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(54) Title: METHOD FOR THE PREPARATION OF CERAMIC COATINGS ON ELECTRICALLY CONDUCTIVE SUBSTRATES

(57) **Abstract:** The invention relates to a process for the preparation of ceramic coatings on an electrically conductive substrates. With the inventive method, the resulting coated substrates show very good tribological properties in terms of friction and wear resistance.

Method for the preparation of ceramic coatings on electrically conductive substrates

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a coating method for depositing ceramic coatings on electrically conductive substrates. It is also relating to ceramic coated conductive substrates obtained by the coating method. The present invention also relates to moving parts of an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system comprising said coated conductive substrate and uses thereof for reducing friction and wear in tribological applications.

BACKGROUND OF THE INVENTION

Ceramic coatings have outstanding behaviors including resistance to wear, corrosion, elevated temperature and oxidation. Especially for tribological applications, the use of oil or grease lubrications is not sufficient to meet wear resistance. Abrasive resistant coatings are very powerful solutions to resolve surface wear issues.

These coatings are usually generated via plasma deposition techniques, such as chemical vapor deposition (CVD), physical vapor deposition (PVD) and plasma spraying (PS).

Chemical vapor deposition CVD process involves depositing a solid material from a gaseous phase. This is achieved by means of a chemical reaction between volatile precursors and the surface of the materials to be coated.

Physical vapor deposition PVD is a vaporization coating technique, involving the transfer of material on an atomic level under vacuum condition. In some aspects, the process is similar to the CVD process, except that in the PVD process, the precursors start out in solid form, whereas in the CVD process, the precursors are introduced to the reaction chamber in gaseous form.

CVD and PVD methods give a homogenous and flexible microstructure with sufficient surface hardness. For instance, AU2012101373 describes that ceramic coatings may be obtained on a three dimensional metallic substrate by the CVD method. The method and apparatus may be used to deposit, for example, titania or alumina coatings on stainless steel substrates. The resulting surface was reported to have sufficient hardness.

However, limitations in part size and uncontrolled surface quality, in particular, in terms of thickness, remain strong disadvantages of these technologies. Additionally, further drawbacks of these technologies are slow deposition rates, which are important hurdles to overcome. For instance, Lackner *et al* reported that plasma deposited layers can grow on metal surfaces with deposition rates between 0,44-11,4 nm/min (Gas Permeation, Mechanical Behavior and Cytocompatibility of Ultrathin Pure and Doped Diamond-Like Carbon and Silicon Oxide Films, (2013), *Coatings, 3,* 268-300). To reach an average thickness of 5 µm, it would take 190 hours to 8 hours, respectively. Therefore, these methods lead to increase of both maintenance and operation costs for industrial applications.

Another alternative technique for deposition of ceramic coatings is plasma spraying PS. From an industrial point of view, the PS process performs with a deposition rate, which is much higher than all the deposition rates available with PVD or CVD processes. However, surface structures are usually found to be porous inducing either vertical or lamellar cracks. This leads to poor adhesion between coating and substrate. In many reports, it is stated that the PS process is a sophisticated process because of complicated process parameters. Indeed, each PS process parameter (gas velocity, nozzle diameter, nozzle distance, gas concentration, temperature, etc.) has significant influence on coating chemical and mechanical properties, but is difficult to adjust. There is a high complexity in optimizing plasma spray processes for ceramic deposition in order to get a less porous surface. Indeed usually the coating obtained by plasma spraying is a porous surface with an uneven layer (Floristan *et al*, (2010), Development of electrically conductive plasma sprayed coatings on glass, *Journal Surface & Coatings Technology 205*, 1021-1028).

Spark plasma sintering (SPS) is a sintering technique that consists in simultaneously applying to a bulk sample or powder sample to be densified, or to the parts to be joined, a uniaxial pressure and current pulses of high intensity, which may be an alternating current (AC) or a direct current (DC). The main characteristic of SPS is that a high current and voltage are used to allow simultaneous densification and bonding of powders with porous bodies. The heat generation is internal, in contrast to the conventional hot pressing, where the heat is provided by external heating elements. The heat treatment allows to join permanently two parts with each other. The main advantages of this fabrication method are the lower processing temperature and shorter duration cycles. The SPS technology allows densifying samples in relatively short time periods of the order of a minutes.

In particular, CN104529498A relates to a multilayer environment barrier coating which is created simultaneously with the basal body from a ceramic matrix composite in a one-step process with spark plasma sintering.

US 2014/004271 A1 both disclose a method of manufacturing a ceramic coating on ceramic or ultra-refractory metal substrates for aeronautic applications, the method comprising the step of sintering the deposited powder on the substrate by spark plasma sintering using a pulsed direct electric current and a graphite mold, which is made out of a conductive material to let the electrical current flows through the mold. The same goes true for US 2006/172073A1 which relates to functionally graded materials (FGM) to be used in medical applications.

FR2941965 and FR2932496 also both describe a process for depositing a coating layer on a metal turbine blade, said turbine blade being placed in a graphite mold before being treated by SPS in order to join the coating with the turbine blade. The coating layer densifies in the space left between the mold and the turbine blade. By using a graphite mold as usually in the conventional sintering processes, diffusion is the leading cause initiated by a higher temperature around the particles. Because of the low thermal conductivity between the mold and the particles to be sintered, there is a big temperature difference from the surface of the particle into the particle center, resulting in thermal stress and crack-building on the coating. To avoid damaging of the coating, the heating rate has to be optimized to achieve a homogeneous heat distribution between the mold and the material to be sintered.

The same problem is also observed when using a graphite die, which keeps in place the ceramic particles to be sintered. As in the case of a conductive mold, the heat distribution is also not homogeneous in the sintered material. The publication, Post treatment of Plasma-sprayed amorphous ceramic coatings by spark plasma sintering, *Journal of Thermal spray technology, vol 24(4),* April 2015, 634, discloses the preparation of a crystalline material out of an amorphous material using a SPS process, in which a pellet is prepared out of a ceramic powder, the heat being generated by pulsed direct current passing directly through a small graphite die that contains the ceramic sample.

Based on the foregoing, there is still a need to investigate further on a new coating process, which would provide high deposition rates by using environmentally friendly chemicals. It would be also desirable to decrease the coating deposition times in the coating process and to find a simplified coating process which would be cost effective and would be easily carried out into practice. In particular, the new coating process should allow to prepare a coated conductive substrate with excellent resistance properties to wear and friction, wherein the coating is a crack free coating with better adhesion to the substrate.

SUMMARY OF THE INVENTION

After thorough research, the inventors of the present invention have surprisingly found that a coating method for depositing a ceramic coating on electrically conductive substrates as defined in claim 1 is very efficient and easy to carry out in industrial scale for preparing coated conductive substrates. The resulting coated electrically conductive substrate shows excellent tribological properties, in particular, high wear resistance and low coefficient of friction. The inventors of the invention achieved to find a coating with excellent tribological properties, the ceramic coating being coated on an electrically conductive substrate. The challenge was even higher because both materials, namely the ceramic material and the substrate, have different thermal expansion coefficient which is the technical problem to overcome in order to get a good adhesion between the ceramic coating and the substrate.

According to the invention, the method for depositing a ceramic coating on an electrically conductive substrate is characterized in that the method comprises the following steps:

a) coating a suspension comprising inorganic nanoparticles or depositing a powder comprising inorganic particles on the conductive substrate,

b) placing the coated substrate of step a) between two electrically conductive punches (3,3) being a part of a spark plasma sintering device, and

c) joining by spark plasma sintering the inorganic nanoparticles with the substrate of step a) by applying joining pressure through the punches (3,3) to the at least one side of the coated substrate of step a) and by applying an alternating current through the punches (3,3) and the coated metal substrate of step a), wherein the two punches (3,3) are exclusively in electrical contact through the coated substrate, forcing the alternating current passing through the coated substrate,

wherein the electrically conductive substrate has an electrical conductivity higher than 0.5x106 S/m, and
wherein the suspension of step a) has a viscosity of 50 to 500 mPa.s, even more preferably 100 to 300 mPa.s measured at 25 °C, and
wherein the ceramic coating has an electrical conductivity in the range of 2×10^{-8} to 1 S/m, and
wherein if a suspension is used in step a) then an additional drying step before step b) is conducted to provide a coated substrate with volatile components less than 5 wt%, preferably less than 2 wt%, even more preferably less than 1 wt%, based on the total weight of the dried ceramic coating.

Preferably, the additional drying step is carried out at a temperature comprised within the range of 20 °C and 450 °C and in a drying time between 5 seconds to 40 minutes.

In a preferred embodiment of the invention, the coating or deposition of step a) is carried out on both sides of the electrically conductive substrate.

In a preferred embodiment of the invention, the coated substrate of step a) is sintered between 5 seconds to 20 minutes, corresponding to the period of time where the sample is sintered, namely, after the rising temperature step and before the subsequent cooling step.

According to another preferred embodiment, the temperature of the oven of the spark plasma sintering device is pre-heated between 40 and 1500 °C, more preferably between 500 and 1200 °C, before applying the joining pressure during the SPS step c).

According to a preferred embodiment of the method, the inorganic nanoparticles of step a) are selected from the group consisting of metal oxide nanoparticle, metal nitride nanoparticle, metal carbide nanoparticle, non-metal oxide nanoparticle, graphite nanoparticle or mixtures thereof.

According to another preferred embodiment of the method, the step a) of depositing the suspension comprising inorganic nanoparticles is made by solvent casting method, in which the concentration of inorganic nanoparticles in the suspension is 1 to 60 % by weight of inorganic nanoparticles, based on the total weight of the suspension.

According to another preferred embodiment of the method, the step a) of depositing the inorganic nanoparticles is made by a dry route using a powder, in which the concentration of inorganic nanoparticles is up to 100 % by weight of inorganic nanoparticles, based on the total weight of the powder.

Another object of the invention is a ceramic coated substrate obtained by the coating method of the invention. All of the characteristics and preferences indicated above for the coating method of the present invention apply to the present coated substrate obtained by the method according to the present invention. The coating is a crack-free layer with a thickness of 10 nm to 500 µm, preferably 100 nm to 100 µm, more preferably between 500 nm to 10 µm.

The present invention also relates to moving parts of an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system comprising at least one ceramic coated substrate of the invention as defined above.

Another object of the invention is the use of said moving parts of an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system according to the present invention for reducing wear and/or friction.

The present invention thus refers to a method for reducing friction and wear of moving parts of an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system according to the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the friction coefficient of a coated metal substrate according to the invention in comparison with coatings prepared using a PVD process or using a Spark Plasma Sintering with indirect electrical current flow, meaning that an electrically conductive graphite die used during the SPS process).

Figure 2 is a graph showing the wear volume after sliding friction tests performed on a coated metal substrate obtained by the claimed coating method and on coated metal substrates obtained by a PVD coating process or by a SPS process with indirect electrical current flow, meaning that an electrically conductive graphite die is used during the SPS process.

Figure 3 is a schematic drawing of the coating method according to the invention.

Figure 4a shows a 3-D microscope image on wear trace after sliding test and Figure 4b is an EDX-analysis (Energy-dispersive X-ray spectroscopy) on TiO2 after sliding test of a coating obtained by the coating method according to the invention.

Figure 5a shows a 3-D microscope image on wear trace after sliding test and Figure 5b is an EDX-analysis (Energy-dispersive X-ray spectroscopy) on TiO2 after sliding test of a coating prepared by PVD.

Figure 6a shows a 3-D microscope image on wear trace after sliding test and Figure 6b is an EDX-analysis (Energy-dispersive X-ray spectroscopy) on TiO2 after sliding test of a TiO2 coating prepared by a SPS process with indirect current flow.

Figures 7a, 7b, 7c and 7d show preferred embodiments of the coating method according to the invention using a Spark Plasma Sintering (SPS) device.

Figure 8 shows a coating method using a Spark Plasma Sintering system wherein the graphite punches (3,3) are in contact with each other, therefore forming a mold. Thus, this leads to an applied electrical current flowing mainly from electrodes through punches and only partially through sample, and thus not exclusively through the coated substrate like in the claimed invention. The coated substrate is heated through the graphite punches forming a mold around the sample to be sintered by means of heat conduction, instead of electrical sintering effects.

DETAILED DESCRIPTION OF THE INVENTION

According to the invention, the method for depositing a ceramic coating, on an electrically conductive substrate having an electrical conductivity higher than $0.5x10^6$ S/m, comprises the following steps:

a) coating an aqueous or organic suspension comprising inorganic nanoparticles on the substrate or depositing a ceramic powder comprising inorganic nanoparticles on the substrate,

b) placing the coated substrate of step a) between two electrically conductive punches (3,3) being a part of a spark plasma sintering device, and

c) joining by spark plasma sintering the inorganic nanoparticles with the substrate of step a) by applying joining pressure through the punches (3,3) to the at least one side of the coated substrate of step a) and by applying a alternating electric current through the punches (3,3) and the coated substrate of step a), wherein the two punches (3,3) are exclusively in electrical contact through the coated substrate, forcing the alternating current passing through the coated substrate,

wherein the suspension of step a) has a viscosity of 50 to 500 mPa.s, preferably 100 to 300 mPa.s measured at 25 °C, and
wherein the ceramic coating has an electrical conductivity in the range of $2x10^{-8}$ to 1 S/m, and
wherein if a suspension is used in step a), then an additional drying step before step b) is conducted to provide a coated substrate with a content in volatile components of less than 5 wt%, preferably less than 2 wt%, even more preferably less than 1 wt%, based on the total weight of the dried ceramic coating, the dried ceramic coating meaning the coating after conducting the drying step.

The viscosity of the suspension is measured using a rotating viscometer (AntonPaar Model MCR302) with plate/plate system at 25 °C.

The electrical conductivity is measured at 25 °C with a 4-point-measurement system. Two current leading needles and two sense needles are pressed on the surface of the layer. Pressure of the needle on the layer and the distance between the needles are given by the measurement system (Lukas Labs 302, SP4 head). The conductivity of the layer was measured with an electrical current of 1 A, a frequency of 10 Hz resulting in a phase of 180° (Zahner electric, potentiostat IM6ex). In case of a powder, the powder is pressed to a pellet.

The volatile components correspond to organic solvents, water and any additional additives used for the rheological and adhesive properties of the suspension (as listed below).

The process according to the present invention is able to provide ceramic coatings on electrically conductive substrates with excellent tribological properties, in particular, high wear resistance and low coefficient of friction. The challenge was even higher because both materials, namely the ceramic material and the substrate, have different thermal expansion coefficient which is the technical problem to overcome in order to get a good adhesion between the ceramic coating and the substrate.

Inorganic nanoparticles

According to the present invention, the inorganic nanoparticle (also referred as “particle” or “nanoparticle” in the present text) is a microscopic particle with at least one dimension less than 100 nm. This particle can either be of individual character or be present in an aggregated and/or agglomerated structure, in the latter the size of the primary particle is less than 100 nm at least in one dimension. The size of the aggregated / agglomerated structure can be between 50 and 600 nm (determined by scattering technologies e.g. DLS).

According to a preferred aspect of the present invention, the inorganic nanoparticle is an oxide of silicon, zirconium, cerium, titanium, aluminum, copper, calcium, magnesium, barium, iron, nickel, zinc, yttrium, boron or carbon. Preferred oxide nanoparticles are ZrO_2, CeO, TiO_2, SiO_2, Al_2O_3, CuO, CaO, MgO, BaO, Fe_2O_3, NiO, FeO, ZnO, Y_2O_3, boron oxides; B6O (boron suboxide) and mixtures thereof.

According to a preferred aspect of the present invention, the inorganic nanoparticle is selected from nitrides of boron, aluminum, chromium, tungsten, or carbon and mixtures thereof. Preferred nitride nanoparticles are hexagonal boron nitride (hBN) or cubic boron nitride (cBN).

According to another preferred aspect of the present invention, the inorganic nanoparticle is selected from carbides of silicon, aluminum, silico-oxy, tungsten, and mixtures thereof.

According to another preferred aspect of the present invention, the inorganic nanoparticle is selected from multi or single layered carbonous structures; multi or single walled nanotubes, carbon fullerenes, graphene, carbon black, graphite and mixtures thereof.

According to a preferred aspect of the present invention, the inorganic nanoparticle is a non-metal oxide. Preferred non-metal oxide nanoparticles are graphene oxide, graphite oxide and mixtures thereof.

According to a preferred aspect of the present invention, the nanoparticle is selected from mixture of above mentioned structures.

Suspension or powder comprising the inorganic nanoparticles

The suspension according to the present invention is a liquid mixture which may be either an aqueous (water-based) suspension or a non-aqueous (mostly in organic solvents) based suspension, both comprising the inorganic nanoparticles as defined above. The suspension comprising the nanoparticles has a viscosity of 50 to 500 mPa.s, preferably 100 to 300 mPa.s measured at 25°C.

Examples of organic solvents used in the non-aqueous suspensions are linear, branched or cyclic saturated, unsaturated or aromatic carbon hydrogens, such as alcohols, ethers, ketones, carbon acids, esters, nitriles, amines and amides. Preferably ethylene glycol, n-butanol, iso-propanol, n-propanol, ethanol, methanol, methyl ethyl ketone, acetone, acetylacetone, or mixtures thereof.

The suspension of the invention comprises 1 to 60 % by weight, preferably 25 % to 45 % by weight of inorganic nanoparticles in the suspension, based on the total weight of the suspension.

The rest amount of the suspension thus corresponds to water for the aqueous suspension or an organic solvent for the non-aqueous suspension.

In a preferred embodiment, the rheological property of the suspension may also be improved for the deposition step a) of the claimed process by adding additional additives, such as rheological or adhesive additives or mixtures thereof. Preferably, these additives are selected from the group consisting of silanes, functional and non-functional (meth) acrylates, polyurethanes, epoxy resins, poly (meth) acrylates, poly acrylamide, poly vinyl alcohols, poly vinyl pyrrolidone, poly alkylene glycole, poly ethylene glycole, cellulose derivatives, metal soaps, poly amides, silane-terminated polymers, or mixtures thereof. According to a preferred embodiment, water soluble hydrocolloid mucoadhesive based on poly (vinyl alcohol) is used to adjust the viscosity of the suspension for the deposition step a).

The coating process may also be conducted using a powder comprising the inorganic nanoparticles. The powder comprises up to 100 % by weight of inorganic nanoparticles, based on the total weight of the powder.

If a powder is used, then two non-conductive dies (7, 7) (see figure 7d) are used to keep the powder in place during the sintering step c) of the coating process. The non- electrically conductive dies are insulators with an electrical conductivity smaller than $1x10^{-10}$ S/m.

Substrate

The substrate for use in the present invention is an electrically conductive substrate made out of any metal, metal matrix composite, or alloy.

The electrically conductive substrate has an electrical conductivity higher than $0.5x10^{6}$ S/m measured at 25 °C. According to the invention, it is essential that the substrate is a conductor, which is made out of a material that allows the flow of an electrical current in one or more directions.

The electrical conductivity refers to the ability of a material to transmit energy. The higher the conductivity, the higher the flow of electrical current through the material.

As used herein, the metal may be selected out of the group consisting of Be, Ca, Sr, Ba, Ra, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, W.

As used herein, the term “alloy” describes a solid comprising two or more elements, preferably an alloy comprising aluminum, magnesium, lithium, silicon, titanium and zirconium and a second metal selected from the list of metals above.

A metal matrix composite is a composite material with at least two constituent parts, one being a metal, the other material may be a different metal or another material, such as a ceramic, graphite or organic compound. In a preferred embodiment, the metal matrix composite is selected from aluminum matrix reinforced with carbon nitride, steel reinforced with boron nitride, aluminum reinforced with silicone carbide.

Coating step a) of the claimed method

The coating step a) of the present coating method corresponds to the deposition of the suspension comprising inorganic nanoparticles on the electrically conductive substrate, or the deposition of a ceramic powder comprising inorganic nanoparticles on the electrically conductive substrate.

The wet route step corresponding to the coating on the substrate of a suspension comprising inorganic nanoparticles may be made following a solvent casting method such as an immersion coating method, a doctor blade method, a printing method or a spraying coating method.

In case of doctor blade method, thickness of the film is determined with blade distance to substrate (as described in A. Berni, M. Mennig, H. Schmidt: Sol-gel Technologies for Glass Producers and Users, Chapter Doctor Blade, Page 89-92).

As shown in Figure 3 (i), during coating step a) of the claimed coating method, the suspension comprising inorganic nanoparticles is deposited in the form of a layer on a substrate. As shown in Figure 3 (i), the suspension is applied on one side of the substrate. According to another preferred embodiment, the suspension may be applied on both sides of the substrate, thus leading after the spark plasma sintering to a substrate being coated on both sides.

After coating the suspension comprising inorganic nanoparticles on the electrically conductive substrate according to step a) and before proceeding with the spark plasma sintering step c), an additional drying step is conducted, in which the suspension of step a) is dried to provide an electrically conductive substrate with a dried coating having a content of less than 5 % by weight ofvolatile components, based on the total weight of the dried ceramic coating, preferably less than 2 % by weight, more preferably less than 1 % by weight. The drying step may be carried out in an oven, preferably at a temperature comprised within the range of 20 °C and 450 °C and in a drying time between 5 seconds to 40 minutes. This drying step is also illustrated in Figure 3 (ii). The dried ceramic coating means the coating after conducting the drying step.

The dry route step corresponding to the deposition of a ceramic powder comprising the inorganic nanoparticle on the substrate may be made by following methods: a dry coating method such as thermal spraying, electro spraying or a sieve process.

In case of a sieve process the thickness of the dry film is determined by the mesh of the sieve, the amount of powder applied on the sieve and the sieving time.

As shown in Figure 3 (ii) during coating step a) of the claimed coating method, the powder comprising inorganic nanoparticles is sieved in form of a layer on a conductive substrate by using a sieve with a mesh of 10 µm to 500 µm, preferably 50 µm to 100 µm. As shown in Figure 3 (ii), the powder is applied on one side of the conductive substrate. According to another preferred embodiment, the powder may be applied on the conductive substrate and the lower punch, thus leading after the spark plasma sintering to a conductive substrate being coated on both sides.

Step b) and spark plasma sintering step c) of the claimed method

In the present invention, during the spark plasma sintering step c) of the coating method, the coated electrically conductive substrate of the step a) is exposed to spark plasma sintering. The spark plasma sintering draws the inorganic nanoparticles together and offers the ability to reach nearly 100% theoretical density. The nanoparticles are then strongly bonded with each other as exemplified in Figure 3 (iii).

As exemplified in Figures 7a, 7b, 7c and 7d, the configuration of a SPS system consists of a SPS sintering device with vertical single-axis pressurization, a water-cooled vacuum chamber, and special sintering high current transformer (2) connected with two electrodes (1). The high current transformer (2) generates a defined voltage and current. The alternating current leads to efficient Joule heating. The uniaxial pressure for SPS may be applied by the top and bottom graphite punches (3) to enhance densification (maximal loads typically between 50 and 360kN). The electrically conductive substrate (4) coated with the coating (5) according to step b) of the coating method is stacked between the graphite punches (3) on the sintering stage and held between the electrodes (1). Under pressure and pulse current (6), the temperature of the coated substrate quickly rises up with a heating rate up to 1000K/min, resulting in a production of high quality sintered compact in a few minutes. The process may take place under vacuum or protective gas at atmospheric pressure. All heated parts are kept in a water-cooled chamber. Control of the processing cycle is usually done by temperature measurement (using either thermocouples or axial/radial pyrometers). Based on this temperature measurement, the electric power injected into sinter object is controlled.

Figures 7a, 7b, 7c and 7d illustrate some preferred embodiments of the Spark Plasma Sintering (SPS) step c) of the coating method according to the invention. In particular, Figure 7a shows a preferred embodiment of the coating method, wherein one side of the electrically conductive substrate is coated. Figures 7b and 7c show other preferred embodiments of the coating method, wherein the electrically conductive susbtrate is coated on both sides.

Figure 7d illustrates another preferred embodiment of the present invention, wherein a ceramic powder is sintered on an electrically conductive substrate. In order to keep in place the ceramic powder before the sintering step c), two non-conductive dies (7, 7) are used to hold the powder.

The non-conductive dies (7, 7) are insulators with an electrical conductivity smaller than $1x10^{-10}$ S/m, thus forcing the electrical current to pass through the coated sample (4 and 5) with a higher conductivity than the dies (7, 7).

The current flow is dependent on the characteristics of different elements which compose the system, such as the electrically conductive substrate (4) or punches (3,3) and particularly on their electrical and thermal characteristics. The temperature distribution is closely related to the current distribution because the heat transfer is generated by the flow of current (6).

In the present invention, the sintering step c) is set up so that there is no direct physical contact between either two punches, and if dies are used to maintain the ceramic powder in place, then the two dies are made out of a non-conductive material with an electrical conductivity smaller than $1x10^{-10}$ S/m.

In contrast, as indicated in the background section above, a classic approach is to use a graphite mold for preparing the coating, in which case the electrical current flow is mostly distributed from two electrodes through the electrically conductive mold, thus passing only partially through the coated substrate. Figure 8 shows such an embodiment, wherein the current flow (6) is mostly distributed through the punches (3,3). The substrate is thus heated through the graphite punches by means of heat conduction, instead of electrical sintering effects as in the claimed process wherein the punches are not in direct physical contact with each other and no electrically conductive die is used.

The innovative idea of the investigators of the present invention is based on having chosen a combination of a coating deposition step a) with a spark plasma sintering step c) wherein the electrical alternating current is only able to flow through the coated electrically conductive substrate. It has been found that the resulting coating shows outstanding wear and friction resistance as shown below in the experimental part. The inventors of the present invention have reached the conclusion that the temperature profile which is homogeneously distributed on the coating (5) and the interface between coating (5) and electrically conductive substrate (4) allows an homogeneous heating of the sinter sample, thus improving drastically the bonding of the inorganic nanoparticles of the coating (5). Moreover, the electrical effects are enhanced, because the high-electric currents flow directly through the electrically conductive substrate/coating (as illustrated in Figures 7a, 7b, 7c or 7d), rather than through the surrounding tools (such as graphite mold or punches (3,3) of Figure 8). Indeed, Figure 8 shows a comparative coating method using a Spark Plasma Sintering system wherein the graphite punches (3,3) are in contact with each other, thus allowing an applied electrical current flowing not only from electrodes through the sample (coated substrate), but also from electrodes through punches, which form a mold around the sample. As a result of using a conductive mold or die (e.g. graphite material), the electrical current does not exclusively pass through the coated substrate. In Figure 8, the coated substrate is heated through the graphite conductive punches by means of heat conduction, instead of electrical sintering effects.

According to the claimed coating method of the invention, the current used for the SPS coating step is a pulsed or non-pulsed alternating current (AC). The pulsed or non-pulsed alternating electric current has an intensity of 1 A to 500 A, preferably of 10 A to 100 A, more preferably of 30 A to 70 A. According to the present method, it is essential that the electrical current is of alternative nature. Both alternating current (AC) and direct current (DC) describe types of current flow in a circuit. In direct current (DC), the electric charge (current) only flows in one direction. On the other hand, electric charge in alternating current (AC) changes direction periodically. The voltage in AC circuits also periodically reverses because the current changes direction. The AC current avoids a separation of ions/molecules because the charged particles (ions/molecules) are moving backwards and forwards and stay nearly in their initial position. Using a DC current means the ions/molecules are moving to one electrode and a separation occurs. This means that the sintered material is not homogeneous anymore, which probably leads to a poorer quality of the resulting coating.

The joining pressure applied by the two punches (3,3) of the spark plasma sintering device is of 1 MPa to 200 MPa, preferably of 10 MPa to 150 MPa, more preferably between 10 MPa and 50 MPa.

During the Spark Plasma Sintering process, the alternating electric current makes the temperature of the parts raise to a joining temperature of 600 °C to 1800 °C, preferably to 800 °C to 1200 °C. The coated substrate of step a) is sintered between 5 seconds to 20 minutes.

According to a particular embodiment of the coating method, after submitting the coated substrate to SPS (step c)), the coated substrate is cooled with a cooling at a rate of 80 °C / minute to 600 °C / minute.

According to a preferred embodiment of the coating method and before proceeding with the spark plasma sintering step c), the coated substrate is placed in the sintering chamber of a spark plasma sintering device according to step b), and then the sintering chamber may be pre-heated between 40 °C and 1200 °C, more preferably 300 °C to 1000 °C, before proceeding with the sintering step c). Optionally, during said pre-heating step, a joining pressure by the two punches (3,3) of the spark plasma sintering device may be applied on the coated substrate to be sintered before proceeding with step c. Preferably, the joining pressure of this pre-heating step before the SPS step c) is of 0.5 MPa to 20 MPa.

Before the SPS step c), the rising in temperature and in pressure take place in a ramp. The temperature has preferably a slope from 20 °C to 200 °C/min, more preferably from 50 °C to 100 °C/min for the rising step from the initial room temperature to the final temperature at which the SPS step c) is conducted.

Coated substrate according to the invention and uses thereof

The present invention also relates to a coated substrate obtained by the coating method according to the invention. The coated substrate has outstanding wear resistance and friction properties as shown in the experimental part. In particular, the coating obtained by the method of the present invention has a substantially uniform thickness. A coating layer having a substantially uniform thickness can be a coating layer having a thickness of 10 nm to 500 µm, preferably of 100 nm and to 100 µm, more preferably between of 500 nm to 10 µm.

The coated substrate obtained by the method of the invention has excellent tribological performance and may therefore be used in a tribological system. The tribological system corresponds to moving parts in an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system. In particular, the moving parts of an engine are for example bearings, shafts, pistons, valves, piston rings and cylinder liners. The moving parts of a gearbox are for example bearings, shafts and gears.

The invention also relates to the use of the coated substrate according to the invention in moving parts of an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system or reducing wear and/or friction.

The inventors of the present invention have come to the conclusion that the use of an electrical current passing exclusively through the coating and electrically conductive substrate to be coated, without having the two punches (3,3) being in direct physical contact with each other, is able to heat up all particles simultaneously and homogeneously with a higher heating rate than in the conventional spark plasma sintering processes using for example a mold. All atoms and ions from the particles are stimulated simultaneously by the electrical current. Besides diffusion at the interfacial as in the case of conventional sintering processes, an ion flow is also generated to build new and strong interfaces between the particles, as well as between the particle and the substrate by a chemical reaction. This does not occur when using a conductive mold (such as graphite mold or dies) because the electrical current then not only passes through the substrate to be coated, but mainly through the mold with a lower electrical resistance.

In the experimental part, it is demonstrated that the coatings on electrically conductive substrates obtained by the claimed process are crack-free coatings, similar to coatings from the prior art using

PVD coating process or standard SPS process. In addition, the coatings obtained by the claimed process have outstanding friction and wear performances, which are much better than the friction and wear performances of coatings from the prior art using PVD coating process or standard SPS process, as shown below.

EXPERIMENTAL PART

For the purpose of better illustrating the advantages and properties of the claimed coating method and coating obtained by said coating method, the invention is further illustrated in detail hereinafter with reference to examples and comparative examples, without any intention to limit the scope of the present invention.

Example 1: Coated metal substrate according to the invention

The following commercial dispersion and polymer were used as starting materials: (1) aqueous dispersion of hydrophilic fumed titanium dioxide (AERODISP® W 740X, Evonik, Germany – CAS No. (TiO_2) 13463-67-7) with a solid concentration of 39 to 41 % by weight, based on ignited material, and mean aggregate d50 of less than 100 nm; and (2) water soluble hydrocolloid mucoadhesive based on poly (vinyl alcohol) (Mowiol® 4-88, CAS no. 90002-89-5; M_w=31000 g/mol). The liquid suspension comprises titanium dioxide dispersion (1) and poly (vinyl alcohol) (2) in a weight ratio of 99:1. The liquid suspension was placed in steering mixer and homogenized for 5 minutes. The rheological behavior of the liquid suspension was determined using a rheometer. The liquid suspension has a viscosity of 300 mPa.s at a shear rate of $100s^{-1}$ at 23°C. The liquid suspension was then applied in a form of a film on one side of a steel substrate by using doctor blade with a 20 µm gap. The steel substrate coated on one side with a 20 µm TiO_2 film was then placed in an oven at 450°C for 1 min for drying. Before the drying step, the dried coated steel substrate has a content in volatile components of 60% by weight, based on the total weight of the applied suspension. After the drying step, the dried coated substrate has a content on volatile components (mainly water) of 5 wt%, based on the total weight of the dried coated substrate. The content in volatile components is measured with an IR drying balance from the company Kern GmbH (Model MLS-C). The dried coated steel substrate was then placed into a spark plasma sintering machine (SPS 515, Dr. Fritsch, Germany) between two planar graphite punches. The two graphite punches were sprayed with a thin layer of Bornitrid Spray LG-080 to avoid diffusion of graphite particles into the coated conductive substrate. The coated area was in full contact with the punch as exemplified in Figure 7a (no direct contact between the two punches and current exclusively passing through the punches and coated substrate). The sintering was conducted inertly under vacuum. The temperature was increased from 20°C to 800°C in 8 min under pre-pressure at 1MPa, and then from 800°C to 900°C in 3 min while increasing the pressure on the coated substrate to 30MPa. The temperature at 900°C was maintained for 60s under constant pressure of 30MPa. The temperature was then lowered to 150 °C over 15 min. The graphite electrodes and sintered substrate were allowed to cool down to 25°C. The resulting TiO_2 coating on substrate was compact and crack free. The coating thickness was determined by X-Ray Photoelectron Spectroscopy (XPS) based on Ti-trace. The resulting TiO_2 coating has a thickness of approximatively 1 µm.

Example 2 (comparative example): Preparation of a coated metal substrate using a PVD coating process

The TiO_2 coating per PVD process was created by commercial Alcatel SCM 601 RF-magnetron sputter unit. The adjusted targets were made out of pure titanium 99.8%. Pure oxygen gas has been used to deposit TiO_2 reactively. Target and the same steel substrate raw material as used in Example 1 were connected with a radio frequency power supply. The distance between target and steel substrate is 100 mm with an adjusted power at 750 W, and a bias voltage of 20 V. After 20 minutes of sputter etching, the oxygen reactive gas flow was increased to create a TiO_2 phase. The deposition was carried on during 15 hours. The coating thickness was also determined by X-Ray Photoelectron Spectroscopy (XPS) based on Ti-trace. The resulting TiO_2 coating has a thickness of approximatively 1.3 µm.

Example 3 (comparative example): Preparation of TiO_2 coating on metal substrate according to Spark Plasma Sintering process, in which the graphite punches are in physical contact with each other (similar to the use of electrically conductive graphite dies).

The test was replicated with the TiO2 suspension prepared in Ex. 1 on steel substrate using doctor blade with 20 µm gap. The graphite punches were modified with inner wall defining the cavity of coated substrate shape as exemplified in Figure 8. The same sintering procedure as in Example 1 was followed. The resulting TiO_2 coating on substrate was compact and crack free. The coating thickness was determined by X-Ray Photoelectron Spectroscopy (XPS) based on Ti-trace. The resulting TiO_2 coating has a thickness of approximatively 1 µm.

Example 4: Friction and wear performances of the coatings

The tribological performances of the coatings of Example 1 (according to the invention), Example 2 (comparative) and Example 3 (comparative) were tested following a standard test method with linear oscillating tribometer (SRV test) to characterize their friction and wear behaviors and their interactions with lubricants, greases, base fluids and additives.

Standard sliding friction test was conducted on a ball-on-disc SRV III test machine from Optimol AG according to the method DIN 51834. The tribosystem consists of a ball mated to the top side of the surface of a flat disk. At the start of the test a point contact is formed. The friction test was conducted with base oil Nexbase 3043, as a lubricant between sliding surfaces. Nexbase 3043 is a commercial product from Neste and is a colorless, catalytically hydroisomerized and dewaxed API Group III base oil comprising hydrogenated, highly isoparaffinic hydrocarbons. Chrome steel 100Cr6 balls (10 mm diameter) were used as the counter face material. The test parameters are described in Table 1 below.

Table 1: Protocol to measure friction and wear (SRV test parameters)

Parameters	**Value**
Load	5 N
Preheating duration	1200 s
Friction duration	3600 s
Frequency	50 Hz
Stroke	1 mm
Temperature	100°C
Lubricant Nexbase 3034	Ca. 2 ml

Figures 1 and 2 show the friction coefficient performance and wear profiles after a sliding test conducted on each TiO2 coating according to Example 1, Example 2 (comparative) and Example 3 (comparative), respectively.

As shown in Figure 1, the TiO2 coating obtained by the process of the invention surprisingly shows a lower coefficient of friction than coatings prepared by a PVD process (example 2) or by SPS with indirect current flow (Example 3).

In addition to excellent friction performance, the TiO2 coating obtained by the process of the invention has also better wear resistance properties in comparison to coatings prepared by a PVD process (example 2) or by SPS with indirect current flow (Example 3) (see Figure 2).

Example 5: Wear scar analysis after friction test

After conducting the friction and wear tests according to Example 4, an elementary chemical analysis of each coating of Examples 1, 2 and 3 after a sliding test was conducted.

Figures 4a and 4b show a 3-D microscope image on wear trace after sliding test and an EDX-analysis (Energy-dispersive X-ray spectroscopy) on TiO_2, respectively, of a coating according to the invention (example 1) after sliding test. Figures 5a and 5b show a 3-D microscope image on wear trace after sliding test and an EDX-analysis on TiO_2, respectively, of a coating per PVD (example 2) after sliding test. Figures 6a and 6b show a 3-D microscope image on wear trace after sliding test and an EDX-analysis on TiO_2, respectively, of a TiO_2 coating per SPS process with indirect current flow (example 3) after sliding test. Thus, Figures 4a and 4b, 5a and 5b, and 6a and 6b show the surface morphology, as well as the results from the elementary chemical analysis of Example 1 (inventive) and Examples 2 and 3 (comparative) after sliding test, respectively.

An EDX-analysis is conducted in the middle of wear trace area on all samples and shows elementary traces left after the sliding test. Comparing the intensity of elements on the surface shows what remains on the surface, either TiO_2-coating (peak of Ti) or just metal substrate (peaks of Fe, Mn, Ni with a weak Ti signal peak).

Figure 4b clearly shows that even after tribological test (sliding test to test the antiwear performance), a Ti signal is received from the surface of the inventive coating from the present invention (Example 1), whereas for the two comparative coatings of Example 2 or 3 the Ti signal has nearly disappeared (see Figures 5b and 6b, respectively). This is a clear proof that the coating on an electrically conductive substrate as obtained by the claimed process of the present invention has superior antifriction and antiwear properties in comparison to a PVD coating (Example 2) or a SPS coating with indirect current flow (Example 3).

Thus, the inventors of the present invention have developed a low-cost coating process, which is environmentally friendly as it does not use any toxic chemicals and which advantageously also allows to produce ceramic coatings on electrically conductive substrate with improved tribological performances.

In contrast, as shown in the comparative experimental data, this is not observed in the coatings obtained by PVD coating process or SPS standard coating process of the prior art. Indeed, the coatings made by conventional coating methods are crack free, but show weaker adhesion to the substrate at the interface as demonstrated in the friction and wear tests, as well as the EDX-analysis on TiO_2 (examples 4 and 5).

The ceramic coated substrate obtained by the process according to the present invention shows not only a lower friction coefficient, but also better wear resistance compared to state of the art coated substrates, which are very interesting properties for tribological applications, especially for reducing friction and/or wear of moving parts.

Claims

1. A method for depositing a ceramic coating on an electrically conductive substrate, characterized in that the method comprises the following steps:
   a) coating an aqueous or organic suspension comprising inorganic nanoparticles on the substrate or depositing a ceramic powder comprising inorganic nanoparticles on the substrate,
   b) placing the coated substrate of step a) between two electrically conductive punches (3,3) being a part of a spark plasma sintering device, and
   c) joining by spark plasma sintering the inorganic nanoparticles with the coated substrate of step a) by applying joining pressure through the punches (3,3) to the at least one side of the coated substrate of step a) and by applying an alternating electrical current through the punches (3,3) and the coated substrate of step a), wherein the two punches (3,3) are exclusively in electrical contact through the coated substrate, forcing the alternating electrical current passing through the coated substrate,

   wherein the electrically conductive substrate has an electrical conductivity higher than $0.5x10^6$ S/m, and
   wherein the suspension of step a) has a viscosity of 50 to 500 mPa.s, preferably 100 to 300 mPa.s measured at 25 °C, and
   wherein the ceramic coating has an electrical conductivity in the range of $2x10^{-8}$ to 1 S/m, and
   wherein if the suspension is used in step a), then an additional drying step before step b) is conducted to provide a coated substrate with a content in volatile components of less than 5 wt%, preferably less than 2 wt%, more preferably less than 1 wt%, based on the total weight of the dried ceramic coating.

2. The method according to claim 1, wherein the coating of step a) is carried out on both sides of the substrate.

3. The method according to claim 1 or 2, wherein the coated substrate of step c) is sintered between 5 seconds to 20 minutes.

4. The method according to any one of the previous claims, wherein the temperature of the sintering chamber of the spark plasma sintering device is heated between 40 and 1500 °C, more preferably between 500 and 1200 °C after step b) and before proceeding with step c).

5. The method according to any one of the previous claims, wherein the suspension of step a) comprising inorganic nanoparticles is a suspension comprising inorganic nanoparticles selected from the group consisting of metal oxide nanoparticle, metal nitride nanoparticle, metal carbide nanoparticle, non-metal oxide nanoparticle, graphite nanoparticle or mixtures thereof.

6. The method according to any one of the previous claims, wherein the ceramic powder of step a) comprising inorganic nanoparticles is a powder comprising inorganic nanoparticles selected from the group consisting of metal oxide nanoparticle, metal nitride nanoparticle, metal carbide nanoparticle, non-metal oxide nanoparticle, graphite nanoparticle or mixtures thereof.

7. A ceramic coated substrate obtained by the method as defined in any one of claims 1 to 6.

8. Moving parts of an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system comprising at least one coated substrate as defined in claim 7.

9. Use of the moving parts of an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system as defined in claim 8 for reducing wear and/or friction in an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system.

10. Method for reducing friction and/or wear of moving parts of an engine, a gearbox or pump of an automobile, a wind turbine, or a hydraulic system by using the moving parts as defined in claim 8.

Figure 1

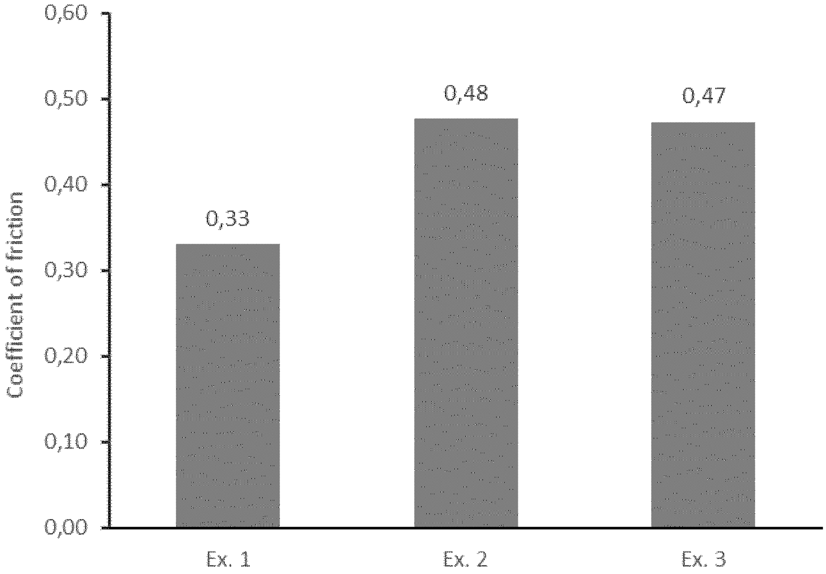


Figure 2

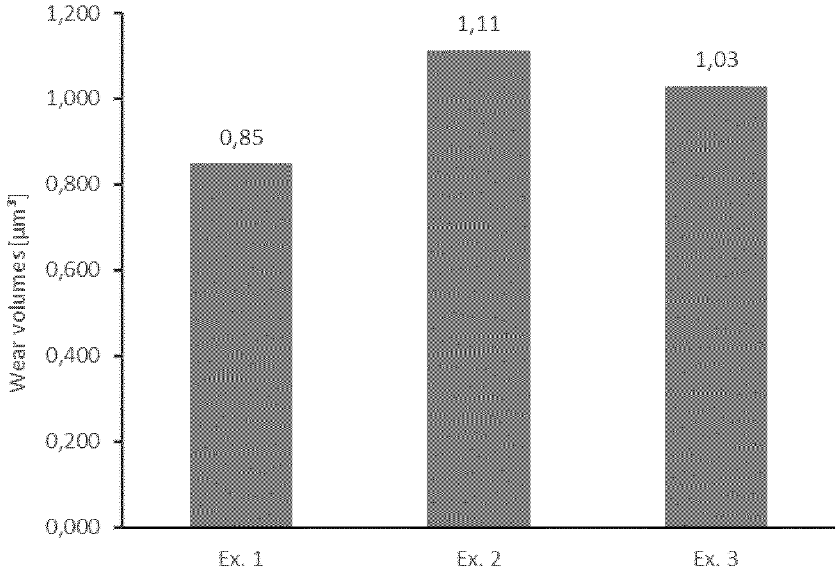


Figure 3

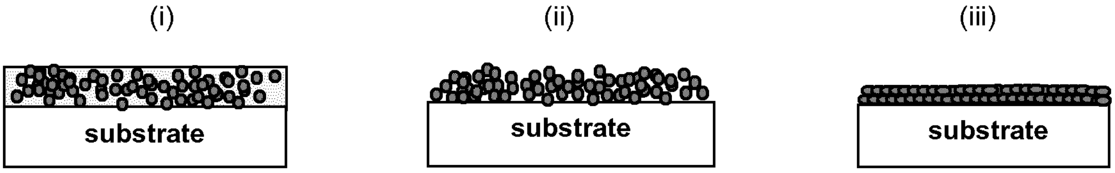


Figure 4a

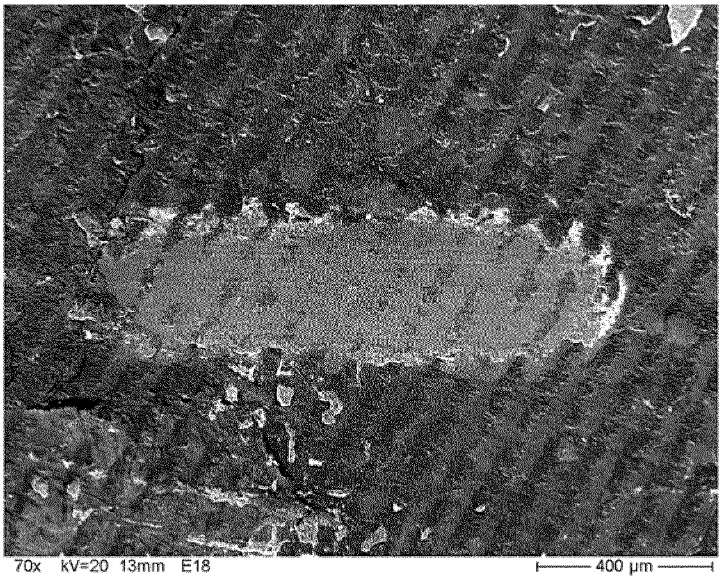


Figure 4b

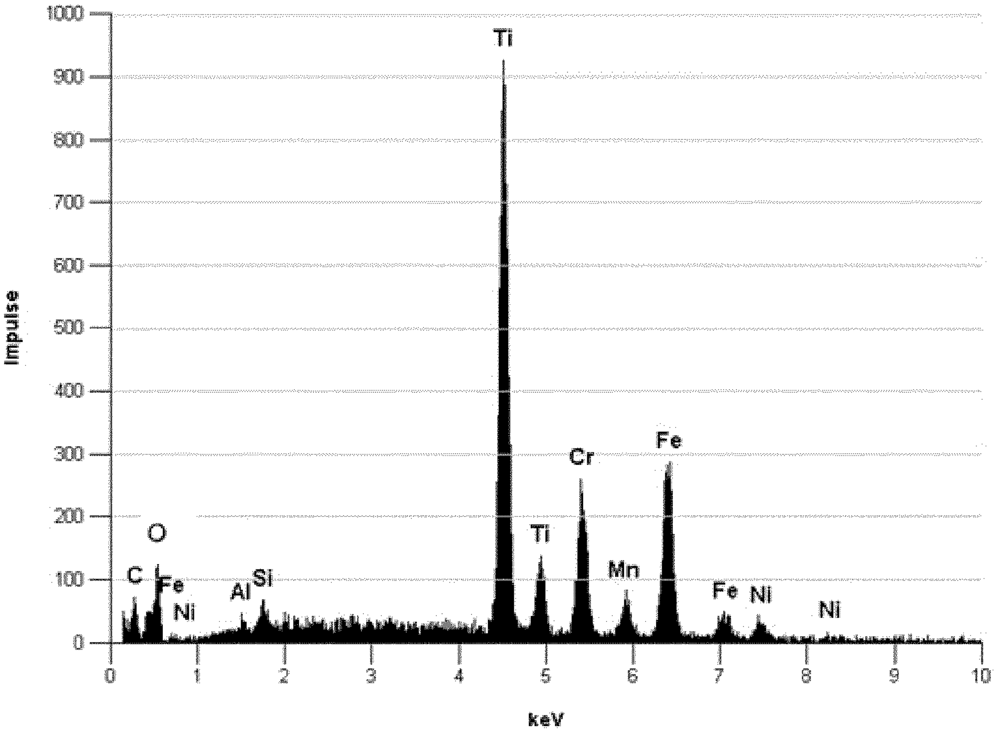


Figure 5a

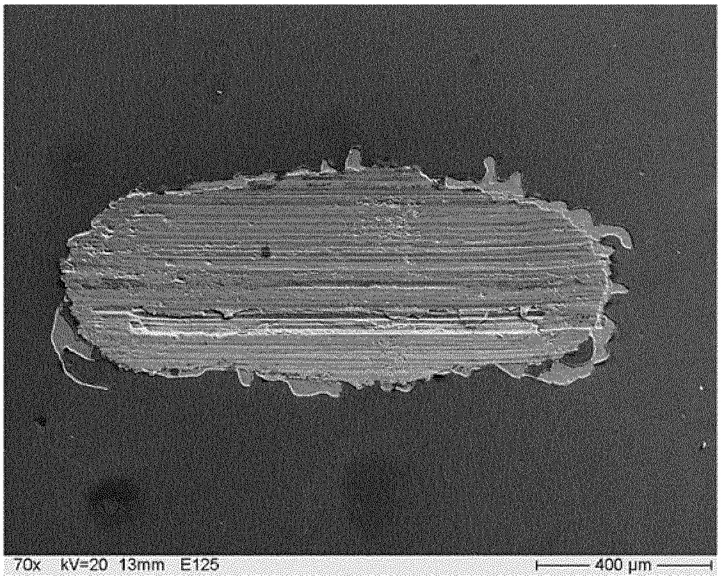


Figure 5b

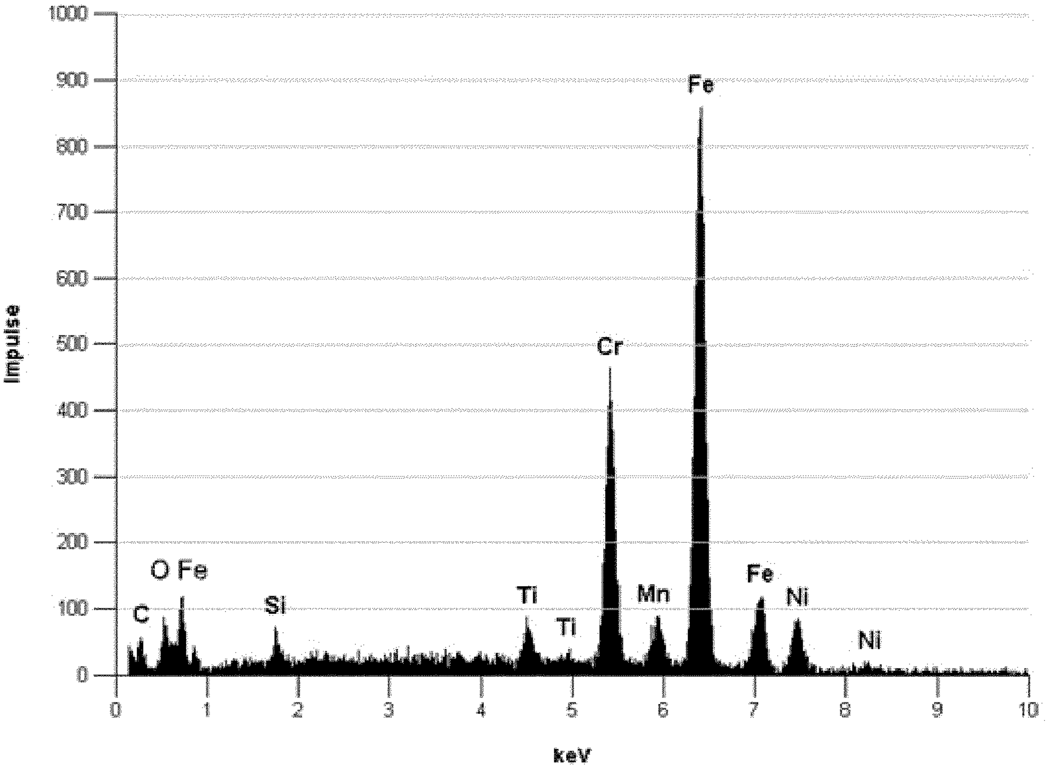


Figure 6a

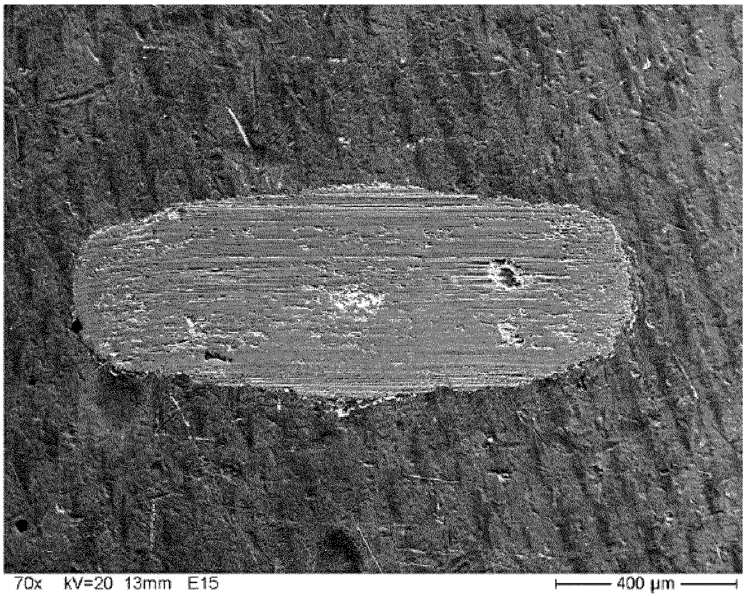


Figure 6b

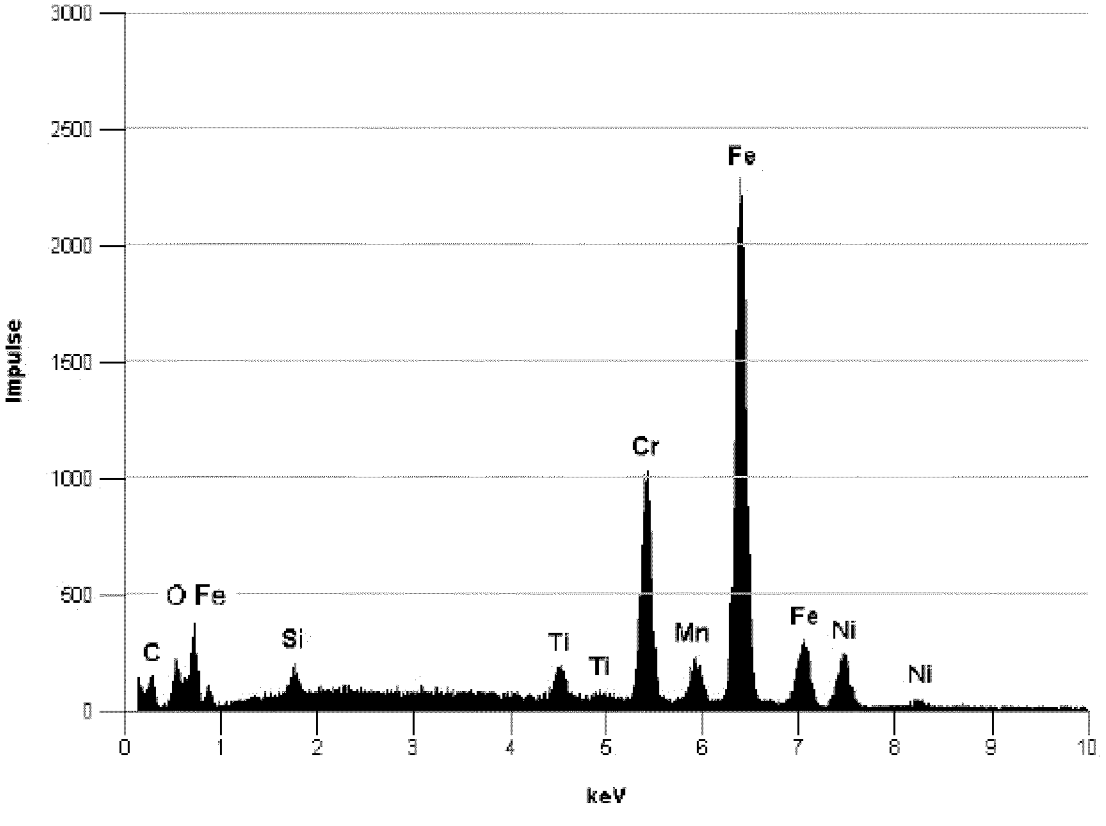


Figure 7a

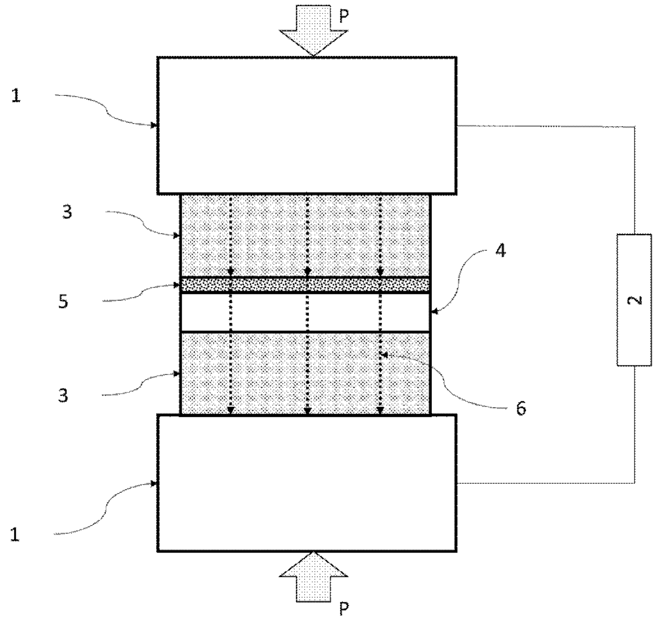


Figure 7b

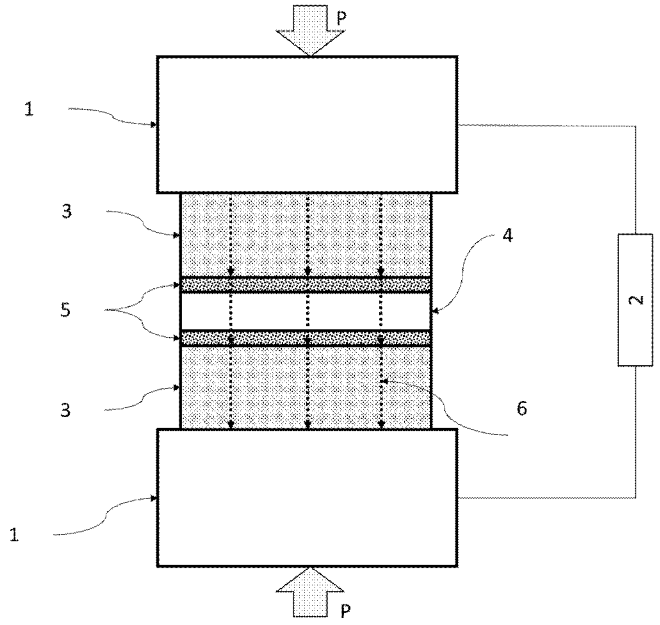


Figure 7c

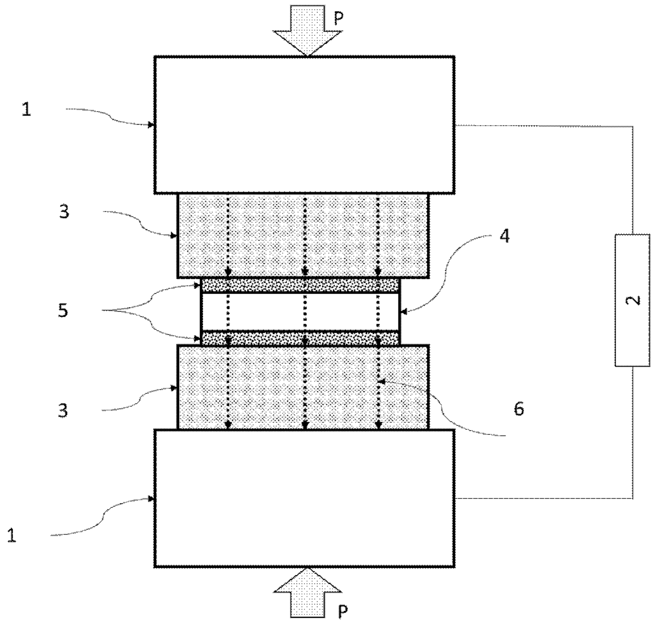


Figure 7d

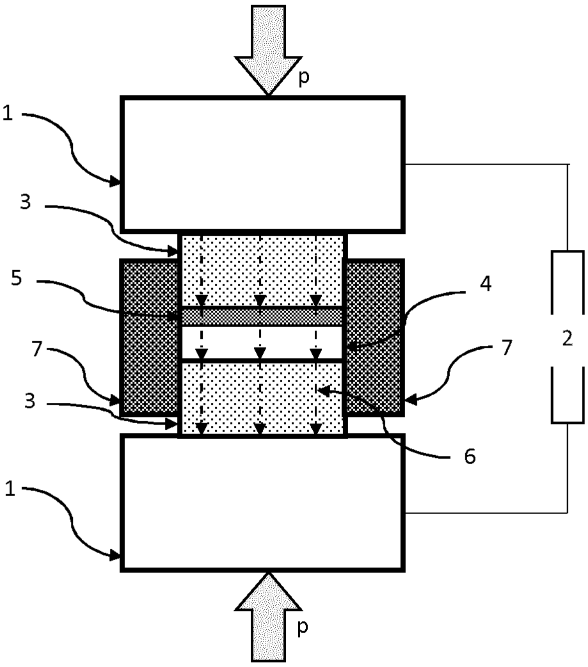
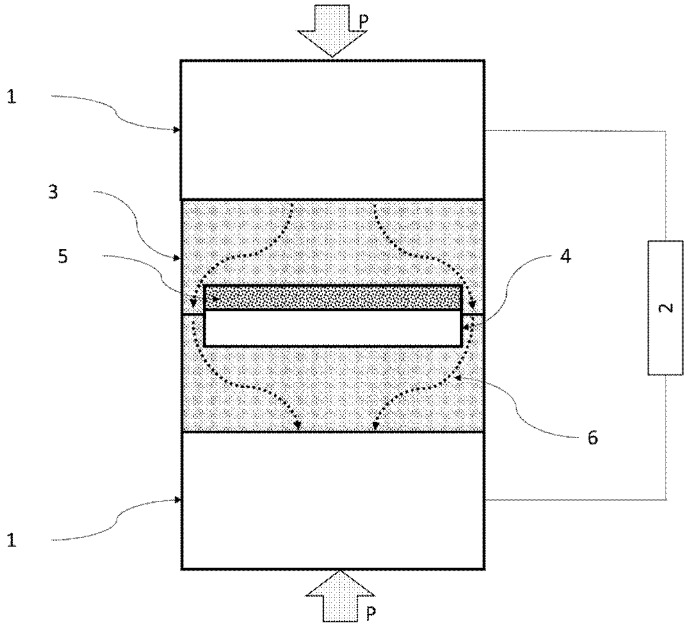


Figure 8



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/069544

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C24/08 B22F3/105
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C B22F C04B B82Y

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/004271 A1 (ALLEMAND ALEXANDRE [FR] ET AL) 2 January 2014 (2014-01-02)	7-10
A	paragraphs [0062] - [0091], [0097], [0106] - [0133], [0142], [0149], [0209] - [0231], [0241] - [0246], [0275], [0276]; claims 1-30; figure 1 -----	1-6
X	US 2006/172073 A1 (GROZA JOANNA R [US] ET AL) 3 August 2006 (2006-08-03)	7-10
A	paragraphs [0019] - [0038], [0043] - [0045]; claims 7-9; examples 1,2 -----	1-6
X	FR 2 932 496 A1 (SNECMA [FR]; TOULOUSE INST NAT POLYTECH [FR]; UNIV TOULOUSE [FR]) 18 December 2009 (2009-12-18)	7-10
A	page 4, lines 3-5 page 6, line 30 - page 8, line 19 ----- -/--	1-6

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 23 August 2017	Date of mailing of the international search report 04/09/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Tsipouridis, P

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	OLIVIER GUILLON ET AL: "Field-Assisted Sintering Technology/Spark Plasma Sintering: Mechanisms, Materials, and Technology Developments : FAST/SPS: Mechanisms, Materials, and Technology Developments", ADVANCED ENGINEERING MATERIALS., vol. 16, no. 7, 30 April 2014 (2014-04-30), pages 830-849, XP055400122, DE ISSN: 1438-1656, DOI: 10.1002/adem.201300409 Sections 1.3, 2.3 -----	1-10

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/069544

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