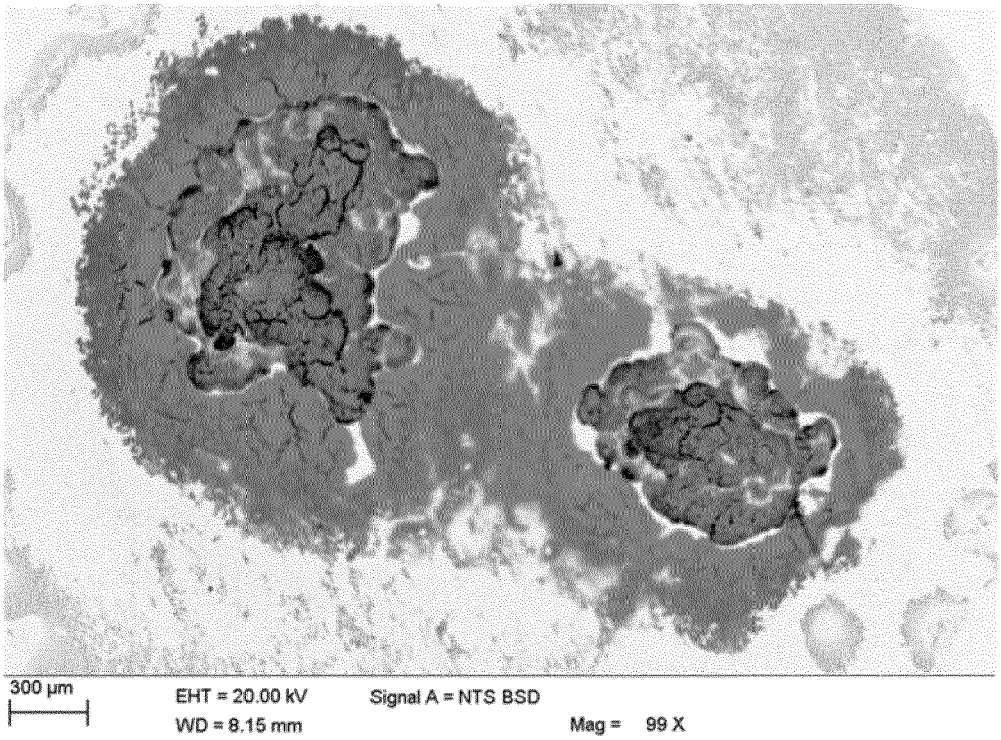

Fig. 6

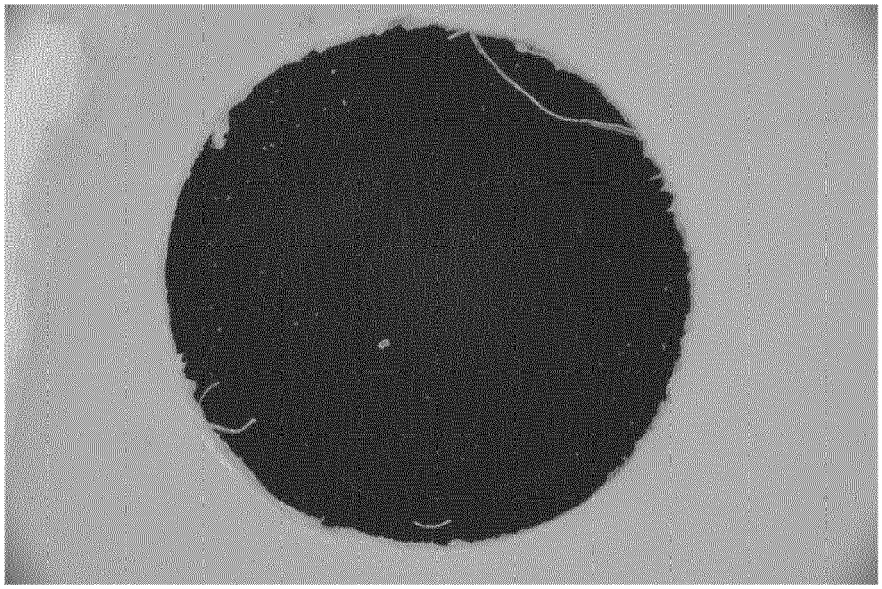

Fig. 7

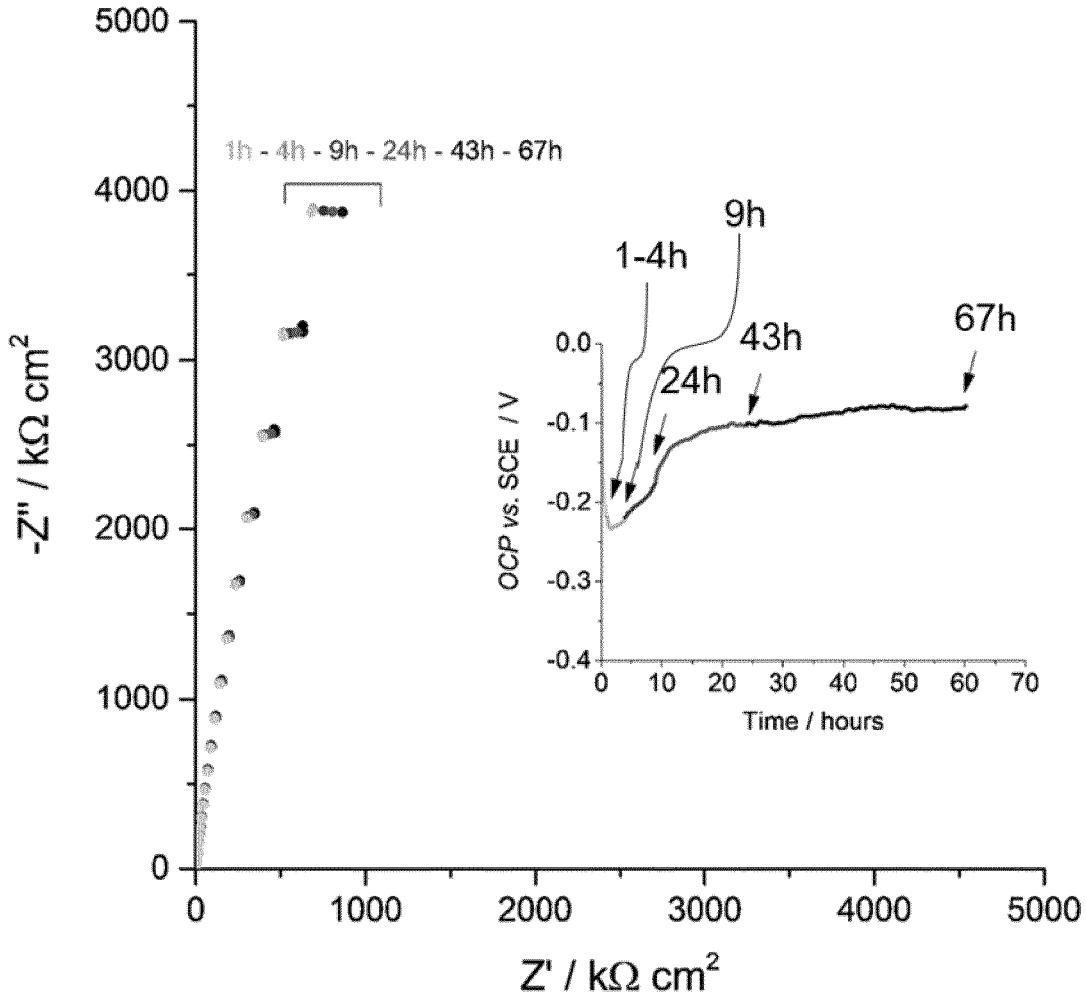
1h - 4h - 9h - 24h - 43h - 67h
-Z'' / kΩ cm²
Z' / kΩ cm²
0
1000
2000
3000
4000
5000
9h
1-4h
43h
67h
24h
OCP vs. SCE / V
0.0
-0.1
-0.2
-0.3
-0.4
0
10
20
30
40
50
60
70
Time / hours

Fig. 8

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EUROPEAN SEARCH REPORT

Application Number
EP 20 19 6233

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 772 535 A1 (NGK INSULATORS LTD [JP]; UNIV TOHOKU [JP]) 11 April 2007 (2007-04-11) * abstract * * table 1 * * paragraphs [0001], [0018], [0042] * * examples 4, 5 * -----	1-3,5,6, 8,9,14	INV. C25D11/26 C22F1/18
X	CN 104 178 716 B (UNIV ZHENGZHOU) 8 June 2016 (2016-06-08) * abstract * * figures 4, 5 * * description of figures 4 and 5 * -----	1,2,6,8, 9	
X	CN 109 680 316 A (UNIV ANHUI TECHNOLOGY) 26 April 2019 (2019-04-26) * abstract * * examples 1-15 * -----	1,2,4,5, 8,9	
X	US 2004/121290 A1 (MINEVSKI ZORAN [US] ET AL) 24 June 2004 (2004-06-24) * abstract * * examples 1-5 * * paragraph [0018] * -----	1-9	

TECHNICAL FIELDS SEARCHED (IPC)
C25D C22F

~~The present search report has been drawn up for all claims~~

Place of search	Date of completion of the search	Examiner
The Hague	18 May 2021	Lange, Ronny

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

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Application Number
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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☒ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

1-8, 14(completely); 9(partially)

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 20 19 6233

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 2, 3(completely); 1, 8, 9(partially)

Inventive concept I regards a process for enhancing corrosion resistance of a metal-based glass substrate, wherein the metal of the metal-based glass is one or more of zirconium, titanium, hafnium, aluminium, magnesium, and gold, and wherein the process comprises a step of exposing the substrate to an electrochemical anodic treatment applying a current density from 0.5 mA.cm-2 to 1000 mA.cm-2 wherein the electrochemical anodic treatment is carried out with a current density from 10 to 500 mA.cm-2 and wherein the current density is applied for 5 and 300 seconds, preferably for 30 to 90 seconds.

---

2. claims: 4-7, 14(completely); 1, 8, 9(partially)

Inventive concept II regards a process for enhancing corrosion resistance of a metal-based glass substrate, wherein the metal of the metal-based glass is one or more of zirconium, titanium, hafnium, aluminium, magnesium, and gold, and wherein the process comprises a step of exposing the substrate to an electrochemical anodic treatment applying a current density from 0.5 mA.cm-2 to 1000 mA.cm-2 and wherein the electrochemical anodic treatment is carried out in an aqueous solution having a pH ranging from 0 to 6 and wherein the electrochemical anodic treatment is carried out in an aqueous solution comprising one or more of sulfuric acid, phosphoric acid, oxalic acid, citric acid, perchloric acid, and nitric acid, preferably a mixture of sulfuric acid and phosphoric acid and wherein the electrochemical anodic treatment is carried out at a temperature preferably ranging from 5° C to 60° C, more preferably from 20° C to 40° C and wherein the electrochemical anodic treatment is carried out in an aqueous solution comprising one or more complexing agent selected from the group consisting of ethylenediaminetetraacetic acid, citrate, ethylenediamine, and oxalate.

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3. claims: 10-13, 15(completely); 1, 8, 9(partially)

Inventive concept III regards a process for enhancing corrosion resistance of a metal-based glass substrate, wherein the metal of the metal-based glass is one or more of zirconium, titanium, hafnium, aluminium, magnesium, and gold, and wherein the process comprises a step of exposing the substrate to an electrochemical anodic treatment applying a current density from 0.5 mA.cm -2 to 1000 mA.cm-2 wherein the process comprises a pre-treatment,

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 20 19 6233

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

carried out before the electrochemical anodic treatment, preferably including the following sequence: a) surface finishing the metal-based glass substrate, b) optionally rinsing the metal-based glass substrate with deionized water, c) degreasing the metal-based glass substrate, d) optionally rinsing the metal-based glass substrate with deionized water, e) passivating the metal-based glass substrate, f) optionally rinsing the metal-based glass substrate with deionized water.

1.2 Inventive concept III also concerns the respective luxury component being provided by the process.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 20 19 6233

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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18-05-2021

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		EP 1772535 A1	11-04-2007
		JP 4482558 B2	16-06-2010
		JP WO2005116301 A1	03-04-2008
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		WO 2004024202 A1	25-03-2004

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REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- **A. GEBERT ; P. GOSTIN ; L. SCHULTZ.** Effect of surface finishing of a Zr-based bulk metallic glass on its corrosion behaviour. *Corr. Sci.,* 2010, vol. 52, 1711-1720 **[0009]**