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(54) **WORK ROLL COATING AND METHOD FOR PRODUCING THE SAME**

(57) The present invention relates to a method of coating a thermally-sensitive metal object with a protective coating, comprising the following steps:

- a first step of applying on said thermally-sensitive metal object a coating layer containing at least one phase having at least one mechanical property that can be improved by heat treatment;
- a second step of performing a superficial annealing on the coated thermally-sensitive metal object;

characterised in that the superficial annealing conditions are selected so that said mechanical property of the coating is increased while the corresponding mechanical property of the metal object is not significantly thermally-affected by the annealing step, so that the coating morphology is not modified during annealing and so that the annealing does not result in the creation of additional layers at the coating/substrate interface due to inter-diffusion.

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Description**Field of the Invention**

5 **[0001]** The present invention relates to an innovative work roll coating for application in cold rolling and temper-mill rolling of steel products and the method for producing such innovative coating.

Background and Prior Art

10 **[0002]** Cold rolling is an industrial process where sheets or strips of metal are passed between large rollers, which compress it and squeeze it under high pressure. This results in grain reorientation and creation of defects in the crystal structure of the metal. Depending on the applied strain, different mechanical properties are achieved after cold-rolling, usually including a higher yield strength and greater hardness of the metal strip. The thickness of the metal strip is hence reduced by processing it through a sequence of rolling mill stands. Multi-stand mills typically consist of three to six pairs of rollers in a series, each pre-set to reduce the thickness by a certain percentage until the final thickness is reached.

15 **[0003]** Hard chrome plating of work rolls is standard practice in the rolling industry since the 1980's. The benefits thereof are an improvement of roughness retention, leading to an increase of rolling length and of service life, the latter up to a factor of 2, strip cleanliness improvement as well as provision of a cheap and robust process.

20 **[0004]** Side benefits of the increased rolling length are obtained for the operation of the rolling mill, namely: less roll consumption and decrease of the cost associated with roll permutation, i.e. stop time of the mill, dismount the chocks, grinding, texturing, coating, remounting the chocks.

25 **[0005]** However the classical electrolytic hard chrome (EHC) plating process makes use of chromic acid, i.e. hexavalent chromium or Cr(VI), which is known to be highly toxic for human health as well as dangerous for the environment. Because of its toxicity, the current chrome plating technology will be abandoned in the coming years due to the banning of Cr(VI) compounds in the European Union (EU Regulation REACH) and possibly outside Europe. So there is currently intensive industrial search for alternative solutions.

30 **[0006]** A wide range of technologies allow to coat rolling mill rolls with protective coatings, for instance powder spraying (thermal spray or cold spray), vacuum deposition (PVD, CVD), as well as chemical and electrolytic processes. Among those, electroplating and chemical plating are of particular interest in the cold rolling industry, since they are well adapted for the application of coatings with thickness in the appropriate range of 5 to 10 μm . The surface morphology of electroplated and chemical plated coatings is also very similar to that of EHC coatings, which is beneficial for the surface quality of the rolled sheet. Finally, the treatment cost and processing time associated with the electroplating process for large parts is advantageous as compared, for instance, to vacuum deposition.

35 **[0007]** From literature, it is well known that a variety of coatings applied by electroplating or electroless plating have been developed that exhibit mechanical properties (hardness and wear resistance) that match or approach those of EHC coatings, in particular alloyed metal coatings and cermet coatings.

40 **[0008]** Electroplated alloyed metal coatings, generally having an amorphous or nanocrystalline structure in as-plated condition, are usually based on co-deposition of an iron group metal (Fe, Ni, Co, Cr) with another alloy forming element. Examples of such alloys include Ni-P, Ni-B, Ni-Fe, Ni-Co, Ni-Cr, Ni-Mo, Ni-W, Co-P, Co-B, Co-W, Co-Mo, Co-Cr, Co-Fe, Cr-P, Cr-C, Fe-C, Fe-P, Fe-B, Fe-P-B.

45 **[0009]** Cermet coatings are obtained by co-deposition of metal or metal alloys and embedded non-metallic particles, which generally belong to, but are not limited to, carbides, nitrides, borides or oxides. The hard particles further enhance the micro-hardness, load-bearing capacity and wear resistance of the coating.

50 **[0010]** It is also well-described in prior art that, in order to achieve mechanical properties that match those of hard chrome, Ni-, Co-, or Fe-based alloys and cermet coatings applied by electroplating or electroless plating require a heat treatment (e. g. US 2,643,221 A, US 2009/0178736 A1, WO 00/61838 A2, WO 2014/111616A1). Heat-treating chromium and chromium alloys plated from trivalent chromium electrolytes has also been demonstrated to increase significantly their micro-hardness. The improvement of the mechanical properties results from the a partial recrystallization of the metal matrix or the precipitation of a distinct crystallographic phase having a reinforcing effect according to the well-known precipitation hardening mechanism. These two effects can be observed separately or in combination.

55 **[0011]** Those heat treatments typically require temperatures in the range 300 to 500°C applied during minutes or hours.

60 **[0012]** Such thermal conditions are incompatible with heat-sensitive metal parts, especially conventional rolling mill rolls, as it would result in an unacceptable softening of the roll core. This is illustrated in FIG. 1 which shows the evolution of the hardness of DIN 1.2363 steel samples during oven-annealing trials performed at different durations and temperatures. The steel samples were initially heat-treated and quenched using a heat cycle representative for cold rolling rolls. It can be observed that, above 250°C, the steel hardness is significantly and prohibitively reduced with increasing annealing time. Another example is given in FIG. 2, which shows the hardness evolution of SIHARD™ R246 steel from SIJ Ravne Systems, initially induction-hardened to 720HV then oven-annealed in air under different conditions (temper-

ature and time). Similarly to DIN 1.2363 steel, it can be observed that the steel hardness is significantly and prohibitively reduced with increasing annealing time, above 300°C.

[0013] Laser-based surface treatments of steel parts are described in the scientific literature and patents. Local heating of the surface by the laser beam has been applied for raising the surface temperature in the austenitisation range or even above the melting point, which can be exploited for surface hardening, texturing, or alloying. Laser-annealing has also been applied in some studies for annealing of steel parts with protective coatings applied by electroplating. In those references, the annealing is applied on the whole part or at least on a part of the substrate.

[0014] For example, US 4,628,179 A to J. Crahay (CRM, Belgium), discloses a method for providing isotropic roughness on the surface of a rolling mill roll by focusing a continuous concentrated corpuscular beam, e.g. a laser beam or an electron beam, on the roll surface, guiding the beam to impinge on the roll surface in a helical path, and regulating the concentration of the beam, the relative speed of rotation of the roll, and the translation speed of the beam.

[0015] In H. Liu et al, "Evaluation of microstructures and properties of laser-annealed electroless Ni-P/Ni-Mo-P duplex coatings", the authors demonstrate the applicability of laser-annealing for crystallisation of Ni-P based multi-layered coatings. They apply a first layer of Ni-P by electroless plating at a pH of 4.6 and temperature of 86°C, followed by a second electroless deposition of a Ni-Mo-P coating at a pH of 9.5 and temperature of 90°C. After plating, their bi-layer coating was laser-annealed at a fixed power of 500W and scanning rate of 6 to 14mm/s. The authors take advantage of the rapidity of laser-annealing in order to minimize thermal diffusion so as to preserve the original chemical composition of graded and multilayer coatings.

[0016] In C.A. Huang et al, "Microstructure study of the hardening mechanism of Cr-Ni alloy deposits after flame heating for a few seconds", Surf. Coat. Technol. 206 (2011) 325-329, Cr-Ni alloy deposits were obtained from a plating bath with trivalent chromium and divalent nickel ions. An amorphous structure was detected from an as-plated Cr-rich alloy deposit in which the micro-hardness could be significantly increased from 550 Hv to 1460 Hv after flame heating for 3 s. Based on the results of microstructure study, the hardening is attributed to the precipitation of nano-sized carbon-related particles, possibly diamond-like particles, which have a high micro-hardness value and cause lattice strain fields at their precipitation sites.

[0017] In C.A. Huang, "Anneal-hardening behavior of Cr-Fe-C alloy deposits prepared in a Cr³⁺-based bath with Fe²⁺ ions", Materials 10 (2017), 1392, Cr-Fe-C alloy deposits were prepared with a current density varying in the 20-30 A dm⁻² range in the Cr³⁺-based electroplating bath with Fe²⁺ ions and suitable complex agents. A Cr-based alloy deposit was obtained with an electroplating current density above 25 A dm⁻², and a Fe-based alloy deposit was obtained for the current density of 20 A dm⁻². Due to the precipitation of crystalline C-related membranes, the Cr- and Fe-based alloy deposits could be significantly hardened after rapid thermal annealing (RTA) at 500°C for a few seconds. The hardness values of the annealed Cr- and Fe-based alloy deposits increase with the increasing degree of crystallization of the C-related membranes. The highest hardness of an alloy deposit was observed after RTA at 500°C for 10 s, and the highest hardness of 1205 Hv was found for the Cr-based alloy deposit prepared with 30 A dm⁻².

[0018] In Q. Zhang, "Pulse laser assisted composite electroless deposit to prepare ceramic coating", Physics Proced. 5 (2010) 327-332, a Ni-P-nano Al₂O₃ plating layer was prepared on C45 steel by composite electroless deposit, and then hardened by pulse Nd:YAG laser. The results show that there is a firm metallurgical bonding between the treated layer and the substrate arising from local melting of the interface. Hard phases such as Al₅FeNi, FeNi and Fe_{0.64}Ni_{0.36} form on the surface due to laser-induced diffusion processes, which contributes to the hardening of coating through fine-crystal strengthening and dispersion strengthening. The hardness of laser treated layer reaches 840HV in the fusion zone, i.e. 1.7 times that of the as-plated coating.

[0019] Document US 2008/0102291 A1 discloses a method for coating a substrate. The method includes applying a coating to a surface of the substrate, such as applying a metallic or cermet coating via a HVOF (High Velocity Oxygen Fuel) coating process, and locally heating the applied coating and a first portion of the substrate, for example via an induction heating process or a laser heating process. The first portion includes the surface of the substrate and less than the entire substrate. The method further includes cooling the applied coating and the first portion, for example by use of compressed or ambient air, or ambient water.

[0020] It appears that no prior art discloses an annealing procedure compatible with heat-sensitive coated metal objects, ensuring that the annealing is essentially limited to the coating, leaving the mechanical properties of the substrate unaffected. In most studies from the prior art, no specific care has been taken thereof while, in some others, a modification of the substrate surface is explicitly sought in order to modify its surface morphology or mechanical properties or promote the formation of a strongly-bonded interfacial layer.

[0021] It appears also that no prior art discloses functional coatings applicable by electroplating or electroless plating, offering a real alternative to the EHC process in terms of hardness and wear resistance and whose manufacturing process is fully compatible with heat-sensitive substrates like, for instance, cold rolling mill work rolls.

Aims of the Invention

[0022] The present invention aims at proposing a methodology for the production of coated rolls, that meet the requirements for application for example in cold rolling for the steel industry.

[0023] A further aim of the invention is to achieve wear resistance of a coating that would match or, preferably, would exceed that of hard chromium coatings applied using the traditional electrolytic hard chrome process based on hexavalent chromium, and would further extend the related benefits thereof.

[0024] Still a further aim of the invention is a direct application to rolls intended for temper-rolling mills, including those at the end of continuous annealing and galvanizing lines and to tandem mills where rolls of certain stands are currently chrome-plated to reduce the friction and/or improve cleanliness.

[0025] The solution of the invention is also intended to bring added value for applications where thermally-sensitive metal objects need to be coated with a hard and wear-resistant coating, for instance to increase the mechanical durability of aluminum parts.

Summary of the Invention

[0026] A first aspect of the present invention relates to a method of coating a thermally-sensitive metal object with a protective coating, comprising the following steps:

- a first step of applying on said thermally-sensitive metal object a coating layer containing at least one phase having at least one mechanical property that can be improved by heat treatment;
- a second step of performing a superficial annealing on the coated thermally-sensitive metal object;

characterised in that the superficial annealing conditions are selected so that said mechanical property of the coating is increased while the corresponding mechanical property of the metal object is not significantly thermally-affected by the annealing step, so that the coating morphology is not modified during annealing and so that the annealing does not result in the creation of additional layers at the coating/substrate interface due to inter-diffusion.

[0027] According to preferred embodiments, the method is further limited by one of the following characteristics or a suitable combination thereof:

- the thermally-sensitive metal object is made of carbon steel, alloyed steel, tool steel, high-strength steel or aluminium alloys ;
- the thermally-sensitive metal object is a rolling mill roll ;
- said coating is a metal coating ;
- said coating is a composite coating comprising, at least, one metallic phase and one dispersed non-metallic phase, usually a ceramic phase, the volume fraction of the dispersed non-metallic phase being in the range of 0.5 vol% to 40 vol% ;
- the coating step comprises a coating application by electroplating or chemical/electroless plating ;
- the metal coating consists of a binary or ternary alloy composed of at least one of the so-called iron-group metals selected from the group of Fe, Ni, Co, Cr, and Mn, and of one or several alloying elements selected from the group consisting of C, B, P, W, and Mo ;
- the composite coating comprises an inclusion of ceramic particles usually selected from the group consisting of carbides, oxides, borides and nitrides ;
- said mechanical property is hardness, Young modulus or wear resistance ;
- upon heating in the superficial annealing step, the mechanical property improvement of at least one fraction or phase of the coating results from recrystallization of said fraction or phase and/or one or several precipitation processes taking place in said fraction or phase ;
- the second step of superficial annealing is performed using a a continuous concentrated corpuscular beam, such as a laser beam or an electron beam ;
- the second step of superficial annealing is performed using induction-heating or flame-heating ;
- the coating layer comprises a Ni-P, Ni-B, Co-P, Co-B, or Cr-P, alloyed metal matrix applied by electroplating or chemical plating and further hardened by laser annealing ;
- the coating layer comprises a Ni-W, Ni-Mo, Ni-Fe-Co, Ni-Cr, Ni-Co, Co-W, Fe-P, Fe-B, Fe-C, Fe-C-P, Fe-C-B, Cr-C, or Cr-C-P alloyed metal matrix applied by electroplating and hardened by laser annealing ;
- electroplating is applied to the metal object during a time comprised between 2 and 15 minutes, with a current density comprised between 2 and 20 A/dm² and with an energy density comprised between 10 and 50 kJ/dm² and characterised in that the laser-annealing step is performed with a contact time between the laser and the surface inferior

- to 1 sec, preferably about 0,1 sec, and with an energy density comprised between 10 and 100 kJ/dm²;
- the thickness of the annealed coating layer is comprised between 2 and 100 μm.

[0028] A second aspect of the invention relates to a coated thermally-sensitive metal object, obtained by the method according to anyone of the preceding claims, characterised in that the thickness of the coating layer with improved mechanical property is comprised between 2 and 100 μm.

Brief Description of the Drawings

[0029]

FIG. 1 shows the evolution of the hardness of DIN 1.2363 steel substrate, initially heat-treated to achieve a hardness of 850HV, then submitted to oven-annealing at different temperatures between 200°C and 450°C and for different treatment durations, according to prior art.

FIG. 2 shows the evolution of the hardness of SIHARD™ R246 steel substrate, initially heat-treated to achieve a hardness of 700HV, then submitted to oven-annealing at different temperatures between 200°C and 450°C and for different treatment durations, according to prior art.

FIG. 3 shows the micro-hardness depth profile, measured on cross-section, of a sample consisting of a DIN 1.2363 steel substrate coated with a NiP alloyed coating, before annealing, the micro-hardness of the coating layer being also shown.

FIG. 4 shows the same embodiment, after superficial annealing. The micro-hardness depth profile of the coated substrate, measured on cross-section after annealing, is given, the micro-hardness of the annealed coating layer being also shown.

FIG. 5 shows the micro-hardness depth profile, measured on cross-section, of a sample consisting of a DIN 1.2363 steel substrate coated with a NiP-SiC composite coating, before annealing, the micro-hardness of the coating layer being also shown.

FIG. 6 shows the same embodiment, after superficial annealing. The micro-hardness depth profile of the coated substrate, measured on cross-section after annealing, is given, the micro-hardness of the annealed coating layer being also shown.

FIG. 7 shows the same embodiment, after oven-annealing. The micro-hardness depth profile of the coated substrate, measured on cross-section after annealing, is given, the micro-hardness of the annealed coating layer being also shown.

FIG. 8 shows X-ray diffraction (XRD) data for the coated substrates corresponding to FIG. 3 and FIG. 4, i.e. respectively after the coating step and after the superficial annealing step. XRD reference patterns for Ni and Ni₃P phases are shown as well.

FIG. 9 shows the micro-hardness depth profile, measured on cross-section, of a sample consisting of a C45 steel substrate coated with a Ni-P alloy by electroless plating (Kanigen™ process), before annealing, the micro-hardness of the coating layer being also given.

FIG. 10 shows the same embodiment, after superficial annealing. The micro-hardness depth profile of the coated substrate, measured on cross-section after laser-annealing, is given, the micro-hardness of the annealed coating layer being also shown.

FIG. 11 shows the same embodiment, after oven-annealing. The micro-hardness depth profile of the coated substrate, measured on cross-section after oven-annealing, is given, the micro-hardness of the annealed coating layer being also shown.

FIG. 12 shows the micro-hardness depth profile, measured on cross-section, of a sample consisting of a SIHARD™ R246 steel substrate coated with a Cr layer using a trivalent chromium electrolyte, before annealing, the micro-hardness of the coating layer being also given.

FIG. 13 shows the same embodiment, after superficial annealing. The micro-hardness depth profile of the coated substrate, measured on cross-section after laser-annealing, is given, the micro-hardness of the annealed coating layer being also given.

Description of Preferred Embodiments of the Invention

[0030] In a particular embodiment of the present invention, a DIN 1.2365 steel substrate, heat-treated to achieve a hardness of 690HV, was used as substrate. A nickel-phosphorus alloyed coating was applied on the substrate by electroplating using a commercial NiPhos 966 electrolyte commercialised by Umicore Galvanotechnik. Electrodeposition of the coating was performed at a current density of 5A/dm² for 30min at a temperature of 55°C. The coating prepared under such conditions consisted of a Ni-P alloy with 10±1w%P, as measured by X-ray fluorescence.

[0031] Table 1 shows the micro-hardness values measured for the coating and substrate prior to annealing. Micro-hardness is measured according to a method which is well-known of the skilled person (Vickers method, ISO 6507/ASTM E384). FIG. 3 shows a micro-hardness depth-profile of the sample measured to a depth of 3mm. The micro-hardness value reported in Table 1 for the substrate is the average of the 30 data points measured for the depth profile. As shown on Table 1, before annealing, the coating is softer than the substrate.

Table 1. Micro-hardness comparison between coating and substrate in non-annealed condition

Non annealed Ni-P coating applied by electroplating on a DIN 1.2363 steel substrate	
	Micro-hardness (HV0.1)
Coating	540±11
Substrate	685±10

[0032] After annealing, the micro-hardness of the coating increased to 1035HV. As shown on Table 2 and FIG. 4, the micro-hardness depth-profile of the substrate is not significantly impacted by the superficial annealing treatment.

Table 2. Micro-hardness comparison between substrate and coating after annealing

Ni-P coating applied by electroplating on a DIN 1.2363 steel substrate after superficial annealing	
	Micro-hardness (HV0.1)
Coating	1035±19
Substrate	678±12

[0033] In another particular embodiment of the present invention, a DIN 1.2365 steel substrate, heat-treated to achieve a hardness of 800HV was coated with a nickel-phosphorus-SiC composite coating by electroplating. For this purpose, 100g/L of SiC powder (Alpha silicon carbide Grade UF-05, H.C. Starck) was added to the NiPhos 966 electrolyte and kept in suspension using appropriate stirring conditions. Electrodeposition of the coating was performed at a current density of 5A/dm² and temperature of 55°C for 30min. The cermet coating consists of a Ni-P-SiC alloy with 9w%P in the metal matrix and 15vol% of incorporated SiC. Table 3 shows the average hardness of the coating and substrate without annealing. FIG. 5 shows a micro-hardness depth-profile of the sample.

Table 3. Micro-hardness comparison between coating and substrate in non-annealed condition

Ni-P-SiC coating applied by electroplating, in non-annealed condition	
	Micro-hardness (HV0.1)
Coating	551±11
Substrate	799±17

[0034] The coated sample was hardened using laser-annealing. Laser-annealing was performed with a laser power of 320W and a linear velocity of the beam with respect to the sample surface of 1300 mm/min. For comparison purposes, the micro-hardness of an oven-annealed sample was measured as well. Oven-annealing was performed by introducing the coated sample in a furnace pre-heated at 390°C. The sample was left at 390°C for 60min in air then withdrawn from the oven and allowed to cool down to room temperature.

[0035] After annealing, the micro-hardness of the coating increased to 920 ± 12 HV in the case of laser-annealing and 855 ± 65 HV in the case of oven-annealing, as shown on Table 4. FIG. 6 and FIG. 7 show the micro-hardness depth profile of the substrate measured, respectively, after laser-annealing and oven annealing. The substrate micro-hardness after laser-annealing is not significantly impacted by the superficial annealing treatment. In contrast, softening of the substrate is observed throughout the sample in the case of oven-annealing.

Table 4. Micro-hardness comparison between substrate and coating after annealing

Ni-P-SiC coating applied by electroplating, after annealing		
	Laser-annealing micro-hardness (HV0.05)	Oven-annealing micro-hardness (HV0.05)
Coating	920 ± 12	855 ± 65
Substrate	776 ± 27	664 ± 14

[0036] The hardening is associated with a recrystallisation of the initially amorphous coating and precipitation of Ni₃P, with the presence of silicon carbide particles, as observed using X-ray diffraction. This is illustrated on FIG. 8.

[0037] In still another particular embodiment of the present invention, a heat-treated AISI C45 steel substrate with hardness 810 ± 25 HV was coated with a Ni-P alloyed coating by electroless plating using the prior art procedure. For the present study, the coating operation was performed according to the commercial Kanigen™ process. The coating consists of a Ni-P alloy with 8.7 ± 0.2 wt%P, as measured by X-ray fluorescence. Table 5 shows the average micro-hardness of the coating and substrate before annealing. As shown on Table 5, prior to annealing, the coating is softer than the substrate. FIG. 9 shows a micro-hardness depth-profile of the sample.

Table 5. Micro-hardness comparison between electroless Ni-P coating and substrate in non-annealed condition

Non-annealed Ni-P coating applied by Kanigen™ electroless plating	
	Micro-hardness (HV0.05)
Coating	592 ± 15
Substrate	827 ± 36

[0038] The coated sample was hardened using laser-annealing. Laser-annealing was performed with a laser power of 380W and a linear velocity of the beam with respect to the sample surface of 1300 mm/min. For comparison purposes, a sample was oven-annealed using the procedure described above.

[0039] After laser-annealing, the hardness of the coating increased to 1050 ± 25 HV. As shown on Table 6 the average hardness of the substrate is slightly reduced. FIG. 10 shows the micro-hardness depth-profile of the samples. A softening of the substrate is observed, limited to a superficial region of 0.5mm depth. FIG. 11 also shows the depth profile of an identical sample which was oven-annealed for 1h at $390 \pm 10^\circ\text{C}$. Hardening of the coating is observed and reaches 1010 ± 21 HV. Softening of the substrate is observed throughout the sample (512 ± 20 HV).

Table 6. Comparison of the average micro-hardness between substrate and coating after superficial annealing and oven-annealing

Ni-P coating applied by Kanigen™ process, after annealing		
	Laser-annealing micro-hardness (HV0.1)	Oven-annealing micro-hardness (HV0.1)
Coating	1050 ± 25	1010 ± 21
Substrate	773 ± 79	512 ± 20

[0040] In still another particular embodiment of the present invention, a SIHARD™ R246 steel rod supplied by SIJ Ravne Systems, induction-hardened to achieve a hardness of 65HRC over a depth of 3mm, was used as substrate. The latter was coated with a chromium layer electroplated from a trivalent chromium electrolyte composed of 0.39 M $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 3.72 M NH_4COOH and 0.81 M KCl. The electroplating process was performed at a temperature of 35°C and a current density of 50A/dm^2 for 45min. Table 6 shows the micro-hardness values measured for the coating and

substrate (average of 30 measurements over a depth of 3mm from the surface) in the absence of annealing. The very high standard error observed for the substrate is a consequence of a significant micro-hardness gradient, as observed on the depth-profile shown in FIG. 12.

Table 6. Micro-hardness comparison between electroplated chromium coating and substrate in non-annealed conditions

Non-annealed Cr coating applied by electroplating from a trivalent chromium electrolyte	
	Micro-hardness (HV0.1)
Coating	907±50
Substrate	720±93

[0041] The coated substrate was superficially annealed using laser-annealing. Laser-annealing was performed with a laser power of 250W and a linear velocity of the beam with respect to the sample surface of 1400 mm/min. After annealing, the hardness of the coating increased to 1119±50. As shown on Table 7 and FIG. 13 the hardness depth profile of the substrate is not significantly impacted by the superficial annealing

Table 7. Micro-hardness comparison between substrate and coating after annealing

	Chromium coating applied by electroplating, after superficial laser-annealing
	Micro-hardness (HV0.1)
Coating	1119±50
Substrate	781±86

Claims

1. A method of coating a thermally-sensitive metal object with a protective coating, comprising the following steps:

- a first step of applying on said thermally-sensitive metal object a coating layer containing at least one phase having at least one mechanical property that can be improved by heat treatment;
- a second step of performing a superficial annealing on the coated thermally-sensitive metal object;

wherein the superficial annealing conditions are selected so that said mechanical property of the coating is increased while the corresponding mechanical property of the metal object is not significantly thermally-affected by the annealing step, so that the coating morphology is not modified during annealing and so that the annealing does not result in the creation of additional layers at the coating/substrate interface due to interdiffusion.

2. The method of claim 1, wherein the thermally-sensitive metal object is made of carbon steel, alloyed steel, tool steel, high-strength steel or aluminium alloys.

3. The method of claim 1 or 2, wherein the thermally-sensitive metal object is a rolling mill roll.

4. The method of claim 1, wherein said coating is a metal coating.

5. The method of claim 1, wherein said coating is a composite coating consisting of, at least, one metallic phase and one dispersed non-metallic phase, usually a ceramic phase, the volume fraction of the dispersed non-metallic phase being in the range of 0.5 vol% to 40 vol%.

6. The method of claim 1, wherein the coating step comprises a coating application by electroplating or chemical/electroless plating.

7. The method of claim 4, wherein the metal coating consists of a binary or ternary alloy composed of at least one of the so-called iron-group metals selected from the group of Fe, Ni, Co, Cr, and Mn) and of one or several alloying

elements selected from the group consisting of C, B, P, W, and Mo.

8. The method of claim 5 where the composite coating comprises an inclusion of ceramic particles usually selected from the group consisting of carbides, oxides, borides and nitrides.
9. The method of claim 1, wherein said mechanical property is hardness, Young modulus or wear resistance.
10. The method of claim 1, wherein, upon heating in the superficial annealing step, the mechanical property improvement of at least one fraction or phase of the coating results from recrystallization of said fraction or phase and/or one or several precipitation processes taking place in said fraction or phase.
11. The method of claim 1, wherein the second step of superficial annealing is performed using a continuous concentrated corpuscular beam, such as a laser beam or an electron beam.
12. The method of claim 1, wherein the second step of superficial annealing is performed using induction-heating or flame-heating.
13. The method of claim 1, wherein the coating layer comprises a Ni-P, Ni-B, Co-P, Co-B, or Cr-P, alloyed metal matrix applied by electroplating or chemical plating and further hardened by laser annealing.
14. The method of claim 1, wherein the coating layer comprises a Ni-W, Ni-Mo, Ni-Fe-Co, Ni-Cr, Ni-Co, Co-W, Fe-P, Fe-B, Fe-C, Fe-C-P, Fe-C-B, Cr-C, or Cr-C-P alloyed metal matrix applied by electroplating and hardened by laser annealing.
15. The method of claim 13 or 14 wherein electroplating is applied to the metal object during a time comprised between 2 and 15 minutes, with a current density comprised between 2 and 20 A/dm² and with an energy density comprised between 10 and 50 kJ/dm² and wherein the laser-annealing step is performed with a contact time between the laser and the surface inferior to 1 sec, preferably about 0,1 sec, and with an energy density comprised between 10 and 100 kJ/dm².
16. The method of claim 13 or 14, wherein the thickness of the annealed coating layer is comprised between 2 and 100 μm.
17. A coated thermally-sensitive metal object, obtained by the method according to anyone of the preceding claims, wherein the thickness of the coating layer with improved mechanical property is comprised between 2 and 100 μm.

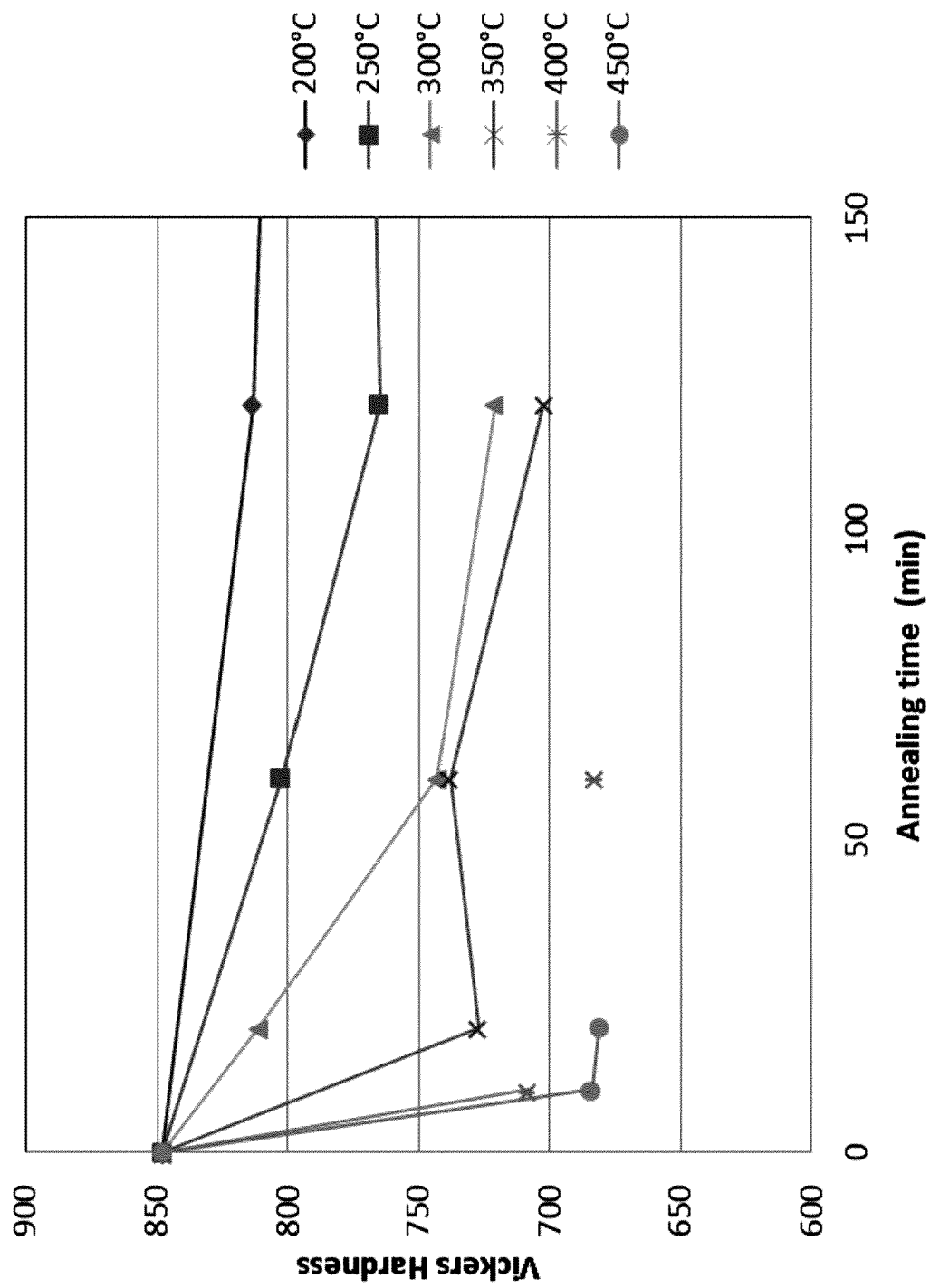


FIG. 1

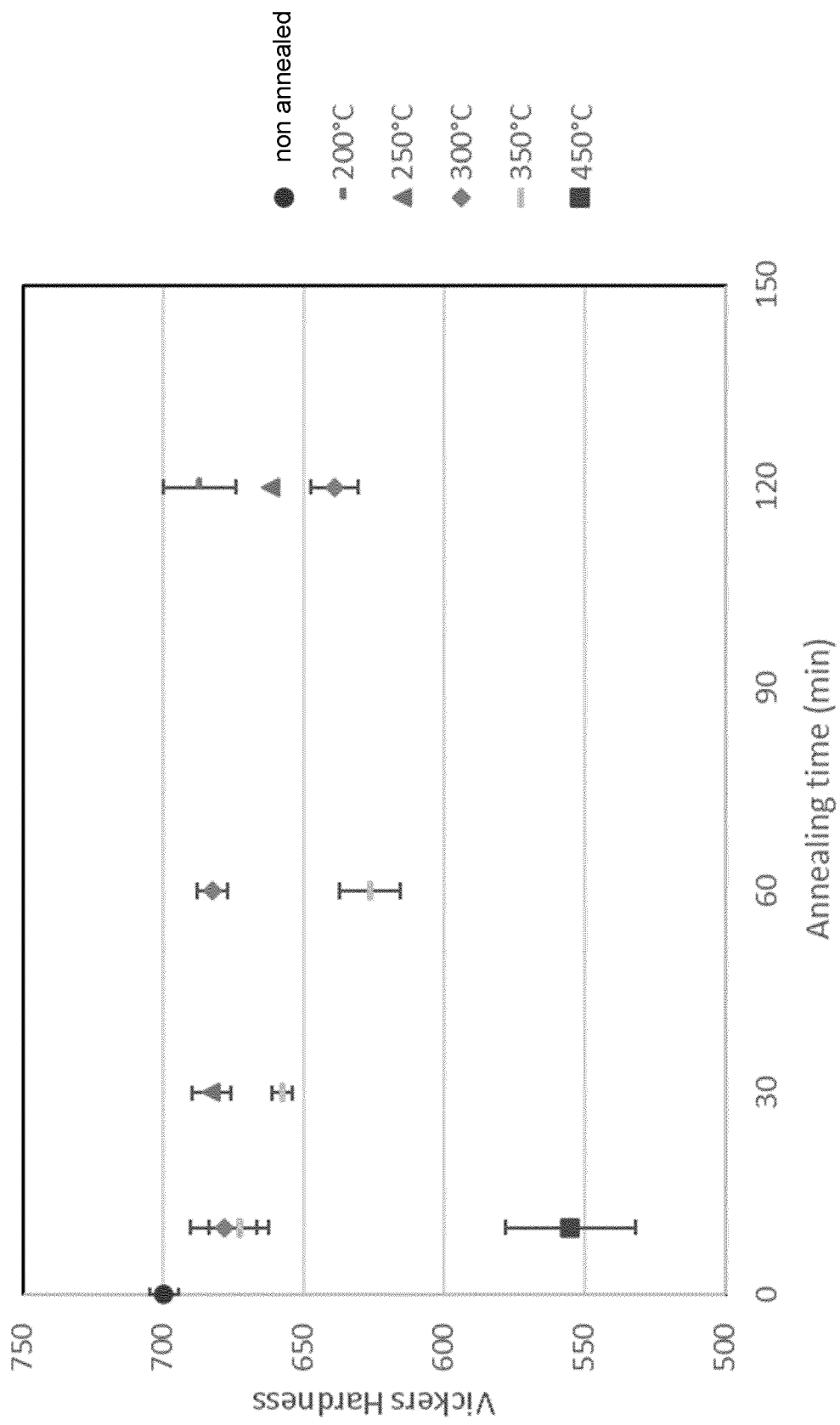


FIG. 2

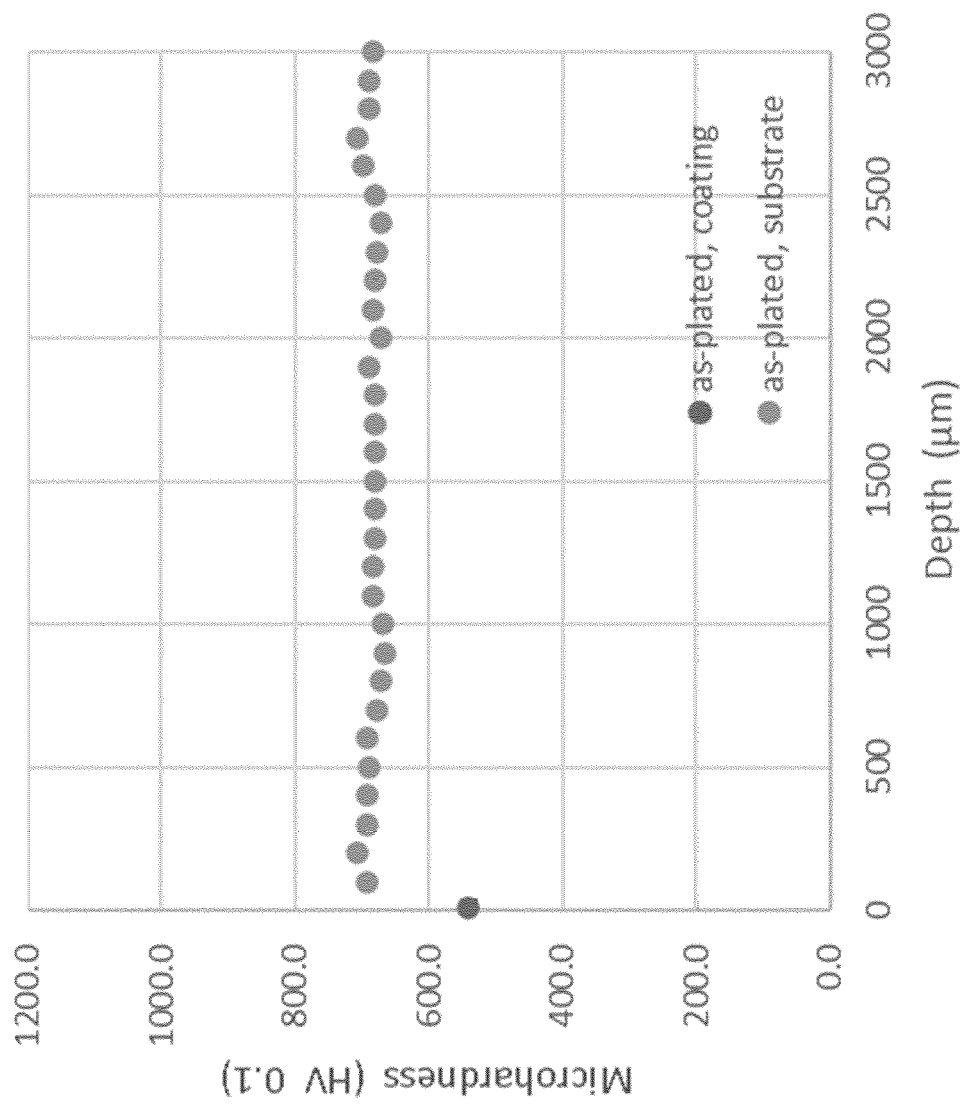
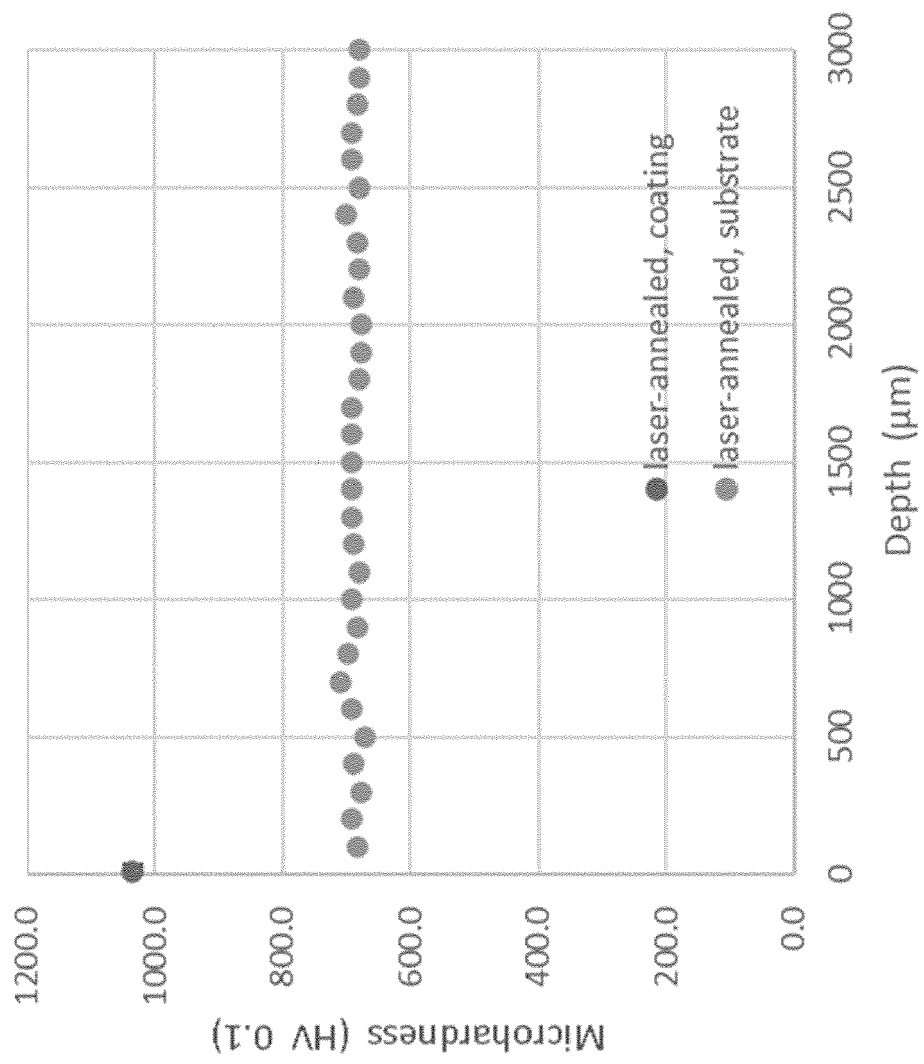


FIG. 3

FIG. 4

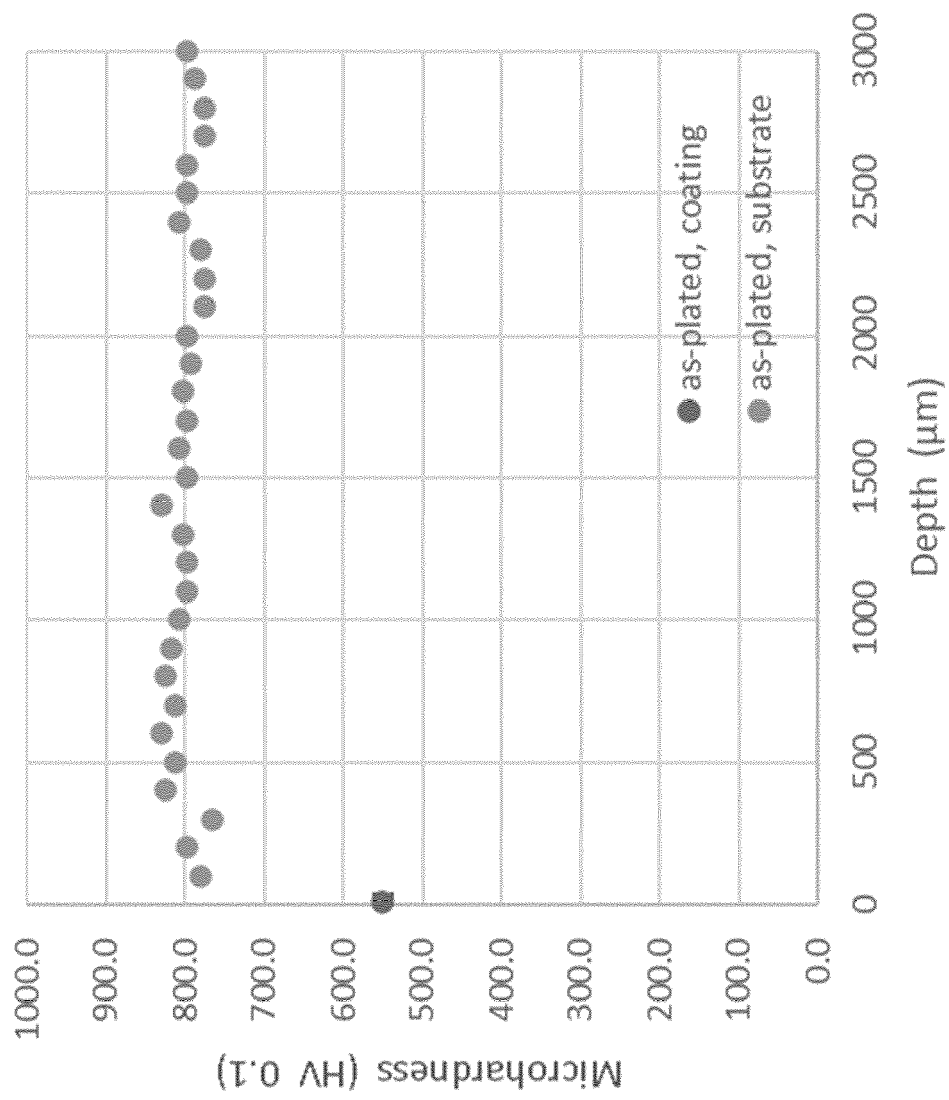


FIG. 5

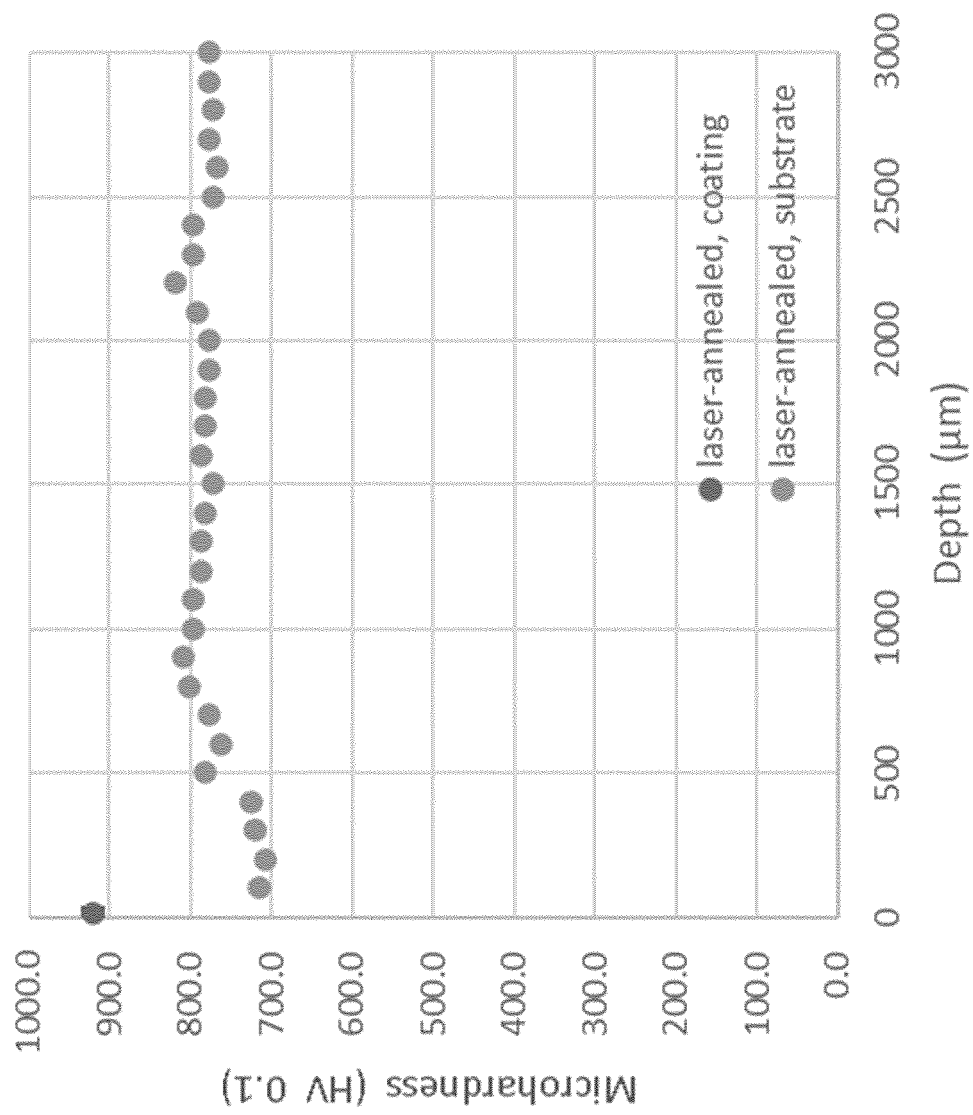


FIG. 6

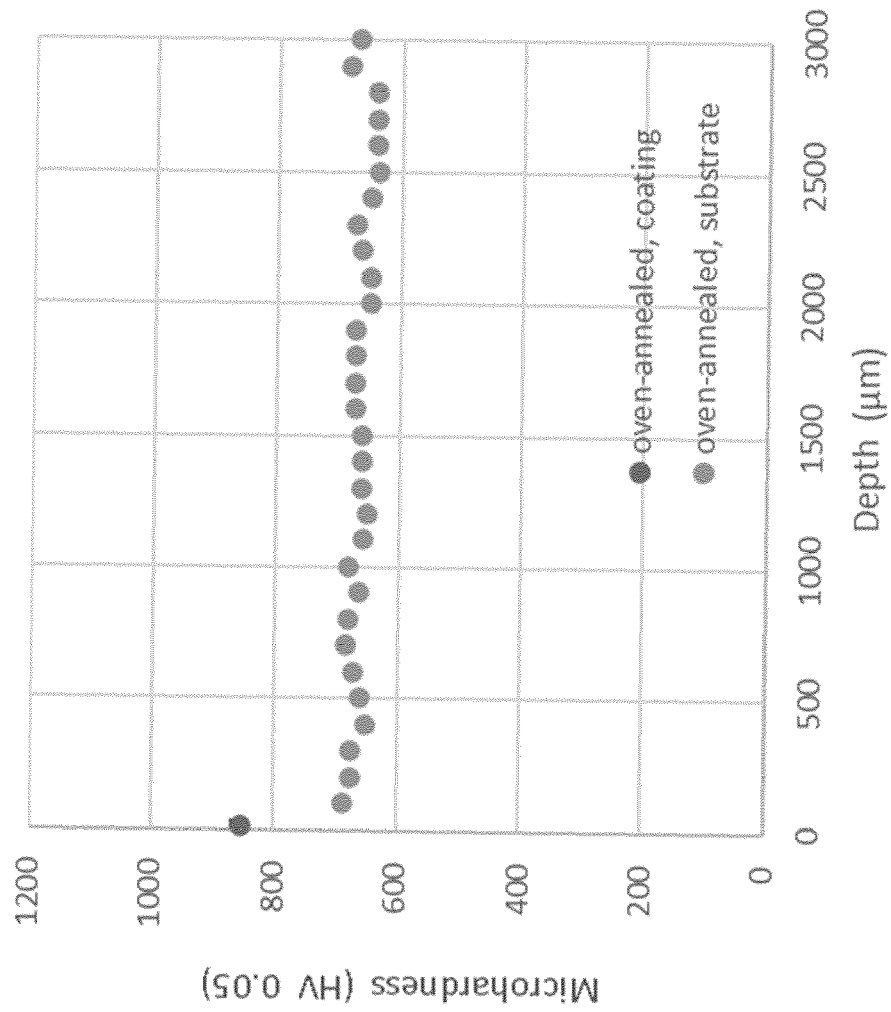


FIG. 7

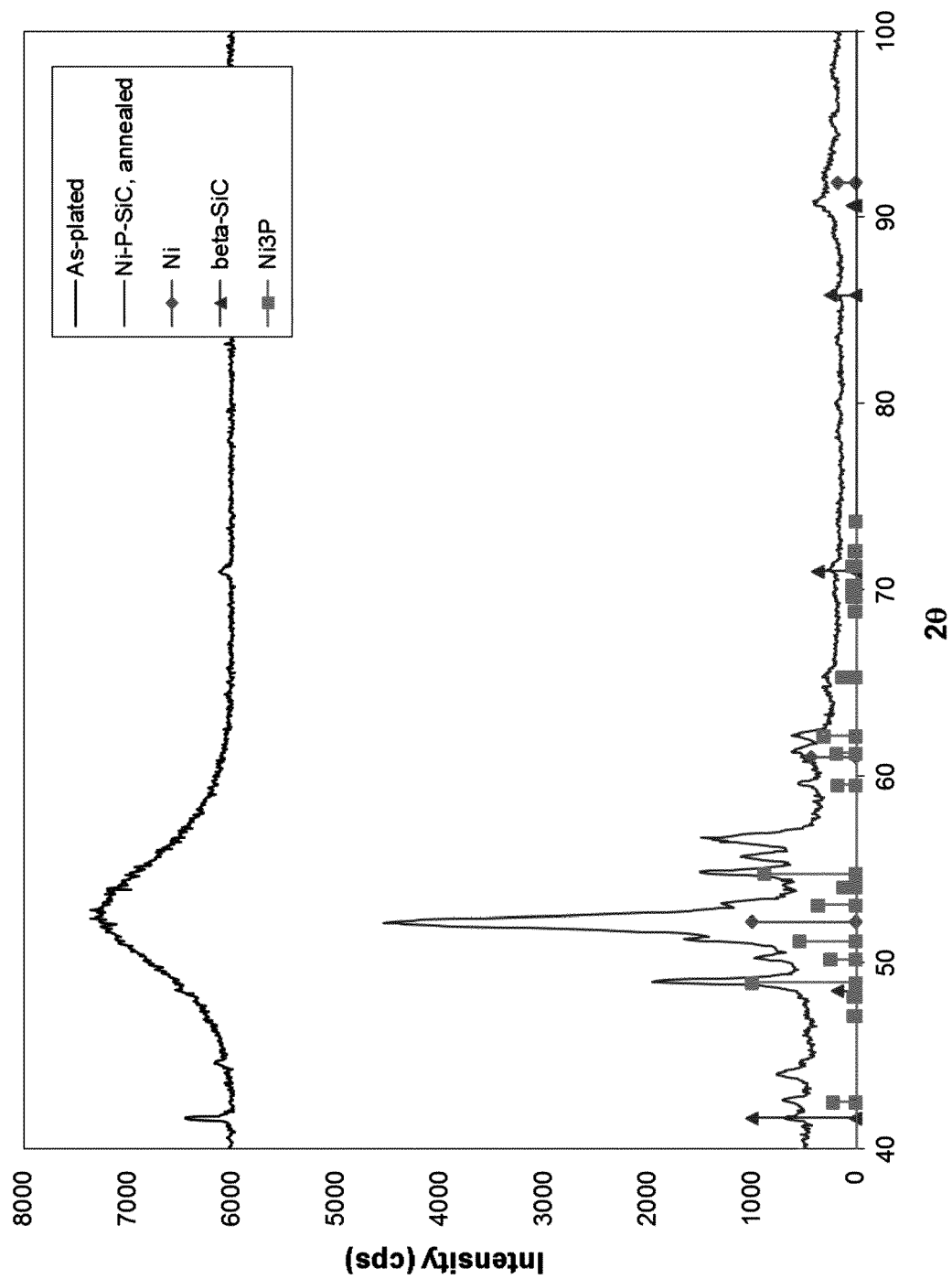


FIG. 8

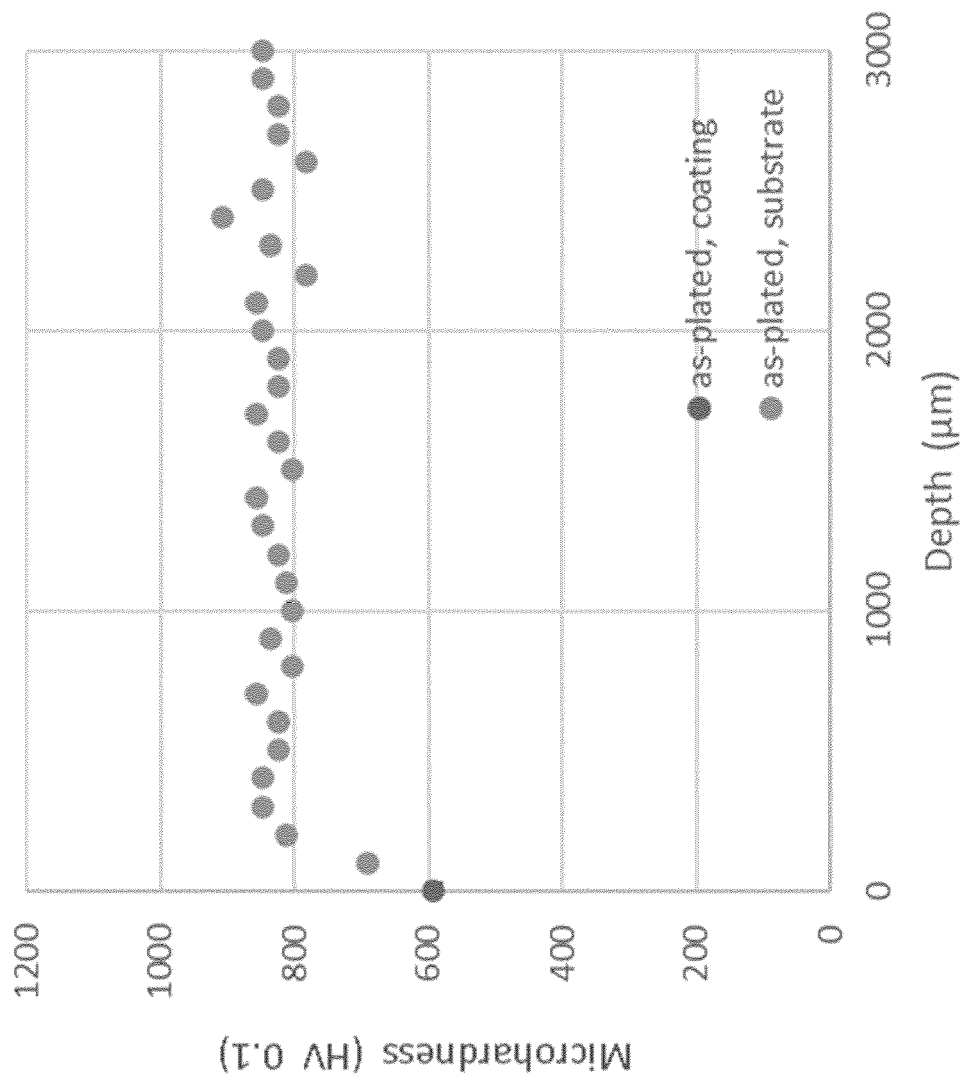


FIG. 9

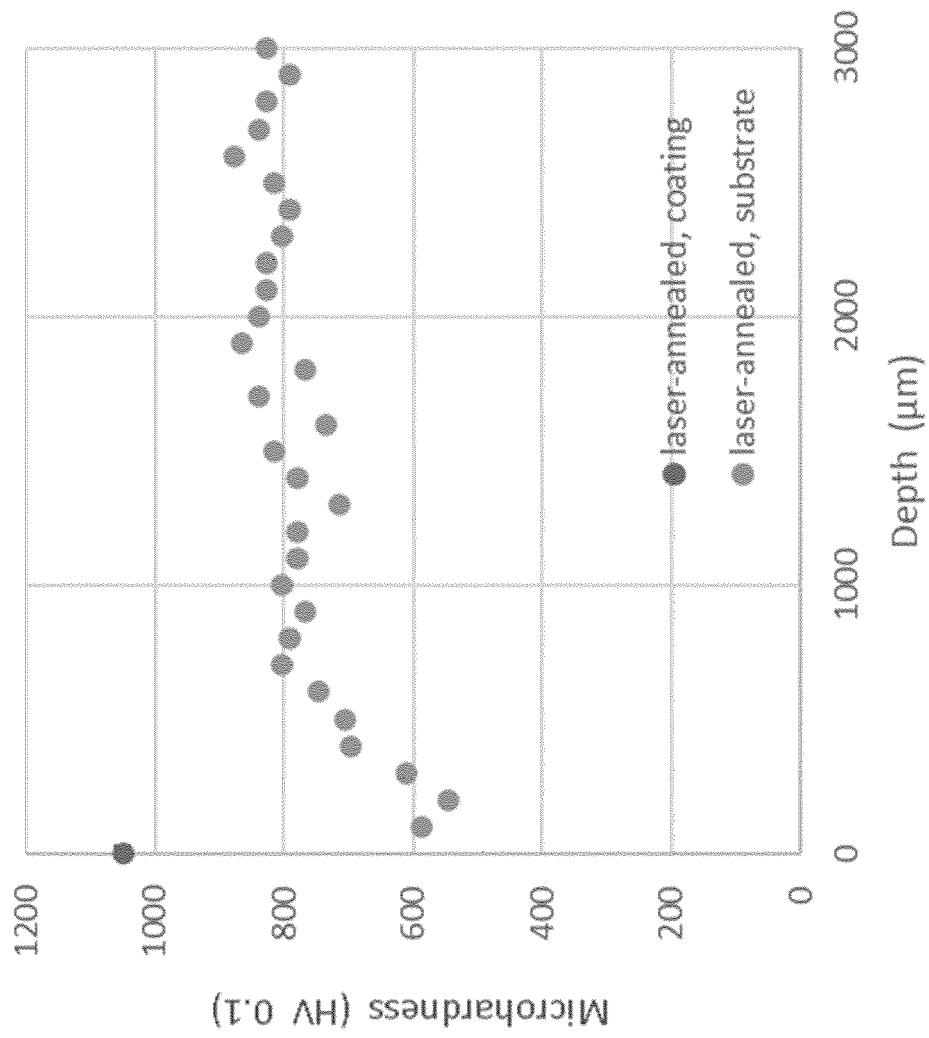


FIG. 10

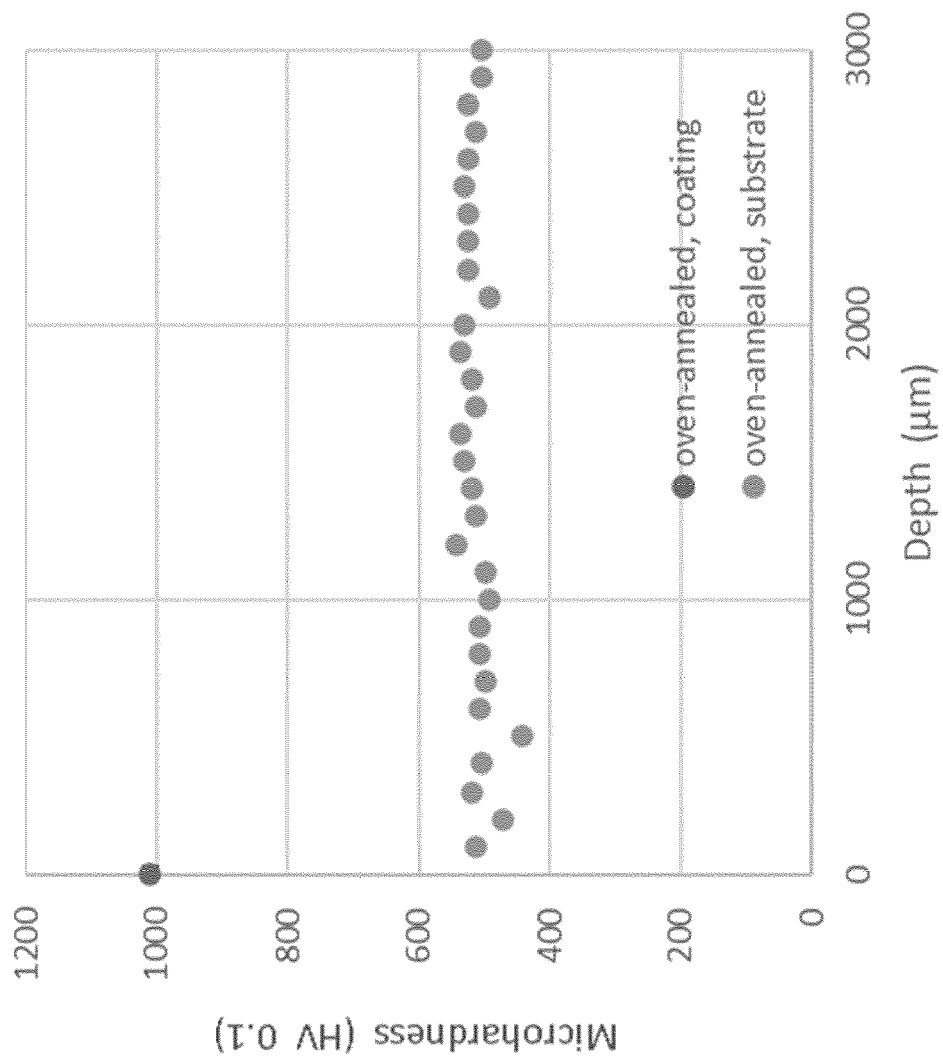


FIG. 11

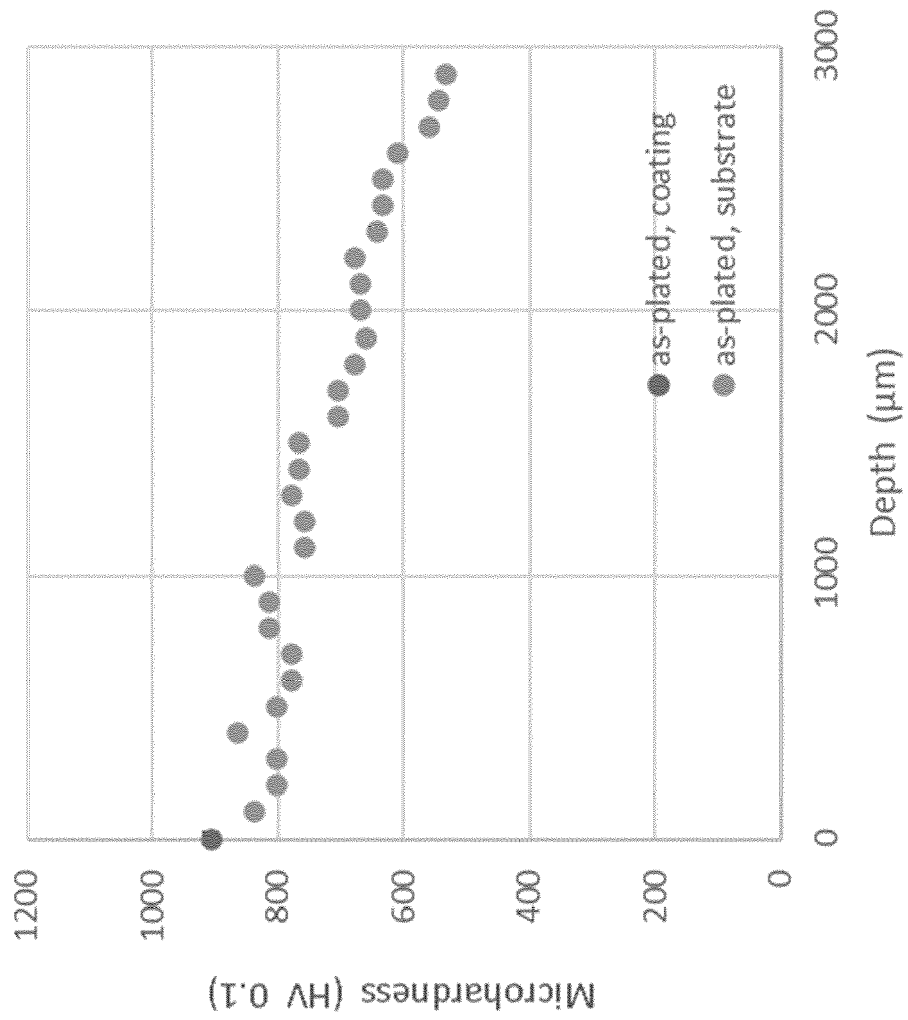
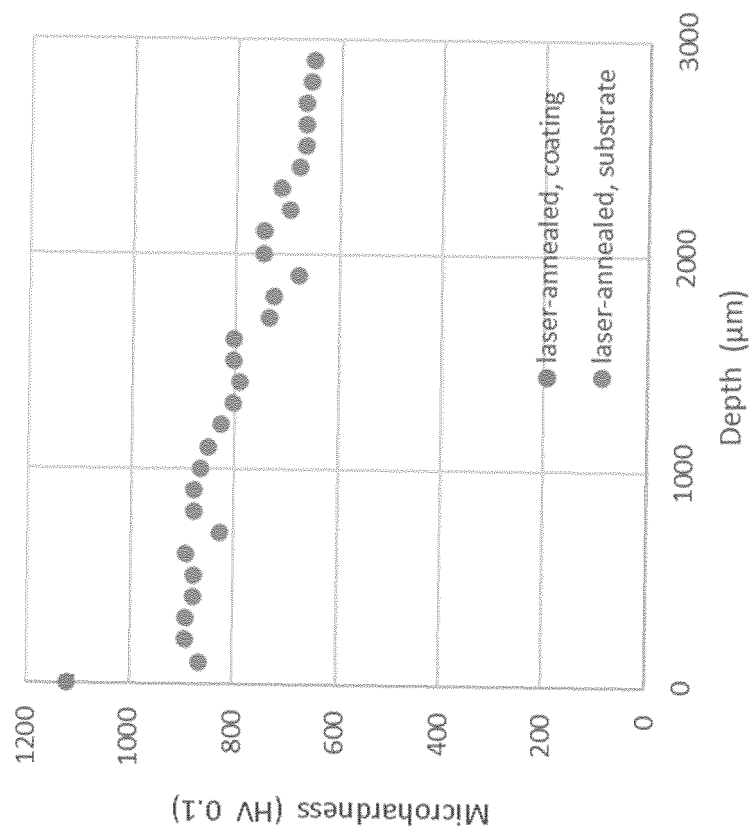


FIG. 12

FIG. 13



EUROPEAN SEARCH REPORT

Application Number

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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,D	ZHANG QUNLI ET AL: "Pulse laser assisted composite electroless deposit to prepare ceramic coating", PHYSICS PROCEDIA, vol. 5, 1 January 2010 (2010-01-01), pages 327-332, XP93029120, AMSTERDAM, NL ISSN: 1875-3892, DOI: 10.1016/j.phpro.2010.08.153 Retrieved from the Internet: URL:https://pdf.sciencedirectassets.com/277348/1-s2.0-S1875389210X00098/1-s2.0-S1875389210005791/main.pdf?X-Amz-Security-Token=IQoJb3JpZ2luX2VjEFoACXVzLWVhc3QtMSJIMEYCIQCxTkwoP8iz9EZUE8g4sBw6Mu37bW/k0qjKXdtR+cMoxQIhAP7baalEop7NSmtWeYlWnEZm2kTeuBjK7ZHu7rQOAJdIKrIFCBMQBROmMDU5MDAaZNTQ2ODY1Igw7LVOYDs3e4LLhM> [retrieved on 2023-03-06] * abstract * * paragraph 2 *	1,2, 4-11,13, 16,17	INV. C25D5/50 C25D15/00 C23C18/16 C23C18/32 ADD. C25D3/06 C25D3/12 C25D3/56
X	US 2018/363147 A1 (KIM YEON-HO [KR] ET AL) 20 December 2018 (2018-12-20) * abstract * * paragraphs [0074], [0081], [0097], [0105], [0107] *	1,2, 4-12, 14-16	C25D C23C
X	EP 3 167 100 B1 (SAVROC LTD [FI]) 26 February 2020 (2020-02-26) * abstract * * example 1 * * paragraphs [0002], [0025] - [0029] *	1-7, 9-14,16, 17	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		24 May 2023	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			



EUROPEAN SEARCH REPORT

Application Number

EP 22 20 2105

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	US 2015/166802 A1 (DIXON RICHARD [GB] ET AL) 18 June 2015 (2015-06-18) * abstract * * examples 1-11 * * paragraphs [0055], [0079] * -----	1, 4-6, 8-11, 16, 17	
X	US 2013/061916 A1 (BAKER-O'NEAL BRETT C [US] ET AL) 14 March 2013 (2013-03-14) * abstract * * example * * paragraph [0077] * -----	1, 4, 6, 9-11, 16, 17	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
Place of search The Hague			Date of completion of the search 24 May 2023
Examiner 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			

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EPO FORM 1503 03.82 (P04C01)



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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:

☐ 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).



LACK OF UNITY OF INVENTION SHEET B

Application Number

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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 (partially)

Inventive concept I regards a method of coating a thermally-sensitive metal object with a protective coating, comprising the following steps: a first step of applying on said thermally-sensitive metal object a coating layer containing at least one phase having at least one mechanical property that can be improved by heat treatment; a second step of performing a superficial annealing on the coated thermally-sensitive metal object; wherein the superficial annealing conditions are selected so that said mechanical property of the coating is increased while the corresponding mechanical property of the metal object is not significantly thermally-affected by the annealing step, so that the coating morphology is not modified during annealing and so that the annealing does not result in the creation of additional layers at the coating/substrate interface due to interdiffusion, wherein the thermally-sensitive metal object is made of carbon steel, alloyed steel, tool steel, high-strength steel or aluminium alloys and/or wherein the thermally-sensitive metal object is a rolling mill roll.

2. claims: 4-8, 13-17 (completely); 1 (partially)

Inventive concept II regards a method of coating a thermally-sensitive metal object with a protective coating, comprising the following steps: a first step of applying on said thermally-sensitive metal object a coating layer containing at least one phase having at least one mechanical property that can be improved by heat treatment; a second step of performing a superficial annealing on the coated thermally-sensitive metal object; wherein the superficial annealing conditions are selected so that said mechanical property of the coating is increased while the corresponding mechanical property of the metal object is not significantly thermally-affected by the annealing step, so that the coating morphology is not modified during annealing and so that the annealing does not result in the creation of additional layers at the coating/substrate interface due to interdiffusion, wherein said coating is a metal coating and/or wherein said coating is a composite coating consisting of, at least, one metallic phase and one dispersed non-metallic phase, usually a ceramic phase, the volume fraction of the dispersed non-metallic phase being in the range of 0.5 vol% to 40 vol%.

Inventive concept II also concerns the respective coated metal object.

3. claims: 9-12 (completely); 1 (partially)

**LACK OF UNITY OF INVENTION
SHEET B**

Application Number

EP 22 20 2105

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:

Inventive concept III regards a method of coating a thermally-sensitive metal object with a protective coating, comprising the following steps: a first step of applying on said thermally-sensitive metal object a coating layer containing at least one phase having at least one mechanical property that can be improved by heat treatment; a second step of performing a superficial annealing on the coated thermally-sensitive metal object; wherein the superficial annealing conditions are selected so that said mechanical property of the coating is increased while the corresponding mechanical property of the metal object is not significantly thermally-affected by the annealing step, so that the coating morphology is not modified during annealing and so that the annealing does not result in the creation of additional layers at the coating/substrate interface due to interdiffusion, wherein said mechanical property is hardness, Young modulus or wear resistance and/or wherein, upon heating in the superficial annealing step, the mechanical property improvement of at least one fraction or phase of the coating results from recrystallization of said fraction or phase and/or one or several precipitation processes taking place in said fraction or phase and/or wherein the second step of superficial annealing is performed using a continuous concentrated corpuscular beam, such as a laser beam or an electron beam.

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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