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(71) Applicant: **Steros GPA Innovative, S.L.**
08030 Barcelona (ES)

(72) Inventors:
• **ROA, Joan Josep**
08030 Barcelona (ES)
• **VALENCIA, Andrea**
08030 Barcelona (ES)

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(74) Representative: **Elion IP, S.L.**
Paseo Castellana, 150-4 dcha
28046 Madrid (ES)

(54) **METHODS TO INCREASE THE LIFE SPAN OF SOLID-PARTICLE BASED ELECTROLYTES**

(57) The invention tackles the degradation of polymeric resins in electrochemical surface finishing, caused by Joule's effect that forms obstructive crust-like layers. This reduces electrolyte flow and polishing efficiency. To prevent or mitigate this, the invention proposes temperature control, phase change materials (PCMs), electrolyte modifications, and process optimization. Heat dissipa-

tion techniques, such as heat exchangers, and adjustments to voltage and current density help minimize thermal effects. Additionally, mechanical recovery methods for crusted resins ensure continued efficiency. These advancements enhance resin longevity and improve electrochemical polishing performance.

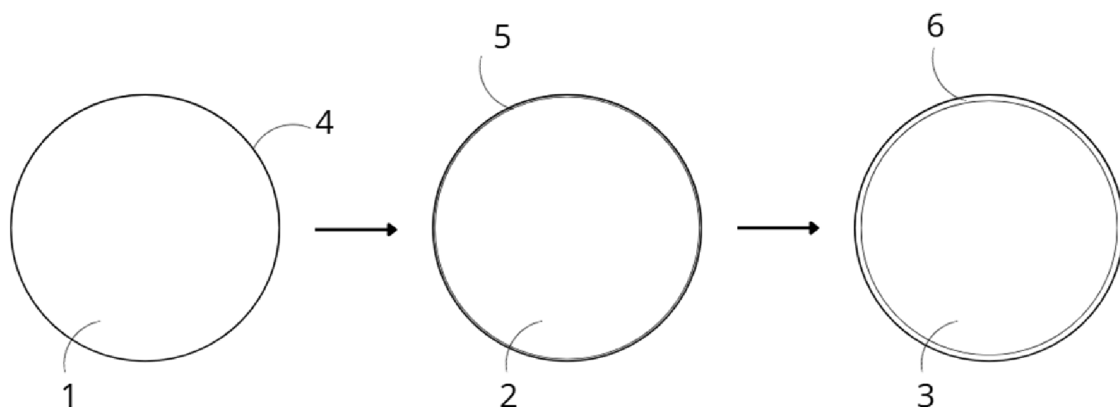


FIG. 4

Description

TECHNICAL FIELD

[0001] The present disclosure relates to the field of surface finishing, specifically to surface finishing by ion transport of conductive surfaces. In particular it relates to surface finishing through ion transport using electrolytes comprising electrically conductive solid active bodies retaining an electrolyte liquid to make them conductive and its sustained performance through time.

BACKGROUND

[0002] In some surface finishing techniques, polymeric resins are employed as the key components for polishing conductive materials; mainly metallic and/or composite materials (inorganic/inorganic materials, like for example metallic/ceramic composite and/or cermet materials), typically through electrochemical polishing or related methods.

[0003] The aforementioned polymeric resins, integral to these processes, are also described in previous advancements in the field. For instance, International Application No. PCT/ES2017/070247 (published as WO 2017/186992 A1) describes a method for smoothing and polishing metals via ion transport using electrically conductive free solid bodies. Similarly, International Application No. PCT/ES2021/070065 (published as WO 2022/123096 A1) discusses treating metallic surfaces using an electrolytic medium comprising solid particles and a non-conductive fluid.

[0004] The ion exchange resins, used in several particular embodiments of the previously described inventions, have a finite lifespan. In some cases, said ion exchange resins are composed of a copolymer of styrene-divinylbenzene with sulfonated radicals, which capture the extracted metallic ions during the surface treatment. There exists a limited value of these radicals; consequently, once all or most of the radicals are saturated, the resin's lifespan is considered to be at its end. However, there are other factors contributing to a decrease on the surface treatment performance which are unrelated to its radical's saturation by metal ions. As a consequence, it can be established that other mechanisms participate on the limited life-span of said electrolytes, decreasing the obtained initial results before reaching the theoretically estimated maximum number of absorbed ions.

[0005] The performance decrease of the resin can be influenced by several factors, including the working current density, operating temperature, voltage, relative movement or agitation, the frequency in alternate current processes, the size of the specimen to be treated and other variables.

[0006] The complex interplay of various operational parameters-such as temperature, voltage, and relative movement speed-could obscure the root causes of per-

formance decline. Without a clear understanding of the involved phenomena's, it becomes challenging to implement effective mitigation strategies to counteract the detrimental effects along the electrolyte's lifespan. Recognizing the source of the problem is crucial, as it not only aids in enhancing the longevity and efficiency of the resin but also ensures consistent and high-quality surface finishes. A systematic approach to diagnosing these degradation mechanisms can lead to significant advancements in the field, ultimately improving the reliability and effectiveness of surface finishing techniques.

SUMMARY

[0007] The present invention relates to an advanced surface finishing method, electrolyte and assembly, capable of achieving a wide range of surface modifications with a prolonged performance through its live span. It has now been observed a new mechanism affecting to the electrolytic performance which is accumulated through the life-span of the electrolyte which will be further described in detail. Several strategies will be disclosed in order to increase the life of the electrolyte related to the present degradation mechanism.

[0008] In particular a method as described herein is a method for treating a surface of a workpiece by means of ion exchange, also referred to herein as a surface finishing method.

[0009] On the context of the present invention, surface finishing may involve altering the condition of a surface, such as changes to roughness, waviness, gloss, presence of oxides, surface tension, residual stresses, coatings, heterogeneities, contaminants, or substances adhering to at least one surface of the container being treated. As a result, surface finishing may include, but is not limited to, processes such as smoothing, polishing, precision finishing, rounding, deburring, corrosion protection, electrodeposition of metallic ions, modifications in surface chemistry, surface morphology or geometry alterations, relieving residual stress, passivation, or any other alterations in corrosion resistant properties, modification of surface tension, cleaning, and sterilization of the surface.

[0010] The invention is applicable to a wide range of surfaces, including those made from materials such as stainless steel, copper, titanium, nickel, metal matrix composites and aluminum as well as their respective alloys.

[0011] During a method for treating a surface of a workpiece by means of ion exchange as described herein, typically resulting in a galvanic surface treatment, according to the present invention, a potential difference is applied between two electrodes, a cathode and an anode, with one of these serving as the workpiece to be polished.

[0012] In a method as described herein, the electrodes may be electrically coupled via a solid-particle-based electrolyte, the solid-particle-based electrolyte compris-

ing solid particles that retain a liquid electrolyte solution, thereby rendering the solid particles conductive, in particular electrically conductive. Optionally the solid-particle-based electrolyte comprises an interstitial fluid between the solid particles.

[0013] To ensure effective interaction, there must be relative motion between the workpiece and the solid particles (free solid bodies) containing the (liquid) electrolytic solution. This relative movement facilitates uniform contact and enhances the ionic exchange processes necessary for achieving a consistent surface finish. The dynamic interaction between the workpiece and the solid bodies promotes efficient material removal and ensures the polishing process is evenly distributed across the surface.

[0014] A solid particle-based electrolyte, according to some embodiments of the present invention, comprises solid particles that retain a liquid electrolyte solution, thereby rendering the solid particles conductive, in particular may be constituted by at least a set of electrically conductive free particles retaining an electrolyte to make them electrically conductive and, optionally, a medium on its interstitial environment, e.g., an interstitial fluid.

[0015] In the present disclosure, the terms "solid particles" and "free conductive solid bodies" refers to electrically conductive particles that may be composed of any non-conductive material capable of retaining liquid, such as polymeric materials, minerals, ceramics, organic or inorganic compounds, and materials of plant origin, with a preference for polymeric substances. In some embodiments, these conductive particles may include ion exchange resins, which can hold electrolytic solutions and have enough galvanic potential to react with metallic surfaces through ionic exchange. In some embodiments, the solid particles are resin particles and/or polymeric solid particles.

[0016] In some embodiments, a solid-particle based electrolyte according to the present invention refers to an electrolyte including a first plurality of solid particles retaining a liquid electrolyte making them electrically conductive, as in the International Application No. PCT/ES2017/070247 (published as WO 2017/186992 A1), introduced herein by reference in its entirety. The environment allocated on an interstitial space between the solid bodies, e.g., the interstitial fluid, can include either a gas a solid and liquid medium, or any possible combination of said mentioned aspects, as mentioned on the previously referenced application, and in combination to aspects from the introduced by reference, in its entirety, International Application No. PCT/ES2021/070864 (published as WO 2022/123096 A1), in which a moderation fluid is present on the interstitial space between the solid bodies is to be understood as any fluid, either gas, liquid, superfluid or any other possible fluid presenting a non-significant electrical conductivity of that presented by the electrically conductive solid particles, preventing them to short-circuit the system and preventing the ion for being significantly carried

out by the free solid bodies. A non-significant electrical conductivity as below 10% of the total conductivity of the solid-particle based electrolyte.

[0017] The solid particles comprised in the solid-particle-based electrolyte retain a liquid electrolyte solution, thereby rendering the solid particles conductive, in particular electrically conductive, also referred to as conductive (solid) particles, or electrically conductive (solid) particles, or free (conductive/electrically conductive) solid bodies.

[0018] In certain configurations, the liquid retained within the solid active particles is electrolytic, with its conductivity potentially enhanced by acids or other additives. However, the invention also accommodates reduced-acid or acid-free alternatives, introduced here by reference in its entirety the International Application No. PCT/ES2022/070649 (published as WO 2023/067214 A1), which details acid-free systems employing electrically conductive solid bodies for polishing composite materials. This approach mitigates environmental risks commonly associated with acid-based polishing methods, making the process safer and more accessible for facilities that avoid handling acids. Additionally, the composition of the fluid can be tailored to incorporate lubricating solids, which adjust viscosity and provide enhanced control during electropolishing. In other embodiments, the medium may consist of a gas, offering further versatility in material selection.

[0019] The interstitial space between the solid active bodies may contain a fluid (e.g., an interstitial fluid) that is preferably non-conductive and/or immiscible with the conductive solution retained by the solid bodies, or any combination of these characteristics. The interstitial fluid is moderation fluid in some embodiments. In embodiments of the present invention, the moderation fluid within the interstitial space between the solid bodies refers to any fluid whether gas, liquid, superfluid, or another type that exhibits a lower electrical conductivity than that of the electrically conductive solid particles. Other configurations or combinations of the fluid environment comprised in the interstitial space between the solid particles may be used, such as conductive liquids or miscible/immiscible liquids with the conductive solution retained by the solid bodies.

[0020] In various embodiments, the conductive particles are composed of materials such as polymers, e.g., polymeric ion-exchange resins, or other substances capable of retaining an electrolytic solution. These materials enable ionic exchange reactions with the metal surface, ensuring a consistent and efficient interaction.

[0021] In some embodiments of the invention, conductive solid particles, free conductive solid bodies, in forms like macro-/microporous or gel-like type structures, designed to optimize fluid exchange and ensure precise surface treatment are used and/or comprised. These particles can incorporate functional groups, including acidic or chelating groups, to enable targeted interactions with metal ions during polishing. For specific applica-

tions, the solid bodies may include ion-exchange resins that are cationic or anionic, strong or weak, depending on the requirements. The system is compatible with various electrolytes, such as aqueous solutions of sulfuric acid (H_2SO_4), sulfonic acids (e.g., methanesulfonic acid "MSA"), phosphoric acids (H_3PO_4), ionic liquids, deep eutectic solvents, inorganic or organic salt solutions, and other electropolishing agents, providing users with a wide range of options for preexisting liquid electrolytes.

[0022] Deep eutectic solvents (DES) according to the present invention refer to liquid compositions comprising two or more components, typically at least one hydrogen bond donor and at least one hydrogen bond acceptor, which upon mixing interact to form a eutectic system exhibiting a melting point lower than that of the individual components, such that the composition is liquid at or near room temperature. Such DES may exhibit low vapor pressure, high thermal stability, and the ability to dissolve a wide range of organic and inorganic species. Non-limiting examples of DES suitable for use herein include mixtures comprising choline chloride with urea, ethylene glycol, glycerol, or organic acids, such as oxalic acid or malonic acid, as well as mixtures comprising metal salts in combination with hydrogen bond donors.

[0023] The conductive particles, the conductive solid particles, themselves may be derived from materials such as acidic cationic resins, anion-exchange resins, or chelating resins that promote metal ion exchange. Specifically, sulfonated styrene-divinylbenzene (S-DVB) copolymers and similar substances are advantageous for their resistance to acids and oxidative conditions. These particles can also feature functional groups like sulfonic or carboxylic groups for retaining metal ions or chelating groups for selective interactions with transition metals.

[0024] Solid particles that retain a liquid electrolyte solution of a particle-based electrolyte comprising as described herein, may lose efficiency over time after being subjected to potential differences, such as in ion exchange methods as described herein, thereby reducing the lifespan of the solid-particle-based electrolyte.

[0025] In particular, the use of solid-particle-based electrolyte under working conditions for ion exchange methods as described herein may result in particles with a blocking crust layer on a surface thereof, which may be regarded as a way of degradation of the particles. In particular, in the present disclosure a specific cause of degradation in polymeric ion-exchange resins used for solid-particle based electrolytes have been identified. It relies on the formation of surface crusts ranging from several nanometers to hundreds of them depending the operational time on the outer layers of the resin particles, obstructing the interconnectivity of the porosity of the solid bodies and thereby preventing them for working according to the method. This crust significantly hinders the transport of ions through the resin, thereby impairing the flow of electrolytic solutions and negatively impacting the performance and efficiency of polishing processes.

[0026] In addition to identifying this critical issue, the invention also addresses the mitigation of the effects of degradation by proposing solutions to prevent or reduce the formation of these crusts. By tackling both the root cause and its consequences, this invention aims to enhance the overall functionality and longevity of polymeric resins in polishing applications.

[0027] In particular, ion exchange methods as described herein comprise at least one of inhibiting, delaying and restoring particles with a blocking crust layer on a surface thereof. Whereby the formation of such crusts in the solid particles of the solid-based-electrolyte is inhibited, delayed or even if such crusts are formed on the particles, the particles are restored, e.g., fully restored or partially restored. Thereby, the reduction in lifespan of the solid-particle-based electrolyte may be mitigated.

[0028] The solid particles, e.g., ion exchange resins, may be susceptible to degradation due to the heat generated (also known as Joule's effect) induced during the surface treatment, e.g., polishing, process. This heat causes the formation of a non-porous and non-interconnected layer stiffer than the virgin or the core of the solid active particles, e.g., of the resin. This layer prevents the retained electrolyte to be properly shuttled from the interior to the exterior of the active solid particle, which is an essential step to carry out the desired performance through the live span of electrolytes according to the present invention, and thereby achieving optimal, replicable and constant surface treating, e.g., polishing, results.

[0029] Building upon these contributions, while the efficiency from the technologies comprised within have been enhanced, its sustained performance through its life-span remain unresolved. The present invention contributes on the optimization of the sustained performance along the lifespan of the solid-particle-based electrofinishing technology, in particular aiming to one critical issue which corresponds to the thermal degradation of the free solid particles under service-like working conditions. Over time, these particles undergo significant microstructural, physical and chemical transformations due to operating conditions, such as the mentioned elevated local temperatures and its prolonged exposure trough, as can be observed from Figure 1.

[0030] The formation of the crust can be triggered by different phenomena. In some cases, the high current densities present in some embodiments of the invention, present a localized Joule effect, focusing the heating of a small area of the particles, reaching local temperatures above the degradation temperatures of the used polymer and generating the formation of the mentioned crust. In some other embodiments of the invention, upon generating a relative movement between the surface to be treated and the electrically conductive free solid bodies, friction forces arises and a global heating of the electrolytic medium results, which may be sufficiently high to reach the threshold for the formation of a crust.

[0031] This ongoing challenge creates a pressing need

in the field for a solution that either delays or mitigates the formation of this crust layer, or alternatively, decreases or eliminates its effects.

[0032] This degradation, consisting on a crust-layer on the surface of the spheres, which reduces the pore density near the surface reducing the interconnectivity and leaves only small gaps on the surface. These gaps do not allow a full passage of the electrolytic solution and hinder the transport of metallic ions. This layer can be formed by different factors, such as due to the Joule's effect experienced by the particles when it is in contact with the workpiece to be post-processed, wherein the electrical energy passing through a conductor is transformed into thermal energy, or because of a temperature increase resulting from friction forces.

[0033] Different strategies are comprised within the present invention to extend the useful life of particles. Some of them focus on controlling, e.g., reducing, the operating temperature during the surface treating, e.g., surface finishing, process through different means.

[0034] In some embodiments, inhibiting, delaying and restoring particles with a blocking crust layer on a surface thereof comprise(s) controlling the temperature of the method, e.g., by ensuring that the solid-particle-based electrolyte is maintained at a temperature within a specific range. In some embodiments, the temperature of the method, also referred to as operating temperature or working temperature, may be from 5 °C to 60 °C, in particular from 20 °C to 40 °C.

[0035] Controlling the temperature at which the method is carried out may be performed by means of a heat exchanger. For instance, the method may be carried out by providing the relative motion between the solid particles and the surface of the workpiece within a recipient, which is provided with a heat exchanger that ensures a specific working temperature and maintaining the particles at said working temperature.

[0036] Accordingly, in some embodiments, a method as described herein further comprises controlling the temperature during the surface treatment, preferably by means of a heat exchanger.

[0037] In some embodiments, a method as described herein further comprises the integration of a heat exchanger to control the temperature of the system during the electropolishing process. In particular, apparatus used in methods as described herein may comprise or integrate a heat exchanger for temperature control.

[0038] While lowering the working temperature may not eliminate the aforementioned effects, it can advantageously prolong the system's lifespan by slowing the formation of an obstructive surface layer (e.g. such as the blocking rust layer as described above). This allows for more efficient operation over a longer period before affecting the integrity of the conductive particles, decreasing its performance or efficiency. Additionally, by controlling the working temperature, the chemical conditions of the system remain stable, minimizing the impact of other variables which contribute to a life-span

reduction.

[0039] Methods according to some embodiments, include alterations in the composition of the electrolyte, the solid-particle based electrolyte, the use of external elements, changes in certain polishing parameters, or/and modifications to the structure of the particles.

[0040] In certain embodiments, the formation of the degraded layer can be further delayed by optimizing the polishing parameters (e.g., voltage, current density, time-pulses, agitation) known in the art, particularly by incorporating longer pause times. These pauses are introduced through duty cycles in the voltage supply, preventing the system from being continuously engaged in the electrochemical process. By intermittently interrupting the voltage application, the system is given time to release and dissipate heat, minimizing localized thermal accumulation. This controlled dissipation helps prevent excessive temperature buildup, which could otherwise accelerate the degradation of the electrolyte resin.

[0041] When the system operates continuously, electrical current flowing through the electrolyte and solid particles generates heat due to the Joule effect. To mitigate this, additional process parameters can be adjusted. For example, reducing the applied voltage or current density lowers the electrical energy converted into heat, thereby decreasing overall thermal stress on the system.

[0042] Accordingly, in some embodiments, methods as described herein comprise modifying one or more operational parameters, selected from:

a) increasing duty cycles ratio within the electropolishing cycles, in particular to a duty cycles ratio from 10 % to 1000 %, in particular between 50 % and 200 %.

b) reducing the voltage applied between the electrodes, in a voltage reduction from the original value to 10 % to 50 % of the original value, that is to say, reducing the voltage by 50 % to 90 %; and

c) lowering the current density, e.g., lowering the current density flowing through the electrodes, in particular to a current density reduction from the original value to 10 to 50 % of the original value, that is to say, reducing the current density by 50 % to 90 %.

[0043] By modifying one, some or all of said operational parameters, the reduction in lifespan of the solid-particle-based electrolyte may also be mitigated, in particular, as these measures may also advantageously contribute to inhibiting, delaying and restoring particles with a blocking crust layer on a surface thereof.

[0044] Furthermore, by carefully controlling both duty cycles and electrical parameters, a balance can be achieved between efficient polishing performance and thermal management. Lowering the intensity of the elec-

tric current, combined with strategic pauses, allows for better heat distribution and dissipation throughout the system. This approach reduces the thermal load on the particles, preventing localized overheating and contributing to the extended lifespan and sustained performance of the electrolyte resin.

[0045] An aspect of the present invention involves incorporating Phase Change Materials (PCMs) into a solid-particle-based electrolyte. In the context of this invention, a PCM refers to any material capable of storing and releasing thermal energy during a phase transition.

[0046] A PCM may thus contribute to at least one of inhibiting, delaying and restoring particles with a blocking crust layer on a surface thereof. Thereby the use of a PMC in methods described herein also advantageously mitigates the reduction in lifespan of the solid-particle-based electrolyte.

[0047] Accordingly, methods as described herein include, in some embodiments, the use of a phase change material (PCM) within the solid-particle-based electrolyte, in particular to regulate temperature fluctuations and thereby delay the lifespan reduction of the electrolyte.

[0048] In some embodiments, the solid-particle-based electrolyte comprises the interstitial fluid between the solid particles and the PCM is included within the interstitial fluid PCM.

[0049] The PCM may be organic, inorganic or a mixture. For instance, the PCM may be selected from organic materials, inorganic materials, or a mixture of organic and inorganic materials.

[0050] In some embodiments, a PCM is selected from paraffins, fatty acids, glycols, eutectic mixtures. Eutectic mixtures, i.e. mixtures of two or more compounds at a specific composition that melt and solidify at a single, reduced temperature compared to the individual components, thereby providing a well-defined and tunable phase change temperature.

[0051] In some embodiments, the PCM comprises ethylene glycol, and in particular the PCM comprises polyethylene glycol (PEG). Ethylene glycol, and in particular PEG, may be preferably present in an amount between 10 and 15 wt. %. with respect to the solid particles, also referred to as solid bodies, of the solid-particle-based electrolyte.

[0052] In embodiments of methods as described herein, the PCM is included, e.g., in the solid-based-electrolyte, in its free form and/or in its encapsulated form, as also described in more detail below.

[0053] The PCM can initially exist in a solid, liquid, or gaseous state and transition to another phase during the process.

[0054] In certain embodiments, the phase change occurs between solid and liquid states at a constant or nearly constant temperature. The system is maintained within a controlled temperature range by utilizing one or more PCMs with either high endothermic or exothermic enthalpy. When a temperature variation occurs within the polishing medium, the PCM undergoes a phase transi-

tion, absorbing or releasing thermal energy corresponding to its enthalpy of phase change. This mechanism enables effective temperature regulation during the process.

[0055] Specifically, in some embodiments, the PCM absorbs a substantial amount of heat as it transitions from solid to liquid, thereby stabilizing the system's temperature. This heat absorption mitigates temperature spikes at the surface of the particles, which result from the Joule effect. By doing so, the PCM helps to reduce the formation and growth of the crust-layer on the surface of the ion exchange resin, ultimately extending the electrolyte resin's lifetime and enhancing ionic exchange efficiency.

[0056] Additionally, in some embodiments, a combination of PCMs with different phase transition temperatures is used to maintain precise control over a broader temperature range. By selecting PCMs that undergo phase transitions at different temperatures, the system can progressively absorb or release thermal energy, ensuring smooth thermal regulation throughout the process. This staged approach prevents abrupt temperature fluctuations that could otherwise impact the performance of the electrolyte resin and the overall efficiency of the ionic exchange process.

[0057] Furthermore, the selection of PCMs with varying enthalpies allows for tailored thermal management, depending on the specific energy absorption or release requirements. Materials with higher enthalpy values can absorb more heat, making them ideal for processes that generate significant thermal peaks, while lower enthalpy PCMs can be used for finer temperature adjustments, preventing excessive cooling or overheating.

[0058] In another configuration, both endothermic and exothermic PCMs are incorporated to regulate temperature not only during heating but also during cooling phases. Endothermic PCMs absorb heat when the temperature rises, preventing overheating, whereas exothermic PCMs release stored heat when the temperature drops, ensuring that the resin remains within optimal operating conditions. This bidirectional thermal regulation safeguards the integrity of the resin, preventing degradation due to excessive heat while also maintaining proper working conditions during cooling cycles.

[0059] Combinations of these strategies can also be implemented to achieve even more precise thermal control. For example, a system may incorporate multiple PCMs with different phase transition temperatures and enthalpy values, along with both endothermic and exothermic properties. This configuration enables highly adaptable thermal management, dynamically responding to both heating and cooling fluctuations to optimize the efficiency of the ionic exchange process while prolonging the lifetime of the electrolyte resin.

[0060] In particular embodiments, depending on the process parameters and surface finishing conditions, a PCM with a high fusion enthalpy is required, as greater energy absorption enhances its efficiency in stabilizing the temperature.

[0061] Additionally, in particular embodiments where, the PCM can operate within a temperature range aligned with the desired operational point to maintain its liquid state while preventing premature solidification during ongoing operations to avoid reiterative solidification cycles that could alter the rheology of the electrolyte. While many PCMs can endure numerous fusion and solidification cycles without performance loss, in some cases, component separation may eventually reduce thermal storage capacity over time.

[0062] In some embodiments, the formation of an obstructive surface layer, e.g., on a surface of the solid particles, has been observed to be an irreversible process. Once established, in some instances, this layer cannot be removed, significantly impacting the performance of the electrolyte resin. During its formation, which is driven by the Joule's effect, small cracks may also develop in some cases. These cracks often result from differential thermal expansion within the resin, caused by temperature variations during the polishing cycle. However, despite their presence, they do not facilitate water penetration. Due to water's high surface tension, a significant increase in pressure would be required to force it through these cracks. In contrast, acidic solutions, which have lower surface tension and a higher affinity for sulfonated chains, are more readily absorbed, reaching the interior of the resin.

[0063] In some embodiments, a method as described herein incorporating means or methods to inhibit, delay or restore particles presenting a blocking crust layer on their surface, e.g., formed during working conditions as described above, comprises adding substances such as acids to the system. Thereby, penetration through the fissures of the blocking surface layer formed on the solid particles, in particular resin particles, may be achieved and thereby their ionic exchange capacity may be restored.

[0064] Accordingly, in some embodiments, a method as described herein comprises adding substances such as acids to the system, preferably to the solid-particle-based electrolyte.

[0065] In particular, a method as described herein may comprise adding substances such as an acid, e.g., in the form of an acidic solution such as an aqueous acid solution, to the solid-particle-based electrolyte, more in particular within the solid particles and/or to the interstitial fluid present between the solid particles of the solid-particle-based electrolyte. In some embodiments, the acid added to the solid-particles-based electrolyte may be the same or different to any acid present in the liquid electrolyte solution retained by the solid particles. To address the issue of obstructive layer formation and extend the usability of the resin particles, a possible solution involves mechanically crushing the particles once the layer has been developed. This crushing process increases the exposed specific surface area that remains unaffected by the obstructive layer, allowing for more effective interaction with the electrolyte solution. By

enhancing the available reactive surface, this method partially restores the functionality of the resin particles, enabling them to continue participating in the ionic exchange process and prolonging their operational lifespan. Accordingly, in some embodiments, previously used resin particles are reused by altering their spherical structure, such as by breaking them, e.g., by crushing, to increase the effective surface area not covered by the blocking surface layer, enhancing their efficiency in subsequent electropolishing processes.

[0066] In some embodiments, in a method as described herein the solid particles of the solid-particle-based electrolyte are previously used resin particles comprising a blocking surface layer, which are reutilized by altering their spherical structure, such as by breaking them, e.g., by crushing, to increase the effective surface area not covered by the blocking surface layer, enhancing their efficiency in subsequent electropolishing processes.

[0067] In some embodiments, in methods as described herein particles comprising blocking surface layers are obtained as a consequence of their use in the methods, even if their presence has been inhibited, reduced or restored, and such particles may be subsequently reutilized by altering their spherical structure, as described above, in the same methods or in subsequent surface treatment methods.

[0068] Experimental evidence has been found linking the thermal degradation of solid-particle-based electrolytes to mechanical property evolution of the polymeric particles. Nanoindentation testing performed on the solid bodies over their operational lifespan demonstrates a progressive increase in elastic modulus, indicative of surface hardening caused by thermally induced structural modifications. This hardening correlates with the formation of a blocking crust layer, which impairs ionic exchange efficiency during electrochemical surface treatment.

[0069] A direct correlation between the thickness of the thermally affected surface layer and the measured elastic modulus of the particles can be established. As operating time increases, localized Joule heating promotes polymer densification and crosslinking near the particle surface, resulting in increased stiffness and reduced permeability. By controlling temperature through the use of phase change materials, heat exchangers, and optimized electrical parameters, the progression of this thermally affected layer is delayed, thereby extending the functional lifespan of the solid-particle-based electrolyte.

[0070] In some embodiments, methods as described herein further comprise the addition of molecules or elements with high specific heat capacity to the solid-particle-based electrolyte or the interstitial fluid present between the solid particles of the solid-particle-based electrolyte. Thereby the general or localized temperature within the electropolishing system may be reduced. In particular, such molecules or elements with high specific heat capacity may be selected from polyols, alcohols,

water, glycols, and mixtures thereof, more in particular from ethylene glycol, diethylene glycol, propylene glycol, glycerol, polyethylene glycol (PEG), and combinations thereof.

[0071] Advantageously, polymeric particles which have reached the end of their useful life for ion-exchange-based electropolishing retain value due to their hardened surface properties. These thermally altered particles exhibit enhanced abrasive behavior and can be repurposed for hybrid galvano-mechanical surface treatments. Such reuse contributes to improved material efficiency, reduced waste, and expanded functional applicability of the solid particles beyond their original electrochemical role.

[0072] Accordingly, in some embodiments in methods as described herein particles comprising blocking surface layers are obtained as a consequence of their use in the methods, even if their presence has been inhibited, reduced or restored, which particles (which may also be referred to thermally altered particles) may be subsequently reutilized, e.g., to benefit from their hardened surface properties in the same method or in subsequent surface treatment methods.

[0073] In particular, in some embodiments, a method as described herein further comprises reusing solid particles, in particular polymeric solid particles, that have undergone thermal surface hardening during electrochemical surface treatment, wherein said particles exhibit increased surface stiffness and abrasive behavior as a result of a thermally induced surface alteration produced under galvanic working conditions, and wherein the re-used particles are employed in a hybrid galvano-mechanical surface treatment combining electrochemical action with mechanical abrasion.

BRIEF DESCRIPTION OF THE DRAWINGS

[0074] To complete the description and to provide for a better understanding of the disclosure, a set of drawings is provided. Said drawings form an integral part of the description and illustrate embodiments of the disclosure, which should not be interpreted as restricting the scope of the disclosure, but just as examples of how the disclosure can be carried out. The drawings comprise the following figures:

Figure 1: Cross section micrographs done by Focused Ion Beam/Scanning Electron Microscopy (FIB/SEM) as a function of the dry-electropolishing time: (a) virgin sample; (b); (c) and (d) after being used for 20, 60 and 100 hours, respectively.

Figure 2. Thermogravimetric Analysis (TGA) evolution for a virgin and degraded solid body based on PST-DVB

Figure 3: Differential Scanning Calorimetry (DSC) evolution for the ionic exchange resin with different

PCM content, from 0 (acting as a reference) to 10 wt.% of PCM.

Figure 4: Illustrative example of the formation of the crust blocking layer in different states of use.

Figure 5: Detailed image of the pore distribution on the surface of the resin, showing a CH densified zone (7), a blocking layer (8) and pores (9).

Figure 6: Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) evolution near the surface for the C-H molecules as a function of the dry-electropolishing time.

Figures 7A and 7B: Sulfur evolution for a degraded particle; after 20 hours (Fig. 7A) and after 100 hours (Fig. 7B).

Figures 8A, 8B, 8C, 8D: Nanoindentation load-displacement curves obtained from the surface of the solid polymeric particles after different operating times: 0h (Fig 8A), 20 h (Fig 8B), 60 h (Fig 8C), 100 h (Fig 8D).

Figure 9: Linear correlation between the thickness of the thermally affected surface layer of the polymeric particles and the corresponding elastic modulus measured by nanoindentation

DETAILED DESCRIPTION

[0075] As previously introduced, one of the most important issues for the life-span reduction of solid-particle-based electrolytes is the formation of a non-porous layer, also referred in the present disclosure as crust-like layer, on the outer surface of the resin particles. This crust is primarily caused by Joule heating effect, a phenomenon resulting from electrical currents generating localized high temperatures. The heat induces local degradation, also known as pyrolytic effect, which involves the thermal decomposition of organic material in the absence of oxygen or under limited oxygen availability. Specifically, pyrolytic effects decompose oxygen-rich groups within the polymer, in some cases, leading to the accumulation of hydrogen (-OH) and oxygen-containing species on the surface of the resin.

[0076] Figure 4 shows the process of formation of the defect mentioned in this disclosure, which involves the creation of a blocking layer or crust on the surface of the resin particles used, caused by the Joule effect they undergo during the electropolishing process. In particular, Figure 4 shows a new particle (1), a particle with approximately 20 hours of use (2), a particle with approximately 100 hours of use (3), an initial particle surface (4) on (1), an initial formation of the crust layer (5) on (2) and a formed crust layer (6) on (3).

[0077] Initially, the resin particle (1) does not show any

visible surface layer (4). The entire surface has a homogeneous composition. Later, after approximately 20 hours of polishing (2), the beginning of a blocking layer (5) can be observed, accompanied by a decrease in polishing performance. At this point, the blocking layer that forms are between 100 and 500 nanometers thick, more specifically, between 200 and 300 nanometers.

[0078] Figure 1 shows the formation of the insulating layer that develops on the surface of the particles. The different images a, b, c, and d, are cross-sectional images of the particle taken with a FIB/SEM.

[0079] In Figure 1.a), the surface of the particle is shown in detail without any polishing process having been performed. Here, a uniform distribution of pores is observed on the superficial edge. In contrast, in Figure 1.b), after 20 hours of polishing, a decrease in the percentage of pores in that area is noted. These pores have collapsed due to the heat generated by the Joule's effect. At 20 hours, this layer has a depth of between 200 and 300 nanometers. In Figures 1.c) and 1.d), the growth of the blocking layer, also called a crust, is observed at 60 and 100 hours, respectively. After 100 hours of dry-electropolishing process, the depth of the layer is between 500 and 1,000 nanometers. As the layer becomes thicker lower ion-exchange rate can be achieved.

[0080] Thermal degradation affects the structural integrity of the resin particles as well. While the core of the particles retains a uniform and functional pore distribution, the outer layers exhibit a nonuniform structure with a low density of non-interconnected pores as represented in Figure 1. This discrepancy is further exacerbated over time as the crust layer thickens, impeding the flow of the electrolytic solution and reducing the overall performance of the particles.

[0081] A test has been conducted using macroporous solid bodies to observe the effect of subjecting them to thermal fatigue generating some heterogeneous cracks distributed along the particle. Different cycles of one and a half hours were performed, where the initial temperature was ambient and then increased due to the Joule's effect, reaching temperatures of up to 80°C. After 20 hours, a blocking layer between 200 and 300 nanometers thick could be observed (see Figure 1b). After 100 hours of operation, the blocking layer reached a thickness ranging between 500 to 1,000 nanometers, greatly reducing the permeability of the particles. In this state, the resin could no longer absorb the electrolytic solution uniformly, as absorption was restricted to the cracks in the crust. These cracks further hindered the effective absorption of the electrolytic solution.

[0082] The formation of the crust layer and the associated chemical changes are irreversible under known typical electropolishing conditions. Attempts to mitigate these effects, such as increasing the acid concentration in the electrolytic medium, in some cases even worsen the situation. Higher acid concentrations elevate the operating temperature, intensifying the Joule's heating and accelerating the crust formation. What is more, with

acid concentrations exceeding 50 wt. %, the pores collapse. This phenomenon occurs because higher acid levels lead to the degradation of the polymer, as the sulfonated solid resins degrades through a dissolution process and therefore the pores collapse.

[0083] This effect is to be potentially confused with fouling, which refers to the accumulation of unwanted material obstructing the pores present on the surface of the particles, often in the form of a crust or layer. However, fouling is caused by the accumulation of foreign particles or substances. In contrast the elemental analysis of surfaces presenting the blocking crust layer revealed that sodium (Na) was absent, suggesting that the formation of the crust is not due to a common fouling mechanism typically associated with sodium buildup. Instead, the degradation observed in the resin is the result of pyrolytic effects induced by Joule heating, which leads to the formation of a crust enriched with hydrogen and oxygen groups (-OH).

[0084] Elemental analysis has revealed the composition of the crust layer formed on the resin particles. Techniques such as Energy Dispersive X-ray Spectroscopy (EDX) and ToF-SIMS have been employed to investigate the concentration and distribution of elements in the non-porous layer as well as at the interface between this layer and the non-degraded region as a function of the dry-electropolishing time.

[0085] The analysis reveals a homogeneous distribution of sulfur in the inner part of the resin particles, while in the non-porous region, the content of sulfur tends to zero, see Figure 7 (region delimited with the white arrows). This highlights that the local temperature reached is higher than 250-300°C in agreement with the TGA conducted on these particles, see Figure 2. In this sense, the local heat induced through the Joule's effect produces a local evaporation of the active acid media present in the contact point region.

[0086] Furthermore, both EDX and ToF-SIMS detect potassium, which is also evenly distributed across the sections of the resin spheres. However, the crust layer shows an accumulation of oxygen and hydrogen groups (-OH), consistent with pyrolytic decomposition and thermal effects during electropolishing.

[0087] As a result, the outer surface of the particles becomes impermeable, significantly reducing their capacity to absorb and transport the electrolytic solution. This limitation directly affects the efficiency of the dry-electropolishing process, as the particles lose their ability to facilitate ion exchange activity, reducing their effectiveness.

[0088] This effect is observed on Figure 6 using techniques such as ToF-SIMS, where the surface after 20 hours of polishing shows an increase in C-H molecules and a decrease in S groups. This is due to the sulfate ions from the radicals on the surface, which, because of electropolishing, oxidize and form other species that ends up within the electrolyte liquid. Additionally, the hydrogen concentration on the surface increases due

to the migration of protons and water molecules during the surface finishing process. Also, there is an increase in the amount of C-H on the surface. While the entire resin structure is composed of C-H molecules, the surface density of CH is enhanced because, due to the temperature, it degrades, causing the pores (9) to compact and eventually collapse (7). Therefore, this blocking layer is formed (8).

[0089] This effect of densification of C-H bonds in the surface layer can also be observed in the various images of Figure 6 obtained by ToF-SIMS. In this figure, the evolution of the formation of this blocking layer is specifically observed as the surface pores collapse and, as mentioned, densify, increasing the proportion of C-H relative to the rest of the molecule. In the first image, a uniformity of C-H bond composition in the particle is observed. After 20 hours, a thin layer of 50 ± 30 nm in thickness is already visible, which increases to 250 ± 25 nanometers at 60 minutes and reaches a thickness of 525 ± 15 nanometers after 100 hours of polishing.

[0090] Finally, after approximately 100 hours (3) of exposure, a crust of around 525 ± 15 nanometers (6) is formed, composed of an increase in C-H density, in addition to oxygen and hydrogen due to pyrolytic causes.

[0091] A first aspect of the present invention refers to a method for treating a surface by means of ion exchange, the method comprising steps of:

applying a potential difference between a cathode and an anode, wherein at least one of the electrodes functions as the workpiece to be treated;

electrically coupling the electrodes via a solid-particle-based electrolyte, the electrolyte comprising solid particles that retain a liquid electrolyte solution, thereby rendering the solid particles conductive;

providing relative motion between the solid particles and the surface of the workpiece, wherein ion exchange occurs through the transport of liquid electrolyte upon contact between the solid particles and the surface being treated; and

mitigating the reduction in lifespan of the solid-particle-based electrolyte by incorporating means or methods to inhibit, delay or restore particles presenting a blocking crust layer on their surface, formed during working conditions.

[0092] A second aspect of the present invention includes the use of a PCM within a solid-particle-based electrolyte to regulate temperature fluctuations and thereby delay the lifespan reduction of the electrolyte. The PCM absorbs or releases thermal energy during phase transitions, mitigating localized overheating caused by the Joule's effect and reducing the formation of a blocking crust layer on the surface of the solid particles, thus enhancing the efficiency and durability

of the ion-exchange process.

[0093] The selection of the most suitable PCM depends on the specific process conditions and the composition of the electrolytic medium. In particular embodiments, the PCM is chosen based on the temperatures reached during surface treatment, which are influenced by the polishing settings and the degradation characteristics of the material comprising the conductive solid particles. These degradation temperatures and enthalpies can be determined through TGA of the solid particles, as illustrated in Figure 2.

[0094] Figure 2 corresponds to a graph that compares the percentage weight value as temperature is applied to resin particles, some in a new, virgin state and others that are already degraded. Additionally, the right axis indicates the derivative of weight with respect to temperature, showing the percentage weight change at a specific temperature point. With this one, different peaks are shown, which represent the temperatures where the evaporation of each substance begins.

[0095] When observing the decrease in percentage weight with respect to temperature, three slopes can be identified: the first corresponds to weight loss due to the evaporation of water, the second to the evaporation of acid, and the third to the pyrolysis effect experienced by the polymer. Three peaks are also visible, corresponding to the derivative. The first peak indicates that the degraded particle began to evaporate water at 48.00°C , while the virgin particle did so at 55.84°C . The second peak indicates that the evaporation of acid in the degraded particle starts at 278°C , compared to 287.02°C for the virgin particle. Finally, the last peak related to the pyrolysis of the polymer is observed to be around 400°C . The peak for the virgin resin is higher, as the degraded resin has already undergone this effect and is therefore in a compromised state. This last peak exhibits a different shape due to the distinct microstructural composition of the surfaces of both particles.

[0096] The required amount of PCM for optimal temperature regulation is determined by comparing its enthalpy with the phase transition enthalpy of the solid particles. The PCM acts as a thermal sink in its liquid state, continuously dissipating heat and stabilizing the system's temperature. This behavior is demonstrated in Figure 3, which presents a DSC analysis of a PST-DVB sulfonated resin incorporating a PCM based on polyethylene glycol (PEG), according to a preferred embodiment of the invention.

[0097] In the DSC analysis conducted under a nitrogen atmosphere, the thermal behavior of the polymer is assessed. When no PCM (0 wt.% PEG) is present, the polymer exhibits a pronounced exothermic peak at its decomposition temperature. However, with the introduction of 1 wt.% PEG, this exothermic peak is slightly reduced, as the PEG absorbs part of the heat released during decomposition. As the PEG concentration increases, the exothermic peak further diminishes, confirming the PCM's ability to absorb thermal energy and

mitigate the polymer's thermal degradation. This demonstrates the effectiveness of PEG in regulating temperature and protecting the solid-particle-based electrolyte from excessive heat exposure.

[0098] In Figure 3, different peaks are observed that indicate the heat released, representing various exothermic processes and how this heat decreases with the addition of glycol-based compounds, in particular polyethylene glycol (PEG). Such compounds act as heat-absorbing media and contribute to mitigating process heat generation that would otherwise be sustained by the solid bodies. It is observed that increasing the content of the glycol-based compound on the surface of the resin results in a reduction of the heat absorbed by the solid bodies. A significant change is observed when increasing the concentration from 5 to 10 wt. %. At higher concentrations, in particular around 15 wt. %, a reduction in peak intensity is observed, which may be associated with thermal effects such as volatilization of lower molecular weight fractions or changes in phase behavior. This indicates that a composition comprising between 10 and 15 wt. % PEG provides a balanced thermal response, minimizing both exothermic and endothermic effects. The peaks are not observed to overlap, as at higher concentrations the thermal response is altered, potentially due to earlier onset of phase transitions or volatilization phenomena. Therefore, ethylene glycol eventually evaporates, resulting in a decrease in the amount present in the resin. To maintain a constant temperature, it should be reintroduced periodically at an optimal concentration of between 10 and 15 wt. %.

[0099] In embodiments with a poly(styrene-divinylbenzene) (PST-DVB) sulfonated resins as a plurality of solid bodies, they undergo thermal degradation in stages, with desulfonation occurring around 200-300°C, followed by degradation of the polymer backbone at 350-450°C, and complete decomposition beyond 500°C. Since the sulfonic acid groups start decomposing at relatively low temperatures, maintaining process conditions below 250-300°C is essential to preserve their ion-exchange properties and structural integrity.

[0100] Particular realizations of the invention include the use of organic PCMs, such as paraffins or fatty acids, which may present challenges due to potential degradation caused by oxidation or uneven melting within the system. For this reason, encapsulation or protective coatings can be employed to prevent oxygen exposure and ensure uniform heat distribution. This encapsulation technique can also be applied to inorganic PCMs, such as hydrated salts, or to eutectic PCMs, which comprise mixtures of different compounds with a melting point adjusted to ensure heat control over a specific temperature range. In particular embodiments, PCMs can either exist freely in liquid suspension or be encapsulated.

[0101] Therefore, some embodiments of the present invention include the use of at least one of organic, inorganic, and eutectic PCMs employed to reduce, mitigate, or eliminate the obstructive surface layer over the

solid particles. In particular embodiments in which organic PCMs are used, paraffins and its specific chemical composition can be used to select the desired working temperature range, where long-chain paraffins (C20-C40) exhibit higher melting points, around 30-40°C, while medium-chain paraffins (C10-C20) have lower melting points, around 20-30°C. The choice over the selected temperature range, in some embodiments, depends on the optimal operating temperature of each electrolyte.

[0102] Among inorganic PCMs, hydrated salts are preferably used in some embodiments due to their higher thermal capacity compared to organic PCMs. For instance, sodium sulfate decahydrate, with a melting point of approximately 32-35°C, or sodium chloride pentahydrate, which has a melting point around 30°C, are suitable options.

[0103] Eutectic PCMs, which are mixtures of different substances with adjustable melting points, are particularly useful when specific thermal properties are required that cannot be achieved with a single component. An example of a eutectic mixture suitable for some embodiment of the present invention is sodium chloride combined with urea, with a melting point between 20-30°C, which can be encapsulated in materials such as polyethylene or ceramic. Another example according to some embodiments comprise a mixture of paraffin and fatty acid, with an adjustable melting point ranging from 25-35°C. Eutectic mixtures can be tailored to achieve a melting point within a specific range. For instance, a mixture of paraffin and oleic acid could exhibit a melting point between 30-35°C.

[0104] There are several embodiments of the invention including other compounds that help controlling the temperature in the electrolyte system, each offering unique properties in terms of thermal management.

[0105] Glycols such as propylene and ethylene glycol are known for their high heat capacities and are often used in cooling applications due to their ability to absorb and store thermal energy efficiently. The enthalpy of fusion varies depending on its molecular weight and physical state. For solid PEG, the typical enthalpy of fusion usually ranges between 150 and 200 J·g⁻¹. For example: PEG 4000 ~ 190 J·g⁻¹; PEG 6000 ~ 180 J·g⁻¹ and PEG 8000 ~ 170 J·g⁻¹.

[0106] Fatty acids, especially those with longer carbon chains, have higher heat capacities, making them effective in absorbing heat. PEG and other materials like oleic acid are also notable for their thermal absorption properties. However, excessive addition of these compounds may result in them not being fully absorbed by the system, causing them to remain outside in the medium. These compounds can be integrated into the system to enhance heat dissipation, thereby preventing the temperature from rising excessively and contributing to the overall efficiency of the electrochemical process.

[0107] A third aspect of the present invention includes a method to mitigate the degradation of the particles involves using a device that facilitates the dissipation

of heat generated by the electrolyte. A potential solution according to some embodiments could be the use of a heat exchanger, where the liquid is recirculated, allowing its temperature to be adjusted, including as an example but not limiting to its use, introduced here by reference in its entirety the International Application No. PCT/ES2024/070344 (published as WO2024246406A1). This process in some embodiments helps to maintain a more stable thermal environment within the system, slowing down the formation of the obstructive surface layer and reducing the impact of the Joule effect on the particles, using a method and equipment for controlling the temperature of particles in polishing processes using solid particles with electrolyte in a liquid environment.

[0108] The method comprises: a stage of absorption of the liquid from the tank where the particles are a liquid temperature control stage externally to the tank; and a stage of reincorporation of the temperature-adjusted liquid into the tank to reduce the temperature of the particles. The equipment includes a circuit of ducts, with an inlet mouth and an outlet mouth in the tank; a suction pump; a filter with a mesh that does not allow particles to pass through; and a heat exchanger.

[0109] Figures 8A, 8B, 8C and 8D illustrate representative nanoindentation load-displacement curves obtained from the surface of the solid polymeric particles after different operating times (0 h, 20 h, 60 h, and 100 h). The nanoindentation tests were performed using a Nanoindenter XP operating in displacement-control mode, employing a ruby spherical indenter with a diameter of 2 mm (elastic modulus $E_i = 350$ GPa, Poisson's ratio $\nu_i = 0.25$). The elastic modulus of the particle surface was extracted by fitting the unloading curves using the Hertzian contact model defined by the relation

$P = 4/3 \cdot E_r \cdot \sqrt{R} \cdot h^{3/2}$, where P is the applied load, E_r is the reduced elastic modulus, R is the indenter radius, and h is the indentation depth.

[0110] The results show a clear increase in elastic modulus with increasing operational time, evidencing progressive surface hardening of the particles induced by thermal effects during electrochemical processing.

[0111] Figure 9 presents the linear correlation between the thickness of the thermally affected surface layer of the polymeric particles and the corresponding elastic modulus measured by nanoindentation. The data demonstrate that as the thermally altered layer grows in thickness, a proportional increase in elastic modulus is observed. This relationship confirms that thermal exposure during operation directly influences the mechanical properties of the particle surface, leading to increased stiffness and reduced ionic permeability. The correlation supports the technical rationale for implementing temperature-mitigation strategies and further validates the reuse of hardened particles for mechanically assisted surface finishing processes.

[0112] Accordingly, the described embodiments de-

monstrate that the degradation of solid-particle-based electrolytes used in electrochemical surface treatment is intrinsically linked to thermally induced physicochemical and mechanical transformations occurring at the particle surface during operation. The progressive increase in elastic modulus and the growth of a thermally affected surface layer, as evidenced by nanoindentation analysis, confirm the decisive role of Joule heating in the formation of blocking crust layers that limit ionic exchange efficiency. Through the integration of temperature-regulating strategies, including the use of phase change materials, heat exchange systems, electrolyte composition adjustments, and optimized electrical parameters, the onset and progression of such degradation mechanisms can be effectively delayed, thereby extending the functional lifespan of the particles. Moreover, the invention advantageously exploits the resulting surface hardening of end-of-life particles by enabling their reuse in hybrid galvanomechanical surface treatment processes, where their enhanced abrasive behavior contributes to efficient material removal. Collectively, these aspects provide a comprehensive and sustainable approach to improving performance, durability, and material utilization in electrochemical surface finishing systems.

Claims

1. A method for treating a surface of a workpiece by means of ion exchange, comprising steps of:
 - applying a potential difference between two electrodes, a cathode and an anode, wherein at least one of the electrodes functions as the workpiece of the surface to be treated;
 - electrically coupling the electrodes via a solid-particle-based electrolyte, the solid-particle-based electrolyte comprising solid particles that retain a liquid electrolyte solution, thereby rendering the solid particles conductive;
 - providing relative motion between the solid particles and the surface of the workpiece, wherein ion exchange occurs through the transport of liquid electrolyte upon contact between the solid particles and the surface being treated;
 - characterized in that** the method comprises at least one of inhibiting, delaying and restoring particles with a blocking crust layer on a surface thereof.
2. The method according to claim 1, wherein the solid-particle-based electrolyte comprises an interstitial fluid between the solid particles.
3. The method according to claim 1 or 2, comprising the use of a phase change material (PCM) within the solid-particle-based electrolyte.

4. The method according to claim 3, wherein the solid-particle-based electrolyte comprises the interstitial fluid between the solid particles and the PCM is included within the interstitial fluid .
5
5. The method according to claim 3 or 4, wherein the PCM is included in its free form.
10
6. The method according to any one of claims 3 to 5, wherein the PCM is included in its encapsulated form.
15
7. The method according to any one of claims 3 to 6, wherein a PCM is selected from: paraffins, fatty acids, glycols, eutectic mixtures.
20
8. The method according to any one of claims 3 to 7, wherein the PCM comprises ethylene glycol, and in particular the PCM comprises polyethylene glycol (PEG).
25
9. The method according to claim 8, wherein the ethylene glycol, in particular PEG, is present in an amount between 10 and 15 wt. % with respect to the solid particles.
30
10. The method according to any one of the preceding claims, further comprising controlling a temperature during the surface treatment, preferably by means of a heat exchanger.
35
11. The method according to any one of the preceding claims, comprising modifying operational parameters, selected from:
35
 - a) increasing duty cycles ratio within the electropolishing cycles, in particular to a duty cycles ratio from 10% to 1000 %, preferably from 50% to 200%;
 - b) reducing the voltage applied between the electrodes, in particular to a voltage reduction from an original value thereof to 10 -50 % of said original value; or
 - c) lowering the current density, in particular a current density reduction from an original value thereof to 10 -50 % of said original value.
45
12. The method according to any one of the preceding claims, further comprising the addition of molecules or elements with high specific heat capacity to the solid-particle-based electrolyte or the interstitial fluid if present between the solid particles of the solid-particle-based electrolyte.
50
13. The method according to any one of the preceding claims, comprising adding substances such as acids to the solid-particle-based electrolyte..
55
14. The method according to any one of the preceding claims, wherein previously used resin particles are reutilized by altering their spherical structure, such as by breaking them, to increase the effective surface area not covered by the blocking surface layer, enhancing their efficiency in subsequent electropolishing processes.
15. The method according to any one of the preceding claims, further comprising reusing solid particles, in particular polymeric solid particles, that have undergone thermal surface hardening during electrochemical surface treatment, wherein said particles exhibit increased surface stiffness and abrasive behavior as a result of a thermally induced surface alteration produced under galvanic working conditions, and wherein the reused particles are employed in a hybrid galvano-mechanical surface treatment combining electrochemical action with mechanical abrasion.

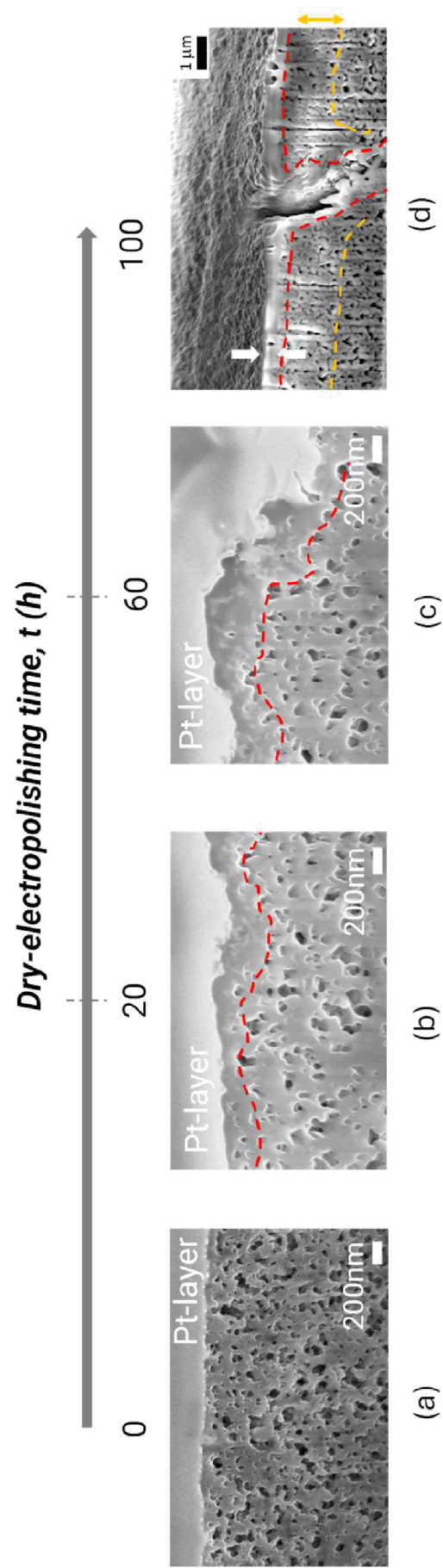


FIG. 1

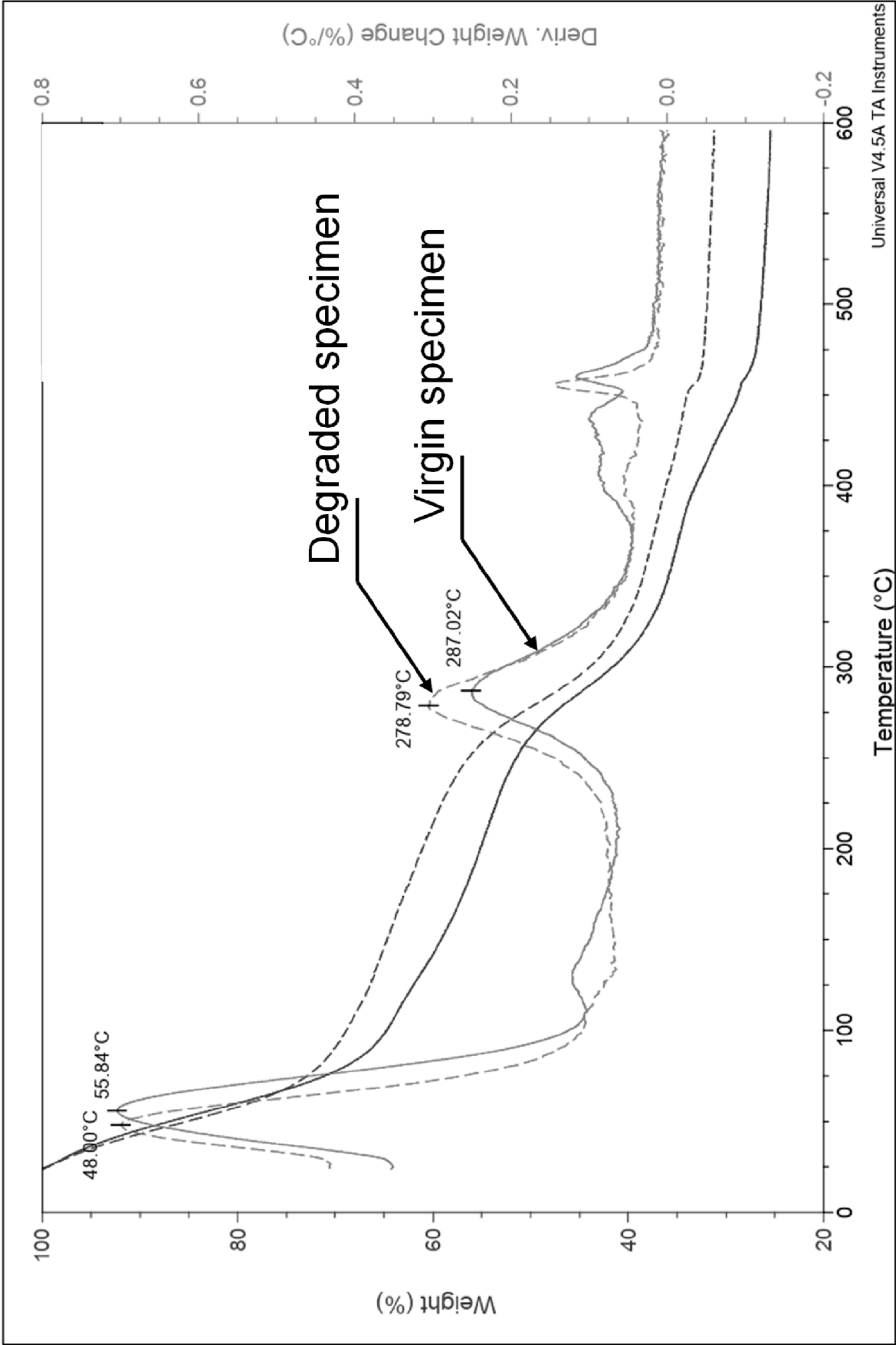


FIG. 2

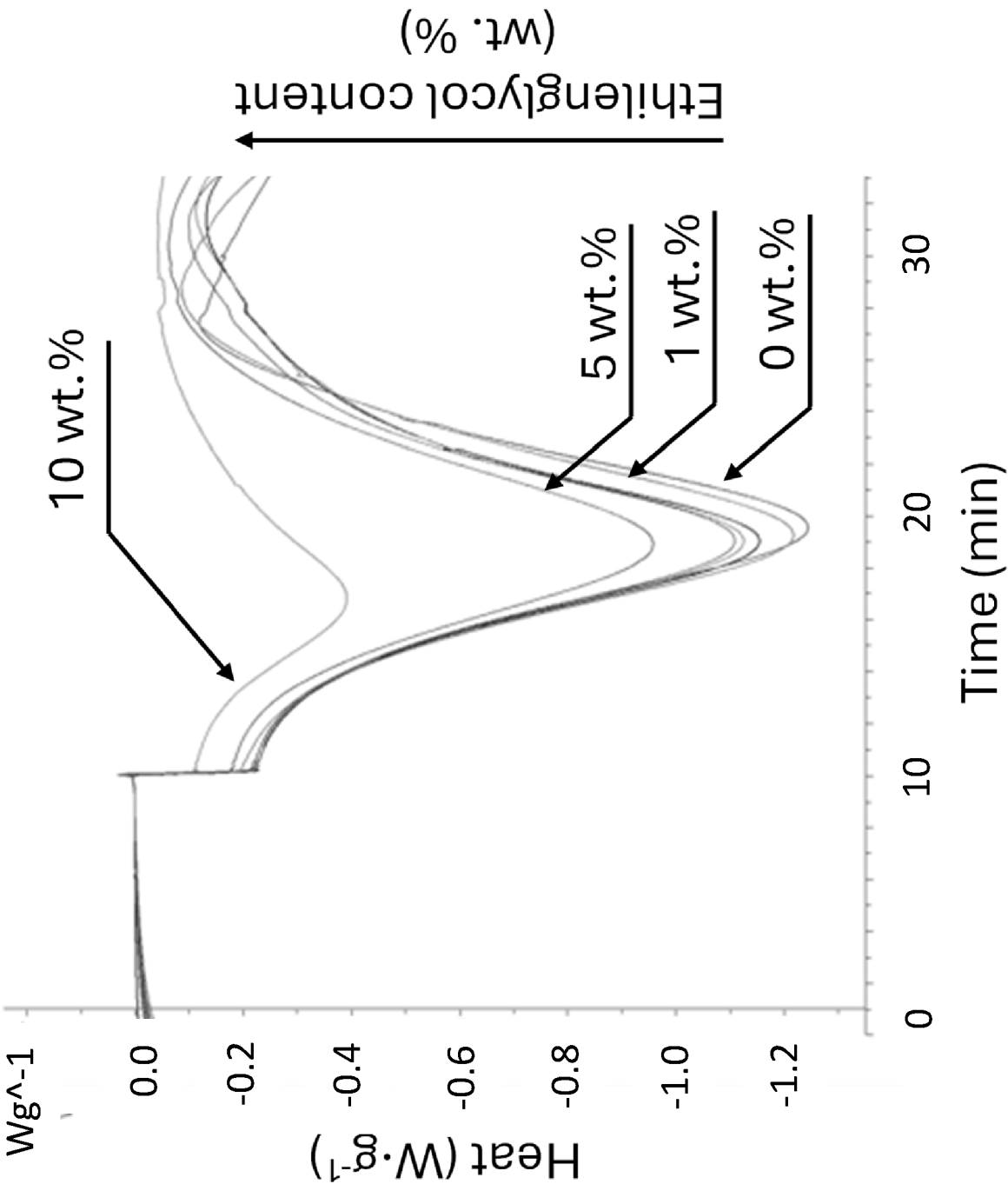


FIG. 3

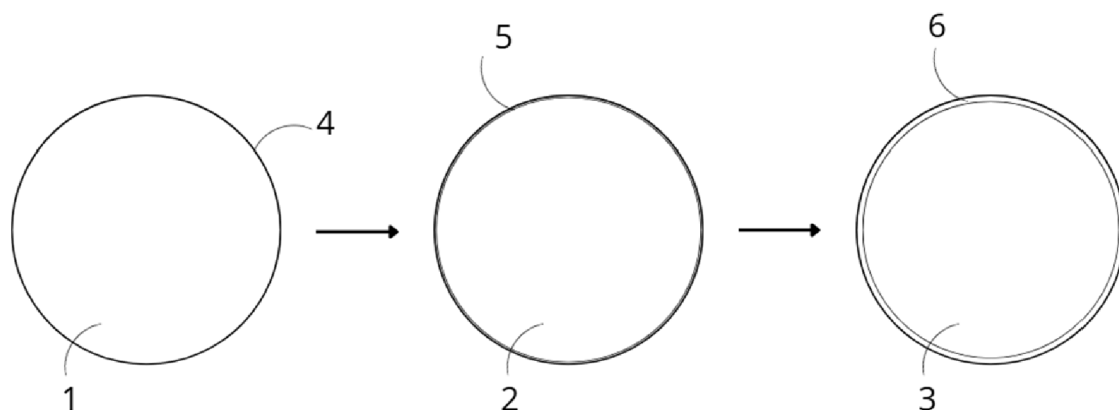


FIG. 4

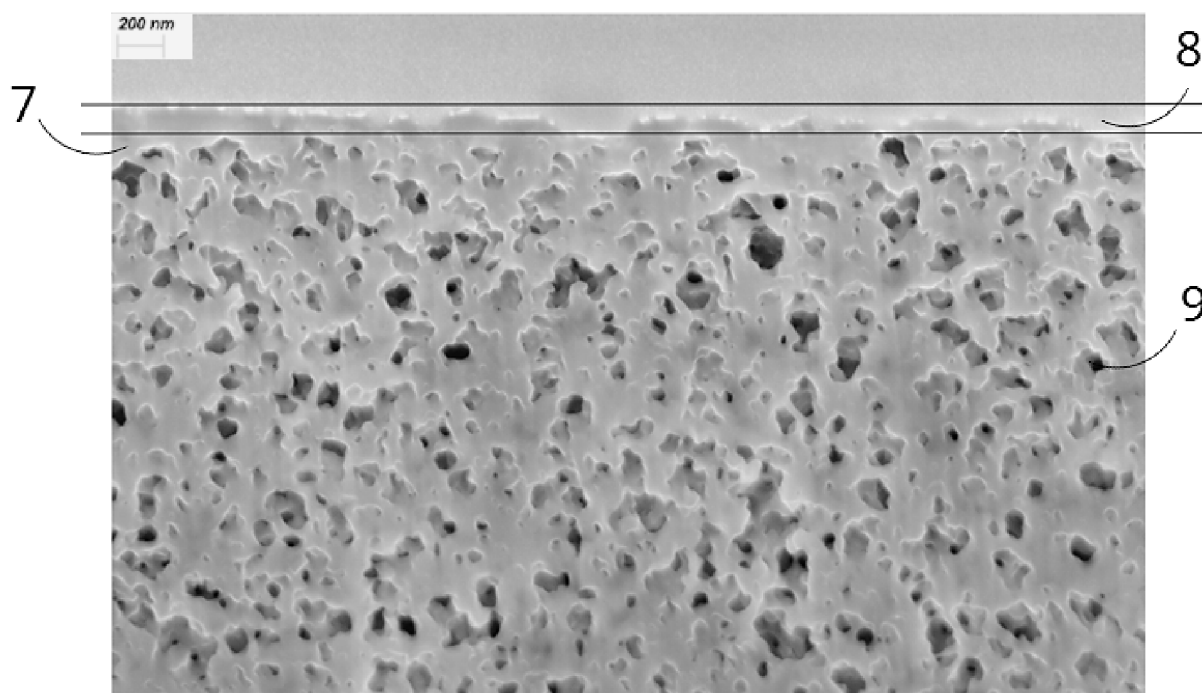


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 Height = 3.430 μm

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 Stage at M = 2.537 mm
 Tilt Corr. = On
 Tilt Angle = 36.0°

System Vacuum = 1.72e-006 mbar
 FIB Gun Pressure = 1.09e-007 mbar
 Gun Vacuum = 3.50e-070 mbar
 19:04:37 10 Jun 2024

Mag = 25.00 K X
 WD = 4.9 mm
 EHT = 5.00 kV
 Aperture Size = 30.00 μm

Signal A = InLens
 Brightness = 49.5%
 Contrast 34.4%
 High Current = Off

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 FIB Mag = 1,64 K X
 FIB Probe = 30K:50pA
 FIB Imaging = SEM
 FIB Scan Rot = 0.0°

FIG. 5

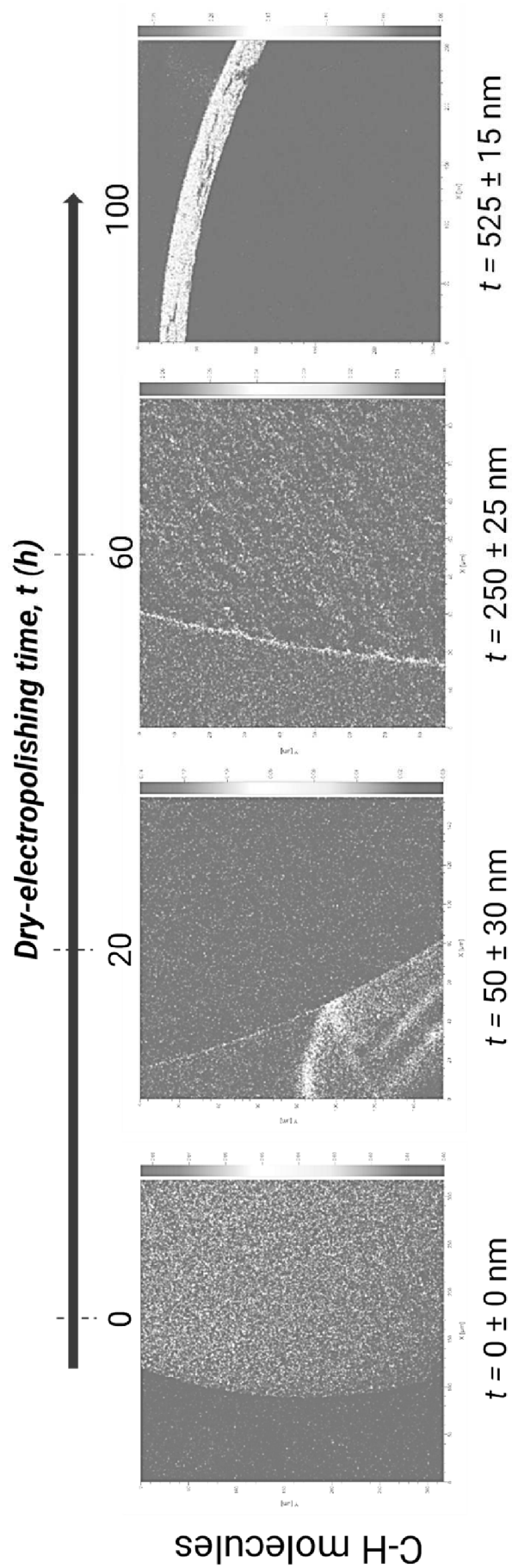


FIG. 6

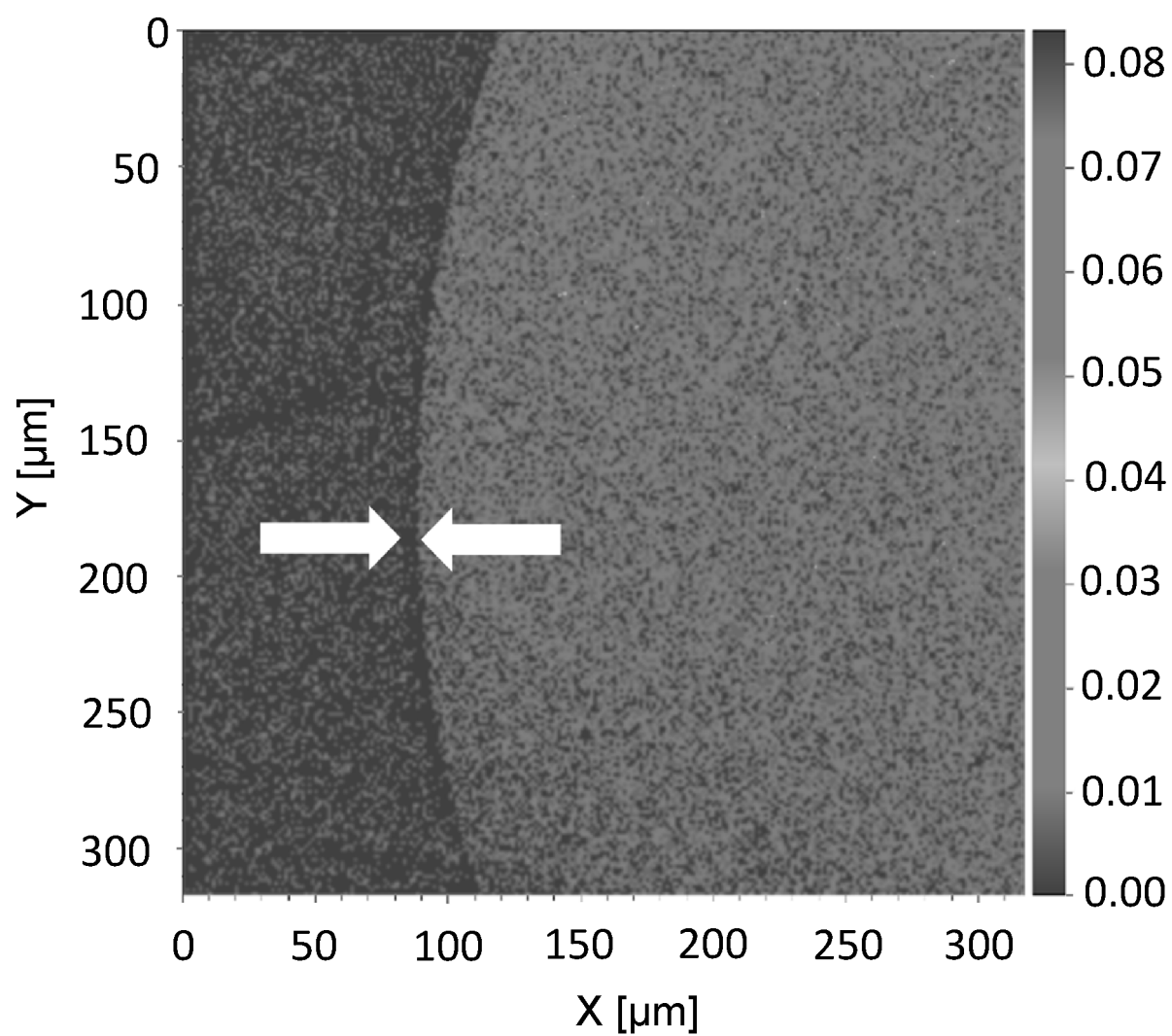


FIG. 7A

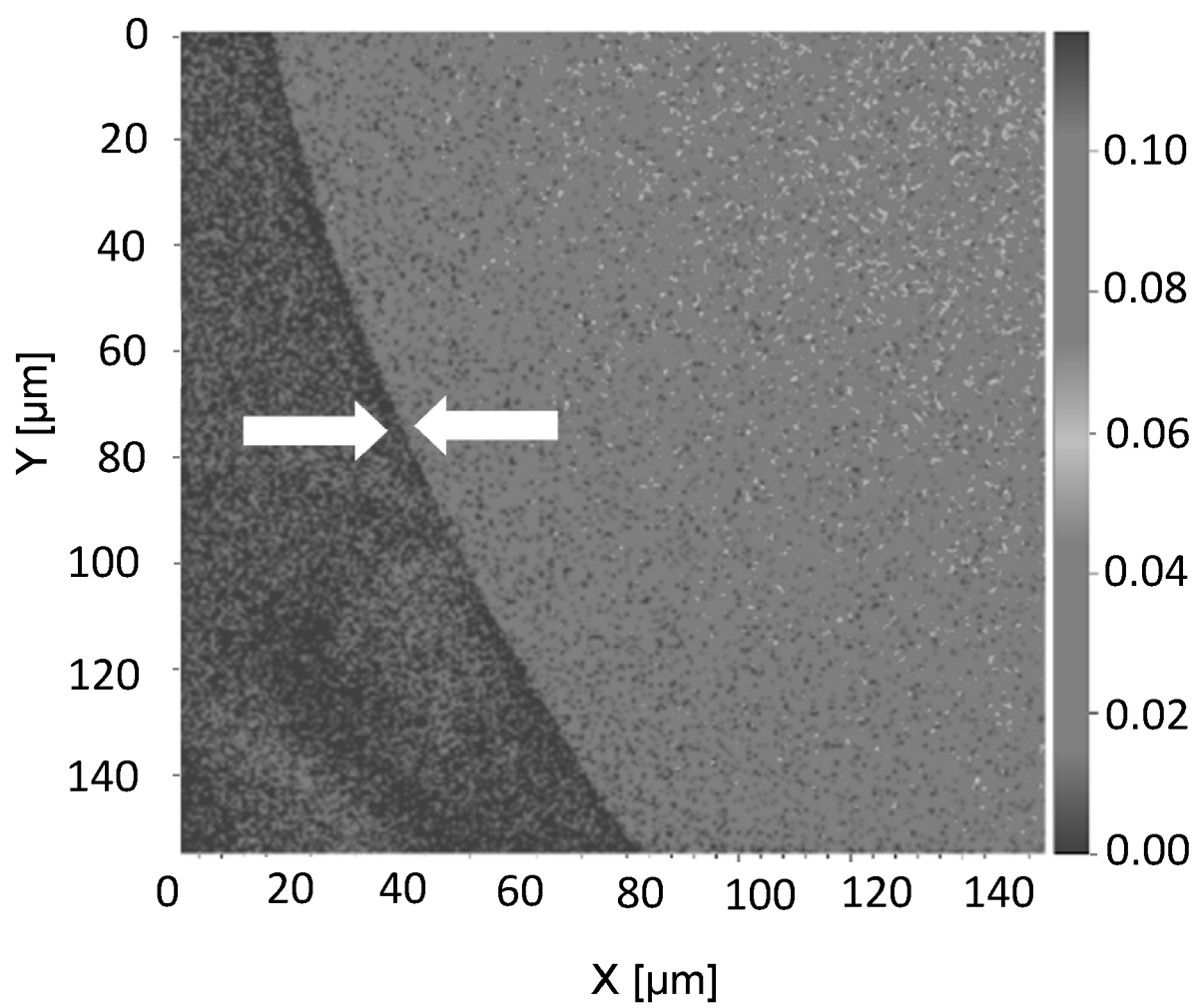


FIG. 7B

POLISHING TIME: 0H.

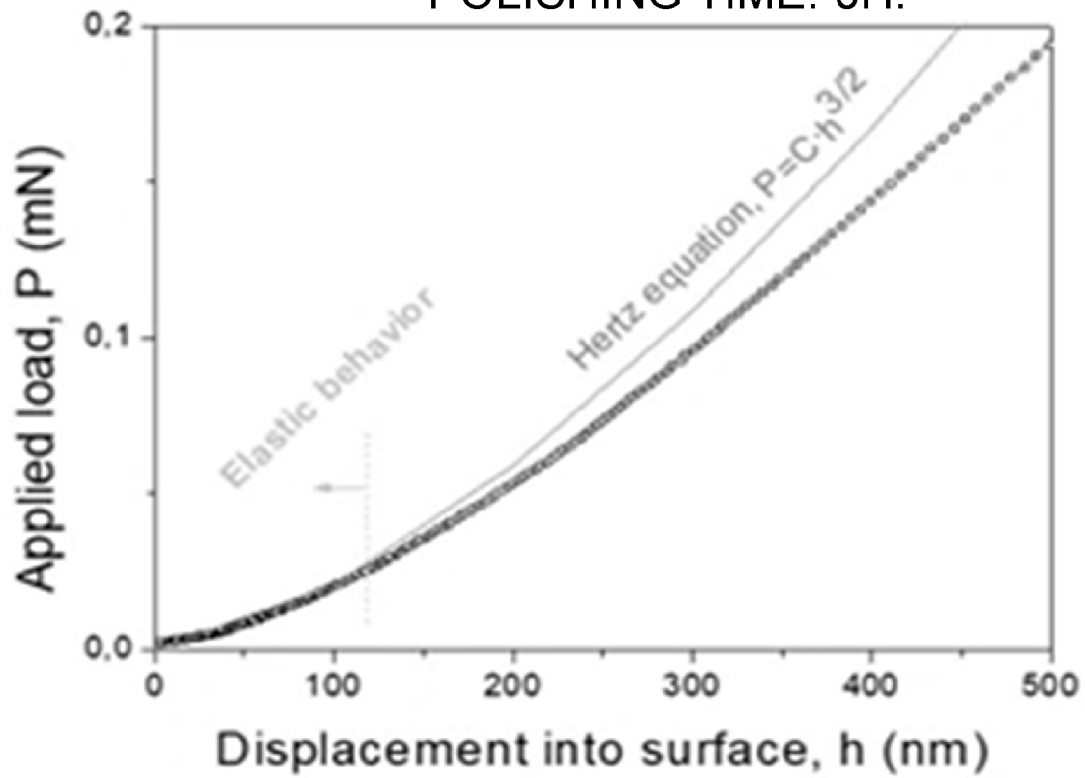


FIG. 8A

POLISHING TIME: 20H.

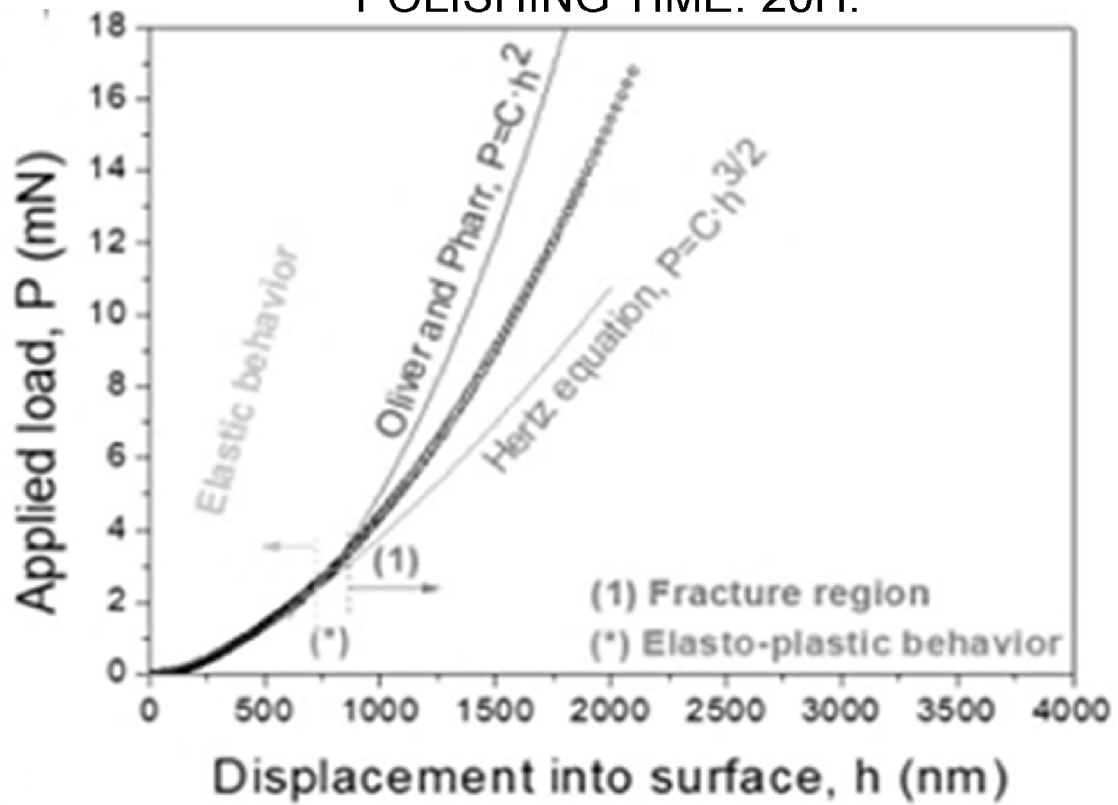


FIG. 8B

POLISHING TIME: 60H.

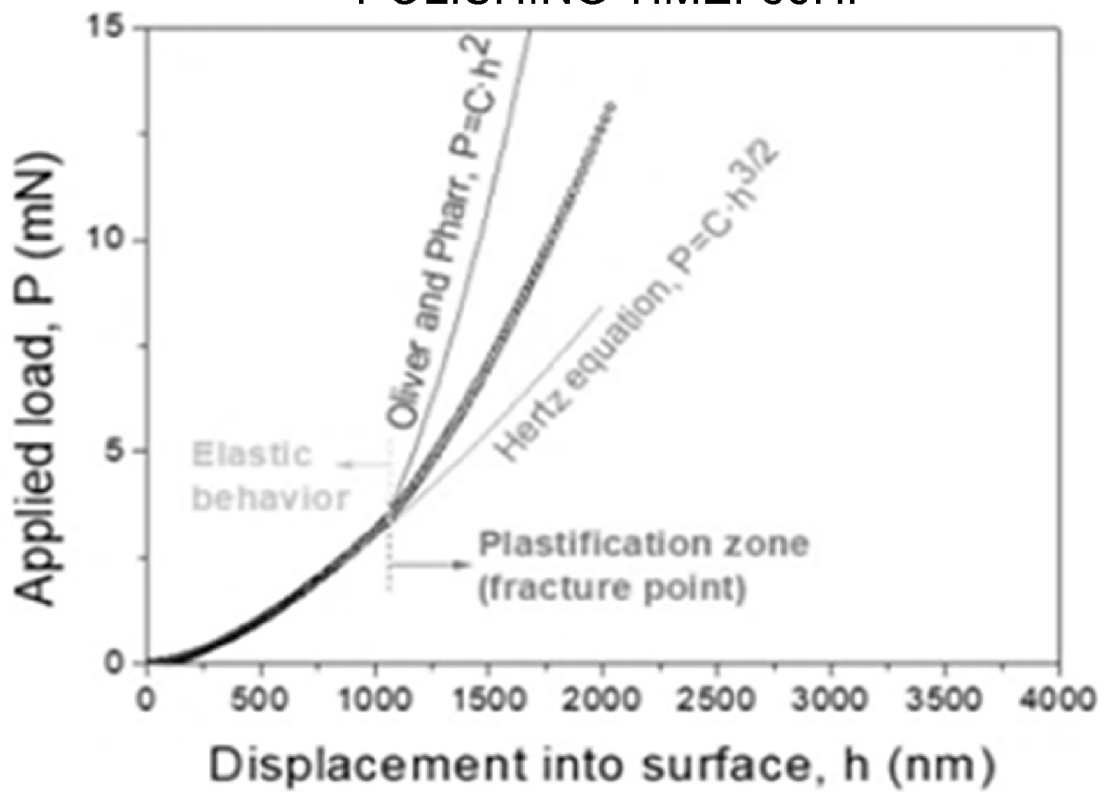


FIG. 8C

POLISHING TIME: 100H.

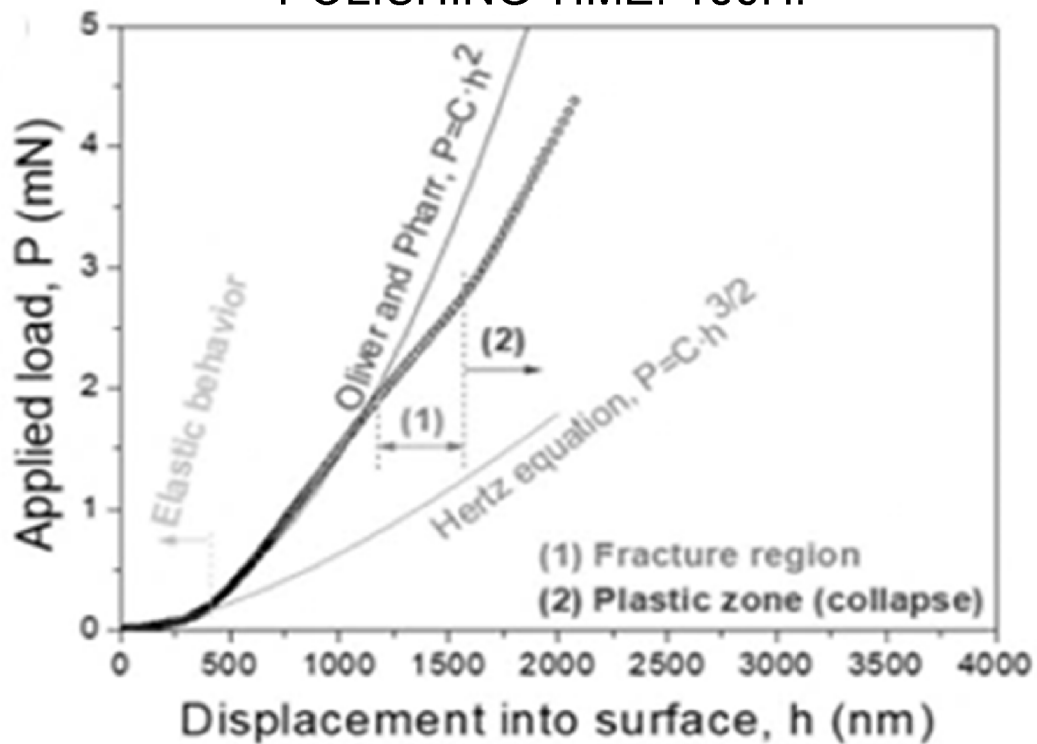
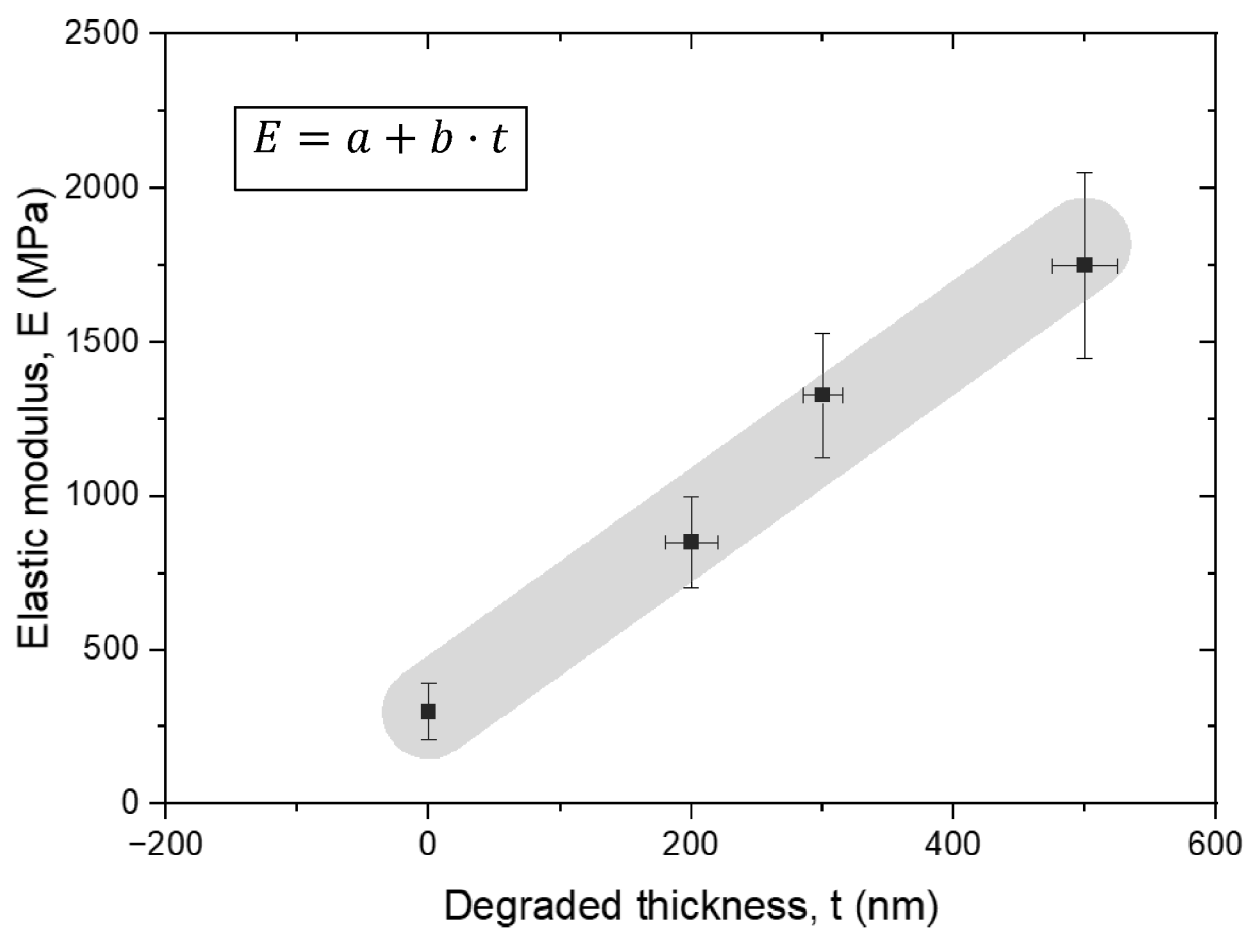


FIG. 8D



Parameter	Value
a	297 ± 45
b	3.04 ± 0.25
R ²	0.9806

FIG. 9

REFERENCES CITED IN THE DESCRIPTION

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