WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.084
Volume 9, Issue 8, 591-600. Review Article ISSN 2277– 7105

NANOSTRUCTURED MATERIALS WITH ELECTRODEPOSITION– A REVIEW

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Article Received on
01 June 2020,
Revised on 22 June 2020,
Accepted on 13 July 2020,
DOI: 10.20959/wjpr20208-18132

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ABSTRACT

Materials with size of few nanometers are known as Nanostructured materials. Electrochemical techniques play an important role in the modern concept of nanotechnology. When it comes to fabrication of nanostructured materials, offering control over the structure, composition and properties, electrodeposition is used which in turn facilitates the preparation of novel materials with enhanced properties which are unattainable by the help of any other techniques. Electrodeposition has an immense potential to grow premium quality ultrathin magnetic layers equipped with magnetic properties. It plays a major role in the development of new magnetic materials while contributing to the micro and nano scaled research of magnetism. Electrodeposition technique was used successfully to synthesize nanostructured electrodes of ZnxCd1-x (O) on ITO glass substrate in an aqueous medium containing Zinc and Cadmium ions for energy generating photovoltaic cell. This process of photovoltaic conversion of solar energy is deemed to be the most promising source of renewable energy, this being the need of the hour.

KEYWORDS: Electrodeposition, Fabrication, Nanostructured, materials.

I. INTRODUCTION

The structural dimensions smaller than 100 nm at the nanometer scale are considered as nanostructured materials. Nanostructured materials of various kinds share two main characteristics:

a) The atomic domains (grains or phases) are confined in space to sub micrometric domains,
b) A high fraction of atoms is found in interfacial regions.

Nanostructured materials can be classified as three-dimensional nanostructures. Metallic systems with every kind of dimensionality can be obtained through the process of electrodeposition but the scope for application is broadest for the three-dimensional ones. Size effects of nanostructured materials can be well integrated by reducing the size of the constituent compounds. Electrodeposition has great potential to change the phase of deposits during the process of heating or cooling. At room temperature, deposits present in the amorphous state after annealing at elevated temperatures change their phase to crystalline. This conversion of amorphous to crystalline phase proves to be useful for rewriting optical storage and solid-state memory.[1] Development in electronic applications with the help of electrodeposition can be acknowledged by stating certain examples like wiring of printed circuits and interconnections of multilayer microchips. This paper covers the topic of electrodeposition of nanostructured metals and provides a comprehensive review on nanostructured materials, their properties and methods of analysis available for the same.[2-6]

II. Electrodeposition Methods of Nanostructured Metallic Systems

Electrodeposition is the most compatible technique for preparation of nanostructured thin films from aqueous solution in the form of nano rods, nanowires, nanotubes, and nano ribbons have special physical properties and potential application in nano devices.[7]

a) Nano electrodeposition[8,9] is a preparation method for reproducibility. The defect introduction mechanism giving rise to the nano crystallinity is intrinsic of the growth method, rather than being built-in by a material post-treatment process. This property exists due to electrodeposition processing routes broadening the range of nano electrodeposited metallic systems which can be then produced.

b) One of the most attractive techniques is the Pulse-electroplating, due to its distinctive structures obtained by the pulse electroplating process and certain novel properties of the nanostructure. Parameters influencing the nanostructures produced by electroplating process are used for better understanding the research objective by the way of how each parameter is involved in the formation and mechanism of the nano crystalline structure. Pulse-plating can produce untutored deposits by the enhancement of the nucleation stage.[10,11]

c) Pulsed electroplating and synchronized ultrasound pulses when combined, the process of sono-electrodeposition is carried out.[12,13] High-density fine powder was obtained, originating from the fact that the electrodeposited nuclei are expelled from the cathode surface by the high-intensity ultrasound pulse, thus impeding their growth.

d) Organic additives through the molecular action of adsorbed species on the electrode behaviour influence the distribution and dimensions of grain. Recent findings highlight the process of electrodeposition as an innovative approach towards the preparation of nanostructured materials. This process proves to be effective in cost reduction and no equipment- intensive method to enable the process of preparation of nano crystalline and metallic materials which are nano sized (metals and their alloys, compositionally modulated alloys and composites) either as coatings or as freestanding objects even in complex shapes (foils, wires, electroforms). Higher deviation from the equilibrium state is expected of nanostructured deposits which are obtained under conditions of much higher electrode polarization which might further result in stabilization of out-of-equilibrium crystallographic systems.

III. Functional Properties of Nanostructured Metals

Nanostructured metals exhibit certain properties which are considered novel such as catalytic, magnetic, electronic and plastic properties along with wear resistance and residual stress. These are seen because of the nano building units and high surface/volume ratio.[14] The properties are stated below:

A. Catalytic properties

The electro catalytic properties are determined by the irregularities on the surface at nano metric level. Reactivity of small metal clusters varies by orders of magnitude when the cluster size changes by a few atoms.[15] Small particle size and a higher surface-to-volume ratio provides nanostructured catalysts with their special properties[44] making them strong competitors for applications like fuel cells and electrode for hydrogen evolution. Distinct electro catalytic effects can be seen when modified electrodes with monoatomic metallic layers are absorbed on to metallic surfaces.[16]

B. Magnetic properties

Nanostructured ferromagnetic materials are expected to exhibit low coercivity. In addition, Grain-size reduction has limited effects on magnetization.[17-20] Strengthened magnetic properties and high wear resistance when combined, leads to an idealistic amalgamation of properties for magnetic recording materials.[21] Metallic multilayers of Nano metric thickness, alternating magnetic and non-magnetic layers, are attractive for giant magneto resistance applications. The hard-magnetic properties for the bulk amorphous alloys are presumably due to the homogeneous development of ferromagnetic clusters with large random magnetic anisotropy.[22]

C. Electronic properties

In nanostructured metals, grain boundaries have large volume fraction which gives rise to an enhanced electrical resistivity[23], acting as an advantage for soft magnetic materials.

D. Wear resistance

A very few systematic investigations on pure nanostructured metals have been made[24,25] while studies on the wear behaviour of nanostructured materials majorly focus on dual-phase alloys and composites.[26] Wear resistance of nanostructured metals and metal-matrix composites would improve impressively if grain reduction is followed through. Nano lamellar systems prove to be considerably better than the coarse-lamellar analogues or corresponding alloys for mild wear situations. These conditions are better described by the Archard law[27] which describes the way wear resistance correlates with system hardness.

E. Plastic properties

The study on the plastic properties is rather biased towards the indention methods, particularly hardness testing due to the limited dimensions of nanostructured metal. While grain dimensions are decreased to a certain point where dislocation sources cannot function under the applied stress field, an increase in hardness is expected to follow. A rapid decrease of the yield stress with grain dimensions can be expected when the inter crystalline flow mechanism is active, which gives rise to grain-boundary flow with the possibility of plastic behaviour of typically brittle systems like intermetallic[28] and low-temperature superplastic behaviour.[29]

F. Residual stress

When the individual nano crystals tend to grow, attractive forces bridge the gap between them but since the process is hindered by the interaction with the substrate or the underlying deposit, stress originates.[30] Thus, grain growth can be used to make the coarse-grained deposits crack-free and also provide stress relief; cracking is the only method to release high internal stresses for nanostructured materials.

Certain electrodeposited materials having both magnetic and electrical properties are used in high efficiency transformers, motor application and power supplies due to their attractiveness as soft magnets. Also, next generation recording head materials can also benefit from having magnetic, chemical and wear properties increasing their application tenfold.

IV. Structure of Nano Crystalline Metals

The structure of Nano sized metals is thermodynamically unstable and prone to changes under annealing[31-33] or at room temperature.[34-37] These changes generally affect the grain size, density of crystalline defects, grain boundary structure and crystallographic orientation. At the nanometer scale, where the atomic fraction of interfacial atoms is comparable to that in the perfect crystalline sites, structure of grain joints remains unstable at room temperature while tending to evolve in a more ordered state. The inter crystalline volume representing a region of stored excess energy with keeping the bulk of a grain in mind, acts as a progressive driving force in nano crystalline materials for grain growth. The variation of inter crystalline volume fraction[38] can be correlated to the nano crystalline structure's enthalpy released due to annealing which can be directly measured by Differential scanning calorimetry[39] and can be related to the variation of the inter crystalline volume fraction. During such process of annealing of Nano electrodeposits, occurrence of quasi-nucleation-growth processes have been reported.[40] Typically, nano sized crystallites grows in a random order, whereas some of them act as nuclei while preferentially growing at the expense of the surrounding nano crystalline material ensuing the occurrence of normal and abnormal grain growth processes, which further depends on the constitution of the original material and the microstructural evolution in the premature stages of the grain growth.[41-43]

V. Methods For The Study of Nano Electrodeposits

There are many experimental methods which have been reported in the literature for the investigation of nano electrodeposition systems. These methods include electron microscopies and scanning-probe techniques, diffractometry, spectroscopy (atomic adsorption, characteristic X-rays, mass, Mossbauer, photoelectron, visible), calorimetric, magnetometer and mechanical measurements etc.

S.no.	Methods for Analysis of Nano Electrodeposits	Application
I.	Atomic absorption spectroscopy	compositional analyses of alloys
II.	Bending test	Ductility test of Nano electrodeposited layers
III.	Characteristic X-rays spectroscopy	compositional analyses of alloys
IV.	Differential scanning calorimetry	evaluation of the thermal stability of nanograined electrdeposits

V.	Differential thermal analysis	crystallization behaviour of alloys
VI.	Extended X-ray absorption	nanocrystalline electrodeposited alloys structures
VII.	Field-emission scanning electron microscopy	Metallographic observation of nanocrystals
VIII.	High-resolution transmission electron microscopy	analysis of the nanocrystallisation of X-ray amorphous electrodeposits
IX.	Inductively coupled plasma optical emission spectrometry	evaluation of some mechanical properties of nanoelectrodeposits.
X.	Infrared absorption spectroscopy	Measurement of the total sulphur and carbon contents of nanocrystalline Ni electrodeposits
XI.	Inductively coupled plasma mass spectrometry	analysis of impurities deriving from bath components
XII.	Time-of-flight mass spectrometry	analysis of samples containing variable amounts of Fe nanocrystals in a Cu matrix
XIII.	Optical microscopy	in-situ monitoring of fractal growth
XIV.	Positron lifetime measurements	evaluation of voids and cavities, mainly located at grain boundaries of nanocrystalline Ni electrodeposits
XV.	Scanning electron microscopy	in-plane morphology of nanoelectrodeposits
XVI.	Scanning-probe microscopy	characterisation of thermodynamic, structural and kinetic aspects of electrochemical interfaces
XVII.	Selected area electron diffraction	discrimination of metallic nanometric phases
XVIII.	Small-angle X-ray scattering	measurement of the dimension distribution of nanometric clusters
XIX.	Superconductive quantum interference device	measurement of the magnetisation of samples
XX.	Surface enhanced Raman spectroscopy	detection and analysis of contaminants incorporated into nanoelectrodeposits
XXI.	Transmission electron microscopy	determination of nanometric features
XXII.	Vibrating sample magnetometry	measurement of coercivity and loop squareness in magnetic deposits
XXIII.	Visible spectroscopy	quantitative determination of the composition of alloy deposits
XXIV.	X-ray diffraction line broadening analysis	estimate of average grain size
XXV.	X-ray photoelectron spectroscopy	detection of incorporated organic species
XXVI.	Nanoscratching	Wear testing of nanoelectrodeposits

VI. Overview of Nano Electrodeposited Metals and Alloys

When, electrodeposition for the fabrication of nanostructured ceramic materials is considered electrochemical deposition of ceramic coatings for biomedical applications has seen the greatest number of advances. Implementation of electrodeposition required preparation of thin films of hydroxyapatite using an electrolytic deposition.[44] or electrophoretic deposition.[45-47] Hydroxyapatite is a permanent material used as an implant material due to its chemical composition which is close to that of bone tissue. Aqueous solutions containing calcium and phosphate ions help prepare nanostructured coatings of hydroxyapatite through the process of electrodeposition.[48] The process of electrochemical deposition constitutes as a fresher perspective to the fusion of biomedical coatings and composites. It is considered to be a valuable contributor to the field of nanostructured compounds. Solar cells, chemical sensors, catalysis and semiconductor diodes have developed a certain usage of nanostructured ZnO proving to be an important part of their application.[49-51] Electrodeposited nanomaterial having composition of Nickel proves to be useful for corrosion control and protection. It can further be used to develop cracking resistance and is also used for purification process. It is also used in fuel cells. Gas sensors, biomedical implant, solar cells and electro chromic devices are a few examples using the electrodeposited Titanium in their outer coating which further raises their value.[52] Films made of Palladium and Iron has nanoscale thickness and due to their malleable composition can grow from the organic solutions through pulsed electrodeposition. Palladium and iron films having 12–98% of iron content is ferromagnetic at room temperature. Basis of magnetization of the films is their iron content which increases linearly with the increasing concentration of iron.

Fabrication of ceramic nanowires through the process of electrodeposition is proving to be an upcoming field of interest. Different bath composition and deposition framework gives control over the morphology and permeability of the films. These nanostructured films have an important application in solar cells.

VII. CONCLUSION

The advances in the field of nanotechnology necessitate the parallel progress of nanometrology which is the application of tools and techniques to characterize and manipulate nanostructures. Electrochemical techniques have an important role in the modern concept of nanotechnology. Electrodeposition is used for controlling the structure, composition and properties during the process of fabrication of nanostructured materials. This in turn facilitates the preparation of novel materials with features unattainable by any other techniques or processes. Also, electrodeposition proves to be an important contributor towards the development of nanostructured compounds. It can be safely said that nanotechnology is an emerging technology with immense potential having the possibility of advancement of pre- existing products and for creation of new range of better products with impressive characteristics and features having a wide range of applications.

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