Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

New Trends in Anodizing and Electrolytic Coloring of Metals

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Abstract
Development of an inexpensive, effective, and technologically simple method to occur natural self-organization of oxide nanopores would become very important in light of the ever-increasing needing. The anodization process has recently attracted a wide extent of research attraction in nanotechnology. An anodizing process is considered as effective technique for fabrication of passive layer, and synthesis of nanoporous metals with new morphology enhanced mechanical and electrochemical performances. Modern fabrication techniques involved in an anodic production of nanoporous metal focus on the variation of exterior properties during the electrochemical process. Fabricating anodic nanoporous metals are constrained by the major parameters are listed. Also, this review discusses a brief generic approach for electrolytic coloring and previous investigations for electrolytic coloring as finishing anodized surface with special metal particles affords appropriate optical properties in the anodized surface of aluminum applicable for solar absorption application. Surface mechanical attrition treatment (SMAT) is a new alternative approach that can facilitate anodization; it is a type of plastic deformation technique, used prior the anodization to convert the metal from polycrystalline into nanocrystalline. The conversion results in grain size refinement and establishment of the high density of grain boundaries. A comparison between the resulting anodic metals subject and not subjected to SMAT will be displayed. The discoveries in this review open a new pathway in the anodic fabrication of nanoporous materials. By the integration of both SMAT and anodization, this setup will be a new perspective in the future developments of nanomaterials.

Keywords: anodization; electrolytic coloring; nanoporous metal; SMAT; nanomaterials

1. Introduction

Anodization is an electrochemical oxidation process that aims to change the exterior of metal through modification of the surface morphology and crystal structure for several metals by increasing the thickness of the oxide layer on their surface e.g., Aluminum, Titanium, Vanadium, Tin, Niobium, Tantalum, Tungsten, Hafnium, and Silicon, etc.[1- 3]. It is not only often used to protect metals from corrosion and abrasion but also allows dyeing them in different colors and coats the metallic surface. The anodized coating is hard, durable, will never peel or wear. Figure (1) shows a simplified anodization setup.

General types of anodized oxide layers depending on conditions and nature of an electrolyte used; one the adherent compact, non-porous, and non-conducting barrier type oxide from neutral electrolytes (pH 5-7); this film was extremely thin and dielectrically. While the other compact thick barrier layer and porous-type oxide made using strong acid (sulfuric, oxalic, phosphoric) [4] as well as to increased the corrosion resistance both types shown in Figure (2a, b) for Al [1] and Ti [5] respectively.

Fig. 1: Schematic illustration showing a simplified anodization cell [6].

Since the last several decades, principally porous-type anodization has occupied attention technological interest in the industry due to its properties such as

*Corresponding author e-mail: omniashehata@yahoo.com
Received date 23 December 2021; revised date 28 January 2022; accepted date 29 January 2022
DOI: 10.21608/EJCHEM.2022.112570.5110

hardness, higher abrasive, good corrosion resistance, and wear resistance needed higher thickness.

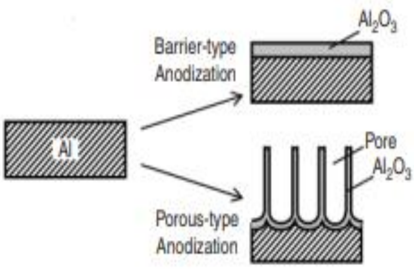


Fig. 2: Different kinds of the anodized oxide layer [1,6].

Anodization Process

It is the public name applied for treating metals or alloys, to form stable oxide film as coating for precise; custom color matching offering and finishing custom pieces with providing consistent color throughout the full production run; by anodizing in one or double process i.e. aluminum substrate. The goal increased performance of the surface by acquiring many advantages such as high durability cheap to produce and maintain and being environmentally friendly. Main parameters required for conventional anodizing process a time of the process, applied potential, current density, types of electrolytes and bath temperature, which determines the structure and properties of the formed oxide film.

Steps of Anodizing Process

- **Cleaning:** to remove all oils and buffering compounds in a bath containing water and mineral acids or alkalis, with dispersants and detergents.
- **Pretreatment:** to improve the appearance of the surface prior to anodizing step through etching, as a results, impart bright and shiny.
- **Anodizing:** to produce actual coatings where metal acts as anode with the passing current to be anodized in electrolyte acid bath of chromic, phosphoric, or sulfuric. As a result, transparent and microscopic porous layer thickness is determined by several parameters.
- **Coloring:** occurred in two ways *"Integral color"* is doing in the anodizing bath which modified for that purpose, imparts black color coating required electrical power create surface more abrasion resistant coating than conventional anodization.

Other *"Electrolytic coloring"* established by two steps, the fresh anodized sample must be immersed in a bath comprised an inorganic metal salt by using applied current that metal deposits in the base of pores, it made for the fresh porous anodized film to be capable of absorbing colorants.

- **Sealing:** to closed pores of surface used in service in many ways.

The conventional anodic process offers a suitable surface for decorative coloration and electroplating but it cannot provide sufficient corrosion resistance, anodic oxide films fractured in the manufacturing process and causes contaminations and particles due to fluctuation of base materials.

2. Types of Anodizing Process

2.1. *A Unique Anodizing Technology*

A unique anodizing technology was developed, it controls cracks at high temperatures when exposed to gas and plasma called "K.PRAS". It has higher physical plasma and gas corrosion resistance at high temperatures of about 450^{0}C. It aimed to increase strength and thermal stability, substrate subject to intermediate annealing with rapid heating and cooling cycle and cold rolling during the manufacturing process as Figure (3).

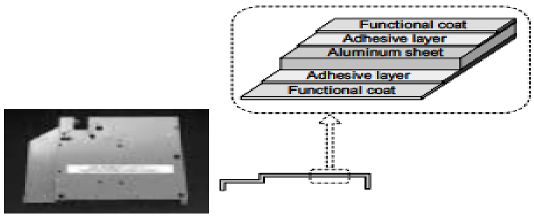


Fig.3: (CD-ROM cover) and composition of functional pre-coated aluminum [7].

This type of technique reduce cracks in the film by controlling microstructures of anodic oxide film through a newly developed electrolytic grinding used for manufacturing semiconductor device tools and print industry [7] and achieved more advantage when it compared to conventional types as noticed from Figure (4).

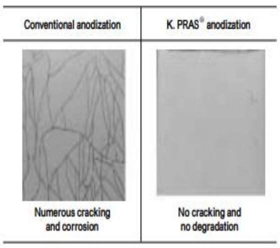


Fig. 4: Appearance of anodized coupons after exposure to Cl_2 gas [7].

2.2. *Mild Anodization (MA)*

Mild Anodization (MA) is known as a self-ordering regime to fabricate ordered anodic aluminum oxide 'AAOs '. It characterized the self-organized growth of ordered nanopores and it prospered in nanotechnology applications [1]. While pore diameter is not the critical parameter as the interplay the exchange between natures of the electrolyte used, the current density, and the temperature. Figure (5) represented the schematic procedure used for Mild anodization [8] and compared SEM micrograph with using various types of acids (Oxalic Acid, Phosphoric Acid, and Sulfuric Acid) [4, 9]. Since mild anodization is done with less voltage in comparison to hard anodization, the pore size will be smaller than the pore size obtained by the hard anodization process.

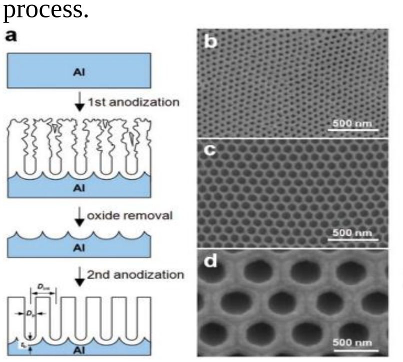


Fig.5: (a) A schematic for self-ordered AAO by MA and (b–d) are SEM of self-ordered AAOs by MA with (b) H_2SO_4, (c) $H_2C_2O_4$, and (d) H_3PO_4 [8, 9].

2.3. *Hard anodization (HA)*

It was technologically advanced in the surface finishing industry under the title hard coat. It becomes extensively used in most industrial applications [10] and offers numerous high-speed oxide film growths (from 50-100 µm/h) with non-uniform structures as self-ordering regimes. So, this technique has not been useful in current nanotechnology research. It faced many difficulties in controlling significant structural parameters i.e., pore size, inter-pore distance, and aspect ratio of the resulting pores. Figure (6) shows a comparison between MA and HA. Lee et al could suppress the controlling reaction heat during HA and establishing a new self-ordering using oxalic acid at anodization potentials > 100V, with the rate of oxide growth 25 to 35 times faster than that in mild anodization (MA) [11].

3.4 Pulse Anodization (PA)

It offers a combination of conventional MA and new HA for tailoring the pore structure of AAOs, using potentiostatic conditions versus changing anodization current in the weak or strong acids. Typical Pause continuously pulse of the high potential pulse (HA) followed by a low potential pulse (MA) respectively. To produce a periodic compositional modulation along the pore axes of AAO [12], it enables to divide a single anodic film into a stack of well-defined AAO membranes sheets as prepared by an extended etching of HA-AAO segments as shown in Figure (7).

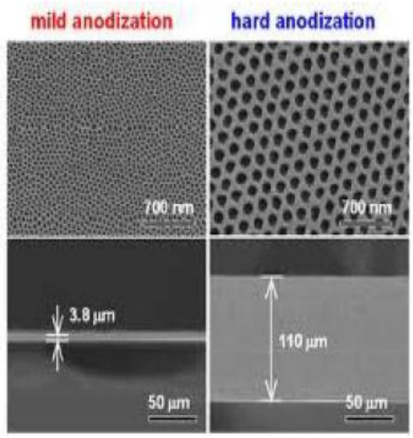


Fig. 6 The Mild and Hard anodization [10].

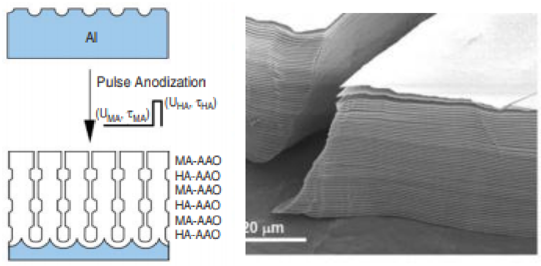


Fig. 7: (a) the fabrication of AAO with modulated pore diameters by pulse anodization**,** (b) SEM image of a stack of nanoporous AAO membranes [14].

Under a galvanostatic condition, Pulse anodization can also tailor the internal pore structure of AAO. In this case applied cyclic current pulses achieve MA and HA conditions also the potential of anodization changed periodically to a value corresponding to each current was pulsed

PA affords a simple and economic way for the bulk production of nanoporous membranes. The preparation of structurally well-defined alumina nanotubes with controllable lengths by a convenient method was succeed since 2008 [13]. Pulse Anodization promises effective dissipation of heat, which is considered of the major causes of the burning of an anodic film.

3. Metals can be anodized

Anodic films are applied to protect pure metal and alloys through numerous different anodizing processes where it is acquiring their high strength to weight ratio and relative availability equipped to its widely used in industrial processes in addition to corrosion resistance and coloring. Anodic oxidation allows prepared oxide film for many metals i.e. aluminum; tantalum, niobium, and many other transition metals. Passive anodic oxide films play an important role in various technical applications in surface protection, micro-systems and nano-systems, and electro-catalysis [15], electro-chromic processes and photosensitive materials [4], dielectrics in electrolytic capacitors. Metals anodized by this process ordered according to their applications aluminum, titanium, magnesium, niobium, tantalum, Vanadium, Iron and zinc, etc.

Anodized "Al" has a variety of commercial uses and diverse consumer applications across a wide range of industries. The benefits of anodization are strong, resistant finish acquires aluminum ability for use in aircraft, automotive products, architecture, and construction. The potential of anodized aluminum products is unlimited [16]. Commonly uses for anodized "Ti" are dental and orthopedic implants [2]. Where anodization has the ability to create numerous colors without the use of dyes, other uses popular for art and jewelry, its Color depended on the thickness of the oxide layer that determined by the anodizing voltage [17]. Magnesium cannot be anodized by strong acid because it is always strongly reacting to the acid environment, so only useful is a light or organic acid, or phosphate, in addition to alkaline silicate. Anodizing magnesium is applicable as paint primer in thin or thick anodic coating but these coatings need to seal with oiler wax for optimum effectiveness, its anodic coatings can improve corrosion resistance. Anodizing magnesium uses park discharge to convert its surface into ceramic oxide however common purpose for magnesium in medical applications [18]. Niobium can be anodized for use a popular material for costume and body jewelry, commemorative coins, the extent of its colors achieved by varying the coating thickness [19]. Anodizing tantalum requires for uses in the manufacture of capacitors, tantalum is similar to titanium and niobium in the process for anodization. It featured by a wide array of attractive colors that can be formed through by altering the film thickness. Vanadium oxide film tends to dissolve when an aqueous solution is used for anodized in the solution as vanadyl ions [20]. Therefore, non-aqueous solutions are necessary for obtaining uniform oxide films on vanadium by anodization. Such films are of considerable technical interest, particularly because of potential applications as an efficient resist material for both photo-nanolithography and electron-beam nanolithography. Carbon steel exfoliates when oxidized under neutral or alkaline micro electrolytic conditions; Ferrous metals are commonly anodized electrolytically in nitric acid, or by treatment with red fuming nitric acid, to form hard black ferric oxide. This oxide remains conformal even when plated on wire and the wire is bent [21]. Anodizing zinc is a difficult process that required voltages of 200V to produce anodized coatings as thick as 80µm on zinc materials, adding hardness and corrosion resistance.

4. New trends in Anodizing

The goal of the anodization process fabricate a thick compact oxide layer on the metal substrate surface, Alumina film is the most commonly used in order to protect aluminum alloy as compared to applied several metals. The phenomenon of corrosion continues to pose a major concern to many industries around the world needing solutions for prevention and control. Corrosion Awareness Day highlights the estimated US$2.5 trillion annual cost of corrosion worldwide. While the potential to reduce that cost by $875 billion annually through appropriate application of existing corrosion abatement technologies is readily achievable a huge portion of the loss can be avoided via convenient proper corrosion control. New trends go to aluminum pure and take increase attraction for its type of membrane, low coast processing, and their importance in major industries. Modern processes can apply a finish to a metal as electrolytic coloring which makes i.e aluminum parts are now being used more hardened than steel and they are being produced at a lower cost.

4.1. *The two-steps anodizing process*

It aimed to obtain self-ordered alumina nanostructured through ordered steps as shown schematically in Figure (8).

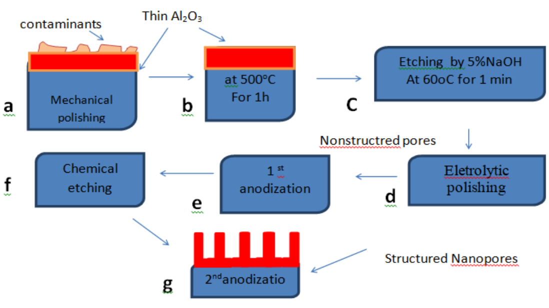


Fig. 8: Schematic of the two-step anodization process

Anodizing in two steps is considered the most widespread process for metal or alloy surface treatment with excellent mechanical properties and a broad market perspective. Anodizing in two steps improves hardness, mechanical properties, and corrosion resistance through thickening passive film and allows enhancing the electric, magnetic, catalytic, optical and sensing properties of the deposited materials for the small size in nm and high-aspect- ratio to produced nanostructures [22]. Recently, attention has been paid to the tunable synthesis of nanoporous 'AAO' by self-organized two-step anodizing with using various acids in order to obtain templates for nanofabrication with desired geometrical features in the production of nanowires, nanotubes, or nanodots from different materials [23-25]. Firstly, Masuda and Fukuda succeeded to obtain a highly ordered metal nano-hole Anodizing in two steps is considered the most widespread process for metal or alloy surface treatment with excellent mechanical properties and a broad market perspective. Anodizing in two steps improves hardness, mechanical properties, and corrosion resistance through thickening passive film and allows enhancing the electric, magnetic, catalytic, optical and sensing properties of the deposited materials for the small size in nm and high-aspect-ratio to produced nanostructures [22]. Recently, attention has been paid to the tunable synthesis of nanoporous 'AAO' by self-organized two-step anodizing with using various acids in order to obtain templates for nanofabrication with desired geometrical features in the production of nanowires, nanotubes, or nanodots from different materials [23-25]. Firstly, Masuda and Fukuda succeeded to obtain a highly ordered metal nano-hole array (Pt and Au) fabricated by a two-step replication of the honeycomb structure of porous anodic alumina (PAA).

5.2 Electrolytic coloring anodic film

Aluminum as extrusion and sheet used for common applications such doors, windows, and curtain walls. Two-step electrolytic coloring processes have been widely used throughout the industry to produce a variety of color-anodized aluminum. All studies in electrolytic coloring for aluminum have been described as patent literature [26-28]. The most common method in obtaining darkening the anodic aluminum surface is worthwhile. This technique is listed schematically in Figure (9), the anodizing and coloring are done separately.

The coloring impact factors as electrolyte concentration, bath temperatures, voltage, and time duration were considered. Tin, cobalt, copper, and nickel are used in coloring processes, but cobalt is considerably more expensive than tin so, Tin becomes very popular for effective implementations. Figure (10) shows schematically present metal used for coloring. Electrolytic coloring is not only fabricated for decoration purposes but also to improve the film's anti-corrosion properties against the environment, the color does not fade away when exposed to the UV light of the sun and applied in the solar energy source plate. This process is based on fact that the surface of a solar energy source plate requires a high absorption and low reflectivity of light in order to efficiently transform solar energy into thermal energy [29]. Moreover, the dark to black anodic film on aluminum features lightweight, low cost, good thermal and electrical conductivities.

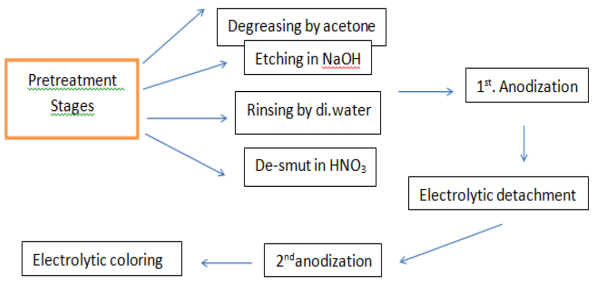


Fig. 9: Schematic of the Electrolytic coloring after 2nd anoidization.

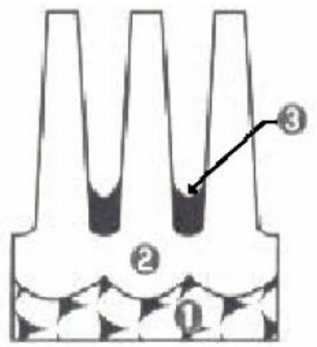


Fig. 10: Sketch of Two Step Electrolytic coloring anodizing on substrate and the metal deposits at the base of the pores (1) Substrate, (2) Anodic coating and (3) metal deposit.

Evaluate the electrochemical stability according to three different cases of electrolytic detachment in electrolytic etching and chemical etching by using either phosphoric acid or Sodium hydroxide solutions in hydrochloric acid as aggressive media before and after coloring with copper nanoparticles in their pores was studied. Results show that etching with NaOH produces nanoporous 'AAO' having the lowest stability due to its thinning barrier layer while etching with phosphoric acid does not act on dissolution of the inner part of grown anodic film. Black colored anodized samples controlled by pore size and filling factor of pores. Etching with phosphoric acid show the lowest stability due to thickness of its outer layer being highest which lead to increased filling factor by metallic nano-copper make the sample more susceptible to galvanic corrosion [30].

Comparing between performances 'AAO' film fabricated by different successive steps electrolytic polished, 1st anodization, 2nd anodization and electrodeposited copper in aggressive media of sulphuric acid with respect to base Al metal were studied [31]. The oxide film thickness (d) is a direct function capacitance of barrier film was represented in Figure (11).

The results revealed that surface stability is strictly influenced by samples preparation; corrosion resistance R_{total} ($R_{outer\ porous}$+ $R_{inner\ barrier}$) decreases in the following order: EP> 1st> 2nd> colored > bare Al. The thickness of oxide film becomes thicker when subject to EP accompanied by highest resistance, 2nd anodization self-organized nanoporous layer stems on the expense of the barrier layer that remains after the electro-polishing step as a result it has a thinner barrier layer covered with a much thicker outer porous layer.

While coloring by copper atoms inside nanopores acquires sample thickening barrier layer may occur during the coloring step due to applied Ac voltage used. Electrolytic coloring by two type's addition of metal ions Sn and Ni was studied in saline solution. Electro-deposition of these metals occurred after 1st anodization and 2nd anodization to discover the impact of ordered and regular nanoporous anodic film than that in non-regular.

Comparing which one of the used metal ions (Sn or Ni) has strong resistance to the chloride ions attack, variation of samples morphologically represented in Figure (12). Variability of metals crystals content into nanocomposite of porous Al_2O_3 in both 1st and 2nd anodized films was noticed. Second anodization constitutes a dense porous film and a great number of hexagonal columns with nano-diameter pores opened. The crystal lattice appearance regularity and a gradual improvement directed to the perfect hexagonal arrangement were observed. Metal ions were deposited and neutralized into columns until the filling of the porous film was controlled by the conditions of anodization and coloring. A dense tin fills the columns of the anodic film more than the amount of nickel; this may be imputed to the difference in atomic radius of both Ni (149 pm) and Sn (145 pm) [32]. Amount of metals deposited after 1st anodization smaller than that formed after 2nd anodization this attributed to 1st anodization comprise of non-ordered, nanopillars oxide film which is decomposed easily and the metal is appeared on the exterior surface, while in case of the 2nd anodization the oxide film characterized by more ordered and the metal ions distributed equally. This explained the variation of the deposited amount of metals on the surface in each case. Strategy modified a nanoporous anodized surface is still needs a lot of work must be done in order to fabricate self-organized oxide nanopores. SMAT is a type of nano-crystallization technique that act on grain-refine of the surface of anodized materials; it is an efficient method to enhance the growth rate of the anodic oxide film on the surface with a controlled microstructure, and improve the hydrophobic uniformity of the anodized surface for various metals and alloys through repeated high-energy ball impaction [33]. This technique was suitable for Aluminum, Titanium [34], and stainless steel [35].

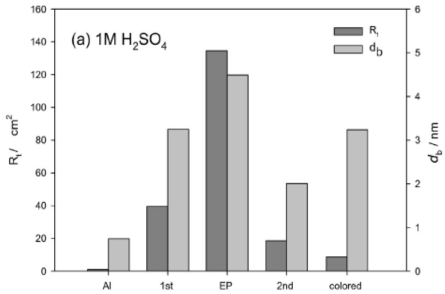


Fig. 11: comparison of the total film resistance (R_t) and its barrier layer thickness (d_b) on uncoated and coated Al samples with different 'AAO' films in sulphuric acid [31].

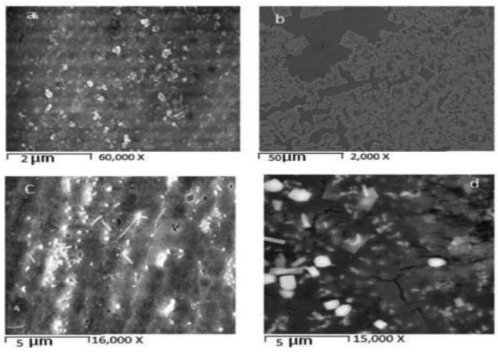


Fig.12: SEM images of colored aluminum after 1st and 2nd anodizing (a, b) Nickel colored and (c, d) Tin colored respectively, after immersion in saline solution [32].

5.3 Surface Mechanical Attrition Treatment (SMAT)

SMAT is applied to an economical anodized surface to generate an anodizing material comprising the anodized surface with an enhanced charge trapping property as compared to the initial material. Since the intrinsic property is material nanocrystallization, a small plastic deformation technique, surface mechanical attrition treatment (SMAT), is used prior to anodization to convert the metal of interest from polycrystalline into nanocrystalline. Novel nanofabrication methods involve two methods surface mechanical attrition treatment (SMAT), and electrochemical anodization. SMAT induces mechanical activation in the form of small plastic deformation to initiate grain refinement [36, 37]. SMAT uses small plastic deformation which is created by random ball bombardment onto the material's surface. Such ball bombardment is induced by the vibration of spherical balls powered by an ultrasonic resonator [38]. The spherical balls are resonated and travel in random directions within the reflecting chamber as shown in Figure (13). The spherical ball is usually in the form of metallic balls or zirconium dioxide balls [40], it was impacted onto the surface of the material. The impact will result in plastic deformation. The balls' movements are multidirectional and random, creating multiple impacts onto the surface of the sample. Repeated impacts result in surface defects and an accumulation of plastic strain, which activates and builds up dislocations [41, 42]. Dislocations will activate grain division. As grain subdivision continues, it will transform from fine to ultrafine, and ultimately completes the process of nanocrystallization, where the grains are in the nanometer regime and cannot be further refined. As the grain size decreases, the density of grain boundaries increases [43]. Therefore a material becomes nanocrystalline.

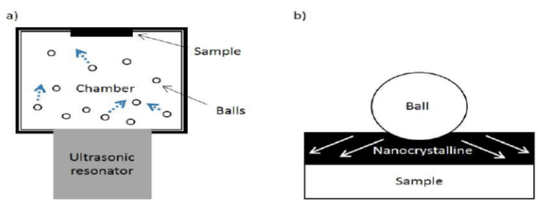


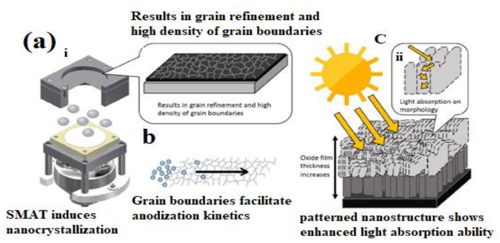
Fig.13: Schematic illustrations of SMAT: a) sample subjected to ultrasonic ball bombardment inside a reflecting chamber, b) localized plastic deformation (with arrows indicated) induced by one ball bombardment on sample [39].

6. *Role of (SMAT) on the Electrochemical and Mechanical properties of Metallic Materials*

Selected three different metals and special alloy represented to demonstrate how nanocrystallization by SMAT contributes in the enhancements of anodization.

6.1 Tin

Tin is a soft and ductile metal. When oxidized, it becomes a highly electrically conductive metal oxide [43]. This makes tin oxide one of the leading candidates in fabrication of nanoporous materials; it is equipped with dual valency. Its cations can be reduced to a state of Sn^{2+} or Sn^{4+} as a result due to its multi-state in surface electronics, the band gap energy can be modified and therefore, increase its flexibility in conductivity. Such property expands the application potentials of tin oxide. Bulk pieces of tin experience grain recrystallization and result in ultrafine nanostructures with a high density of grain boundaries as shown in Figure (14a). The established network of grain boundaries facilitates anodization kinetics by serving as "shortcuts" during chemical diffusion as shown in Figure (14b). Therefore, the thickness of tin anodized oxide film from SMAT pretreated was revealed to be significantly improved up to 72% compared to its coarse grain counterpart. The tin oxide consists of paralleled nanostructures displays a zigzagged patterned morphology as shown in Figure (14c, d) schematic of Tin oxide layers after anodization. In addition, this novel patterned nanostructure was more enhanced light absorption ability through its morphological characteristic and thus it improved photocatalytic performance. Tin oxide performance increased to 76% in the kinetics of photocatalytic degradation. The fabrication of this novel patterned Tin oxide opens an advanced pathway in the development of functional nanoporous monolithic metal oxides [44].



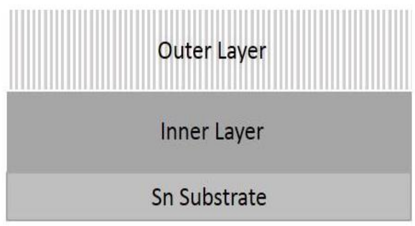


Fig.14: Tin sample nano-crystallization during SMAT and anodization, (d) schematic of tin oxide layers after anodization [39].

6.2 Aluminum

Aluminum is one of the most abundant metallic materials and its oxide state serves in many applications. Its surface is very sensitive to the most exposed environments, especially towards oxygen. Once exposed, an oxide film is formed to prevent further corrosion. Up till now, pore dimensions and geometries of aluminum oxide film are influenced solely by varying the parameters in electrochemistry [45]. The novelty in fabrication has reached saturation with new methods (SMAT + Anodization). SMAT process can be controlled the diameters of the anodic pores and tune them. The pore diameter in anodic aluminum subjected to SMAT is 5.6 times smaller than normal aluminum under the same anodic conditions. Moreover, the anodic pores tuned by SMAT demonstrated better mechanical properties in hardness and elastic modulus when compared to their counterpart. This is represented as a sketch in Figure (15) for fabricated AAO before and after treatment. The bulk of aluminum is subjected to plastic straining through ultrasonic ball bombardment causing a grain refinement process known as nanocrystallization Figure (16 a i and ii). During SMAT, ultrasonic balls induced plastic strain energy onto the surface Figure (16b i), and initiated nanocrystallization until the grains are refined to the nanometer regime. Grain refinement results in a vast network of grain boundaries. Such network serves as "shortcuts" for chemical diffusion and facilitates anodization Figure (16b ii). By imposing higher strain energy through the usage of smaller diameters of balls in ultrasonic ball bombardment, it results in the buildup of more "shortcuts" for faster anodic kinetics and consequently the formation of porous anodic aluminum structure. This novel fabricated 'AAO' by SMAT demonstrates improved mechanical and scratch resistance properties Figure (16c). The tuning of pores results in porosity within the anodic structure.

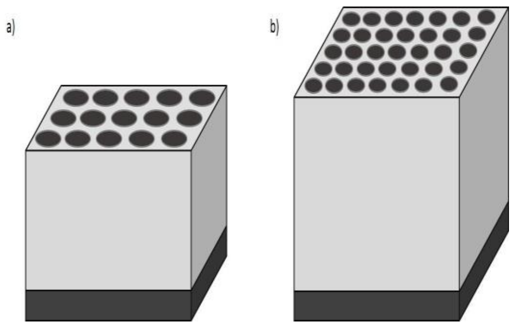


Fig. 15: Schematics of the fabricated AAO: a) without the pretreatment of SMAT, b) with pretreatment of SMAT [39].

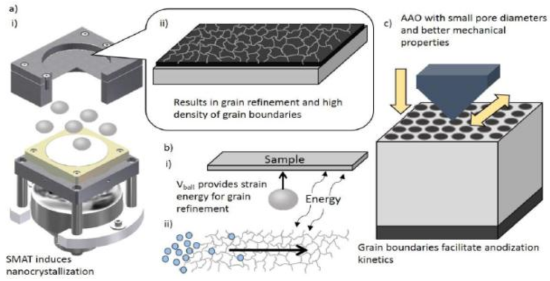


Fig.16:a i) aluminum are subjected to plastic straining, ii) grain refinement in nanocrystallization, b i) ultrasonic ball induce plastic strain energy onto sample, ii) grain boundaries as "shortcuts" for anodization kinetics, c) AAO with smaller pore diameters and improved mechanical properties [39].

6.3 Nickel

Nickel oxide, a transitional metal oxide with the chemical formula NiO, is a semiconductor with band gap energy of 4.0 eV [46]. It consists of octahedral Ni^{2+} and O^{2-} sites. The merits of such lattice structure allow nickel oxide to exhibits outstanding electrochemical stability and durability. Moreover, nickel oxide is relatively low in price, giving it an economical leading edge in fabrication and production [47]. Up till now, various fabrication techniques employing nickel oxide have been used. The goal is to fabricate nanocrystalline NiO achieved by SMAT prior to anodization as shown in Figure (17) that shows the process of treatment and its results. Finally, it will be obtained nanostructures size and morphology, with considered some effects of optimum surface volume, quantum size, and macroscopic quantum tunnel [48]. Such effects stem from novel results and introduce new applications. For example, supercapacitors, gas sensors, and electrochromic films [49-52]. Nanocrystalline NiO has many undiscovered findings, new fabrication methods (SMAT + anodization) will be the key in future developments of nickel oxide.

6.4 Nickel Titanium alloy (NiTi)

The metal alloy of $Ni_{56.1}Ti_{43.9}$ applicable in various applications SMAT is a novel method for conveniently treating delicate nanostructures. It can be tailored to treat the delicate and brittle substrate nanomaterials using anodization procedures as TiO_2NT arrays grown. Figure (18 a, b) shows SEM micrographs sample subject to anodization after a 1 and 5 min. respectively. Stating difference attributed to edge effect of the electrical field.

Time of anodization and SMAT treatment has important effect on changing color from tan to black and morphology of treated surface, indicating its modified electric structure. It should be pointed out that SMAT is able to induce strain facilitated doping as well which created by the continuous and repeated collisions of the tiny SMAT balls with nanostructures.

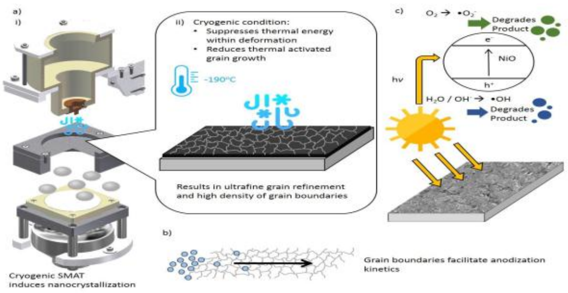


Fig.17:a i) nickel sample nanocrystallization during SMAT, ii) SMAT induces grain refinement and buildup of grain boundaries efficiently without any thermal activated grain growth under the merits of cryogenic cooling, b) grain boundaries serve as “pathways” in transporting ions and atoms in anodic kinetics, c) nickel oxide with enhanced light absorption ability for photocatalytic degradation [39]

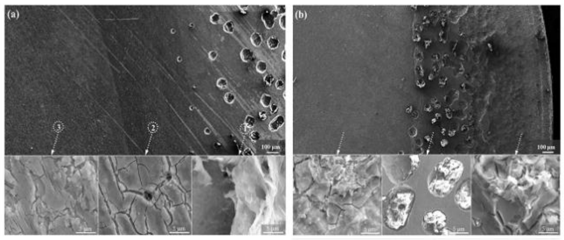


Fig.18: SEM of NiTi subjected to SAMT then anodization for (a) 1min and (b) 5 min [٣٣].

5. **Applications**

The key aspect in many applications is the efficient design ordered of nanopores which self-organized growth for suitable nanotechnology applications and avoid the undesirable cons that can be properly suppressed. Widespread efforts are underway to promote their effective use in the realm of corrosion control. The integration of SMAT and anodization can open up an opportunity to create new nanostructures, improve existing mechanical and electrochemical properties, thus creating better applications for the world. In the following years, researchers had investigated a variety of applications for using aluminum in Transportation about Automotive to reduce vehicle weight for fuel savings by offering a corrosion- free material with the design flexibility to combine multiple functions in one part. Development of the fuel cell can convert the chemical energy from a fuel into electricity through an electrochemical reaction as Al-air energy storage systems which has a variety of applications as power sources for electric vehicles (EVs) [53, ٥٤], military communications [55], unmanned underwater vehicle (UUVs) [56], and unmanned aerial vehicle (UAVs) [57]. Anodic Tin oxide used for hydrogen gas sensing [58], fabricated as coatings with super-hydrophobic abilities on anodic aluminum oxide for self-cleaning applications [59], is one of the anodic oxides that are applicable in Photocatalyst. Whereas Photocatalytic reactions, activated by light energy consists of ultraviolet or visible light, suitable for applications such as water-splitting and hydrogen production [60], Also the one-dimensional, vertically oriented pores with intersecting microgaps and nanochannels can be fabricated through controlling the anodization current for application in Na-ion battery [61] ·and removal of contaminations in the environment [62].

Currently, titanium and its alloys are widely used for the fabrication of implants to replace hard tissue in orthopedics. In November 2017 the data performed implant failure rate reached more than 25% [63]. The anodization method received specific attention due to its versatility in creating nanophase topographies by tailoring the electrochemical parameters. In the following years, scientists reached to improve bone cell functions in vitro and in vivo on anodized nano-featured titanium oxide film; making it one of the promising materials in the depth-orthopedics field [64]. In order to identify a suitable and modern market for the future, this related to response to the market and its detailed analysis of uses anodic oxides are required. So, an optimum material system shall be selected for scale up in fabrication for more realistic results. Nowadays, anodic aluminum oxide layers have motivated considerable scientific and technological interest, because they constitute an organized porosity at a nanoscopic scale till 5-10 nm of diameter, to form self-organized layers made up of nanotubes or nano-channels perpendicular to the metal over a thickness of several micrometers. These nanostructured oxides are exploited in many applications. There are exists of other effects from SMAT which are yet to be discoverd. The future of SMAT consists of many pathways like the surface mechanical alloying that means fabricated anodic oxide coatings on pure aluminum. These are suitably used for space environment applications, these provide specific thermo-optical properties to spacecraft surface; in addition to it is used extensively for a wide range of applications.

Surface mechanical alloying (SMA) applied to modification the composition of metal by alloying with other nanomaterials its particles as nano size through SMAT prior to anodization to fabricated Nano-composites coating. Composite coatings increased generally corrosion resistance and wear resistance. Surface alloying of powder mixture was carried out inside newly designed SMAT machines with a modified cylindrical cavity (Egyptian patent no. 527, 2016). The additions of any powder sample with SMAT method (second SMAT process) to the pre-treated Al substrate subject to the SMAT method (first SMAT) will enhance the insertion of this powder sample through the micro-cavities of the Al substrate that previously induced with the first SMAT process at a certain vibration. Those powder sample additions could be easily taken up by the deformation formed (micro-cavities) on the Al surfaces during the second SMAT processing (SMAT surface alloying). Where the pressure exerted on the powder additions was due to the mass flow of numerous spherical stainless steel balls. The alloying of a powder mixture of Al_2O_3 [64], MWCNTs [65], Fiber Glass [66], and nitrite were prepared. SMAT treatment improves the strength and aesthetics of aluminum extrusion products for easy maintenance and long life in any conditions

Conclusion

Nowadays electrochemical process has drawn attention in academic research, particularly in the field of nanotechnology. An anodizing process is not only dedicated to the improvement of the technical quality of the anodic films for various marketable applications but also, to the production of the film at an efficient rate and cost. This review takes a look at some of the latter advances in anodizing process for several metals; it has long been necessary processes in the surface finishing industry, nowadays become one of the supreme important processes in nanotechnology for developing nanostructured and advanced nano-devices. Modern fabrication techniques involved in anodic nano-porous metal production focus on the variation of extrinsic properties. SMAT before anodizing is a new tool for fabricating anodic metal oxide with new morphology.

Funding

No funding is available.

Declarations

Conflict of interest No conflict exist and the authors declare that they have no conflict of interest

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