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Characterization of Composite Material with Prepared Nanoparticles by Laser Ablation As Anti-Corrosion Material

A Thesis

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بسم الله الرحمن الرحيم

﴿ وَفَوْقَ كُلِّ ذِي عِلْمٍ عَلِيمٌ ﴾

صدق الله العظيم

سورة يوسف الآية(76)

DEDICATION

To my kind father..... who taught me how to live with dignity and honor.

To my dear mother..... I can't find words that can give her right, she is the epic of love and the joy of a lifetime,

An example of dedication and giving.

To my husband..... the highest symbols of sincerity, loyalty, and companion on the way (Noor-Aldeen).

To my brothers.....my support who shared my joys and sorrows.

To my children..... So that is my heart (Marwan and Lareen).

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I dedicate this work to you...

Quds

Thanks And Gratitude

Praise be to God, and thanks be to God for His, mercy, and grace for me to complete the work of this message, and for which no effort and work is completed except by His grace, praise be to God, a great thank you, as it should be worthy of the majesty of His countenance and the greatness of His authority. The envoy is a mercy to the worlds, the master of creation and the imam of the prophets and messengers, our master Muhammad and all his family and companions.

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And to the soul of my deceased grandfather, how I wish you were by my side, may God have mercy on you and put you in peace.

In conclusion, I tell them all my love and affection for you, and I ask God Almighty to protect them and bless them.

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List of Symbols

Symbol	Description	Unit
ρ	Density	Kg/m^3
ΔG	Change in free energy	joules/mol
d_{hkl}	space between two parallel planes inside the crystal	A°
θ	is the angle of incidence	Deg
β	Full Width at Half Maximum	Rad
λ	The wavelength of X-rays falling on the target	A°
a_0	lattice constant	A°
CR	corrosion rate	g/m^2day
Ea	the activation energy and it is defined as the minimum amount of energy that a substance must possess in order for the collision to be effective	joules/mol
A	Arinos constant	-
R	The general constant of gases and its value	J/k.mol
C_i	The Heat Capacity of The Lattice	Joule/Kelvin
T	Temperature	C°
Z	Depth	m
∝	Absorption Coefficient	cm^{-1}
K	Thermal Conductivity Coefficient	$^{w}/_{m^2k}$
D	Heat Diffusion Coefficient	-
τ	Pulse Duration	ns

List of Abbreviations

ABBREVIATION	MEANING
PLAL	Pulsed Laser Ablation in Liquids
YSZ	Yttria Stabilized Zirconia
CSZ	Ceria-Stabilized Zirconia
Al-NPs	Aluminum Nanoparticles
DW	Distilled Water
SPR	Surface Plasmon Resonance
Fcc	face-centered cubic
XRD	X- ray diffraction
hkl	Miller indices
FTIR	Fourier Transform Infrared
FE-SEM	Field Emission Scanning Electron Microscopy
PLD	Pulsed Laser Deposition
GNP	Gross National Product
UV	Ultraviolet
NZVI	Nanoscale Zero-valent Iron

Abstract

In this study, aluminum nanoparticles (Al NPs) were successfully obtained by pulsed laser ablation in liquid (PLAL) with different pulse frequencies (500, 600, and 700 pulses/s). showed that the resulting Al NPs have a polycrystalline structure and a cubic phase. Planes (111) and (200) correspond to peaks at (2θ=38.08° and 44.03°). The average size of nanoparticle crystallites was estimated by the Scherrer method and amounted to (17.52) nm. Field Emission Scanning Electron Microscopy (FE-SEM) images of Al samples were taken at counts (500, 600 and 700). From these pictures, it can be seen that the particle size is approximately (177.4 nm). Al NPs prepared with 600 pulses are in an aggregated form. Agglomeration makes particles appear much larger than they really are. It can be seen from these images that the particle size is approximately (136.0 nm). Al nanoparticles obtained using 700 pulses have a shape close to spherical and cubic, and different sizes. Aggregation of Al nanoparticles occurs due to strong interactions. The average NP grain size observed in FE-SEM images is (123.1 nm). Chemical analysis using energy dispersive spectroscopy (EDS) was used to confirm the chemical analysis of Al NPs. It shows that the only visible peaks are oxygen (O) and aluminum (Al), making up 85.2% and 14.8% of the total atomic percent, respectively. Appearance High percentage of elemental oxygen as a result of thin film oxidation during manufacturing. Fourier Transform Infrared Spectroscopy (FTIR) ranges for the aluminum metal test: 419.18 and 443.27 cm-1 Crossover and longitudinal examples of AL-OH retention groups are seen at low frequencies. aluminum has 1637.93 cm-1 (C-O). 2076.25 cm-1 (C=C) for aluminum. The hard top at 3466.02 cm-1 corresponds to the OH elongation. In the absorption spectra of Al NPs at 500, 600, and 700 pulses, it was noted that the Surface

Plasmon Resonance (SPR) shift shifted toward shorter wavelengths (blue shift) as the number of laser pulses increased. This indicates smaller nanoparticles. As the number of pulses increases, the bandwidth and the maximum absorption wavelength change insignificantly. As the number of pulses increases, the position of the peak becomes unstable. Epoxy resin and aluminum nanoparticles have been used to mitigate the corrosion of iron. The X-ray diffraction pattern of metallic Fe shows that the pattern shows diffraction peaks around ($2\theta \sim 44.62°$ and $64.89°$), called the preferred directions (110) and (200) respectively. The position of the peaks and the presence of multiple diffraction peaks are given. We came to the conclusion that the metal is polycrystalline with a cubic structure. Reinforcing an epoxy coating with aluminum nanoparticles leads to an increase in the corrosion resistance of iron, and FE-SEM of metallic Fe also proves that the effectiveness of an epoxy coating is improved after reinforcement with aluminum nanoparticles. We also test the hardness and corrosion rate of iron in saline environments (1%, 2% and 3%) and acidic aqueous environments (pH=1, pH=2, pH=3) at various temperatures. (30,40,50°C).

CHAPTER ONE

Introduction and Literature Review

1-1 Introduction

The application of nanotechnology in the field of corrosion protection of metals and alloys attracts the attention of researchers. Many of these applications require good understanding of the corrosion behavior of the materials as a function of microstructure. Significant progress has been made in various aspects of synthesis of nano scale materials. In addition, nanostructures promote selective oxidation, forming a protective oxide scale with superior adhesion to the substrate. Nanostructured materials of 1–100 nm are known for their out- standing mechanical and physical properties due to their extremely fine grain size and high grain boundary volume fraction [1]. They are important due to their unique properties that may lead to new and exciting applications [2]. Nanocomposite of polymer coating can effectively combine the benefits of organic polymers, such as elasticity and water resistance to that of advanced inorganic materials, such as hardness and permeability. The nanostructured silica coating showed comparable or better performance than hexavalent chrome pas- sivation [3, 4]. Anti-corrosion describes the measurements that are used to combat the occurrence and progression of corrosion. These can be techniques that are applied to reduce the negative effects of corrosion. There are many anti-corrosion techniques such as inhibitors, coatings or the utilization of cathodic protection systems by which the consequences of corrosion can be prevented [5].

Among which the laser-assisted fabrication of nanocrystals and functional nanostructures has received great attention over the last decade. Although lots of nanomaterial can be synthesized by conventional production processes, such as metal-organic vapor phase deposition, molecular beam epitaxy, the synthesis technology of pulsed laser ablation in liquid (PLAL) is gradually becoming an attractive approach because it is a chemically simple and clean method with high product purity. Moreover, it can be achieved at normal temperature and pressure, and the properties of the products are controlled by experimental conditions such as laser parameters. solutions, external environment and target material [6]. Among various physical vapor deposition techniques, Pulse Laser Deposition (PLD) is a simple and convenient method for deposition of films and coatings [7]. Corrosion of materials is burning problems for industry, railways, housing, transport vehicle, bridge and sensitive equipment's. It is generally takes place with metals, alloys, polymers, woods, glass and ceramics due to interaction of material with pollutants, effluents, industrial waste, human waste, biological waste, municipal waste, sea water, humid environment, acid rains, emissions, chemical by product, micro-organic and macro-organisms as well as sun light (UV radiation) and heat. Materials possess interfaces structures so they have grain boundaries and interfacial cracks. Other factors like impurities, surface morphology and lattice imperfection in material structures can also increase corrosion rate.

Basically, corrosion starts at the surface of material and reduce their lifetime used regularly in aircraft and spacecraft, land and sea transportation vehicles, bridge, building, antique, museum, sculpture, technical equipment, infrastructure and electronic devices. The corrosion of materials can also lose their mechanical, physical and chemical properties as well as they tarnish their appearances. Industrialized nations are spent 5% of GNP (gross national product) for corrosion protection, replacement of corroded parts, maintenance work and environmental protections.

Surface coating of materials are popular approach for corrosion control. For this purpose, thin film coating is applied on the surface of metal against corrosion attack. Corrosive species such as Cl”, H+, H2O, O2, pollutants and pigments, with substances being suppressed by organic epoxy thin-film coatings are important for metal surface protection.. Protective coating on metal surface is partly control development of electrochemical cell. Otherwise coating substances detach from the metal surface through chemical or electrochemical reactions. It is noticed that corrosion rate is deaccelerated by high polarization and coating resistance, low capacitance and high Warburg impedance that can be achieved by organic films coatings.

Organic coating substances on the metal surface are surrounded by hostile environment so its physical, chemical and physicochemical deterioration starts. Such degradation of coating materials can produce in the form of swelling by water absorption, dissolution, cross-linking, oxidation and color changes due to the heat, radiation, acid rain, global warming, ozone depletion, oxidative chemistry and other factors [8].

1-2 Previous studies

Daroonparvar et al. in (2013)[9] studied the hot corrosion of yttria stabilized zirconia(YSZ), normal Al2O3 and YSZ/nano-Al2O3 coatings was studied in the presence of molten mixture of Na_2SO_4+V_2O_5 at 1000 C. Their results showed the presence of the Al2O3 nanostructure layer on the conventional YSZ layer that coudsignificantiy reduced the salinity of corrosive salts to the YSZ layer during hot corrosion .

Negate et al. in (2014)[10] studied three forms of active hot corrosion of plasma sprayed, normal ceria-stabilized zirconia (CSZ),CSZ/Micro Al2O3, compsite layer and CSZ/ NanoAl2O3 layer composite, in which Al2O3 was a CSZ layer topcoat. The analysis indicated that no harm to the surface of the coating layer due to hot corrosion (CSZ/Nano Al2O3), while a small fraction of the coating layer (CSZ/Micro Al2O3) occurred compared to the usual (CSZ) layer.

Keyvani et al.in (2014)[11] compared the stability of the traditional yttria stabilized zirconia (YSz) coating with the nano sensitive composite (YSZ+Al2O3) coating .On a nickel-based super alloy (Inconel738) base using the plasma spray method. Oxidation and hot corrosion were tested at 1100C and 1050C using Na2SO4 and V2O5 molten salts were performed on the coatings. The results showed that YSZ+Al2O3 structural nano composition layer has batter oxidation resistance than conventional YSZ layer. YSZ+Al2O3 nano composite also showed better resistance to hot corrosion test.

Khadom et al. in (2015)[12] evaluate the high temperature of external corrosion of boiler pipes using weight loss technique. They reported that samples of low carbon steel were supplied from north of Baghdad thermal station and used in their study. Locally supplied fuel ash was used as corrosion environment. Corrosion rate were determined as function time in the absence and presence of fuel ash. The results showed that the corrosion of boiler steel pipes was higher in the presence of fuel ash.

Ismardi et al in (2016)[13] prepared the alumina nanoparticles successfully using the Sol-Gel method. They reported that some properties revealed that the size of the nanoparticles was about 6 nm, with high crystalline structure. The alumina nanoparticles were used with the base liquid to lower the engine cooling model system temperature. It has been show that the thermal properties of nano-fluids were linearly proportional to the concentration of Al2O3 nanoparticles, and the higher concentration in the nanostructure, the less time it takes to reduce the temperature.

Enza Fazioa et al.(2016)[14], studied Iron oxide nanoparticles prepared by laser ablation: Synthesis, structural properties and antimicrobial activity, Pulsed laser ablation of iron rod target in water-based solutions were carried out, varying the ablation parameters. The structural, morphological and compositional characteristics of the nanoparticles were studied by micro-Raman, dynamic light scattering (DLS), X-ray photoelectron (XPS) spectroscopies and electron scanning microscopy (SEM/STEM). Slight changes in the ablation parameters result in significant variations in the nanoparticles morphology. As observed by STEM imaging, particles size and distribution was tuned from agglomerated to nearly spherical structures, mainly changing the medium (water or polyvinyl alcohol PVA water solution). On the other hand, the polymeric phase increases the iron oxide nanoparticles stability, biocompatibility and interactive functions on the surface. Antimicrobial activity of iron oxide nanoparticles on Staphylococcus aureus was studied by means of MTT assay. The results indicate that the iron oxide nanoparticles are interesting for potential applications as vector for drug delivery and as constituent of specific platforms for drug targeting.

Karabasa et al. (2017) [15] studied hot corrosion behavior of alumina-yttria stabilized zirconia particle composite coatings produced by thermal spraying, for use as a thermal barrier by plasma sprayed coating have been exposed to 50 wt % Na2So4 +50 wt % V2O5corrosive molten salt temperatures at 1050C for 60 hours. Their results have shown that the amount of YVo4 crystals on the surface of YSZ coating while Al2O3 increasing in YSZ +Al2O3 composition, therefore, the hot corrosion resistance of TBC improves with the addition ofAl2O3.

Rajeh,et al.in (2017)[16] studied hot corrosion for the alloys used in high temperature . The end of this experiment was to study two types of steel used in steam boilers. The ordinary oxidation processes conducted for specimens of steel in the temperature (550,650,750,850, and 950 $\overset{o}{C}$) for different time and then different temperature are used with constant time (3 h). Coating process for specimens by impurities material in the following percentage (67%wt. V2O5:33wt. Na_2SO_4) were performed. After oxidation of the samples, the change in weight was calculated and then used the inhibitor material (MgO) to decrease the effect of impurities on the steel samples and the oxidation processes doing and calculated the change in weight, the ratio (3Inhibitor:1Ash) inhibitor give best results .

Kadhim et al. (2018)[17] used plasma spraying to investigate the chemical corrosion of super alloy of IN-738 LC coated with zirconia containing 20% wt ceria and 3.6 percent wt yttria and coated on a medium coating layer of Ni24.5Cr6Al0.4Y percent (Wt). Ceria yttria stabilized zirconia (CYSZ) upper surfaces were coated with a salt mixture containing 45 wt percent Na2SO4-55 wt percent V2O5 and tested at temperatures ranging from 800 to 1000 ° C for 1 to 8 hours. An electronic scanning microscope, an energy differential spectrometer, a roughness measurement device, and X-ray diffraction were used to determine the topography of surfaces, roughness, chemical composition, phases, and corrosion products of the top surfaces of the spray layers The phase transformation of non-transformable tetragonal (t') into monoclinic phase was confirmed by XRD analyses of plasma sprayed coatings after hot corrosion. The phase shift was from tetragonal to monoclinic.

Singh et al. in (2020)[18] coated ASTM-SA213-T-22 steel using the plasma spray process with (100Al2O3) and (20 TiO2-Al2O3). In a molten salt setting (Na2SO4- 60 per cent V2O5), the effect of hot corrosion was studied at 900 °C. Each cycle involved heating at ambient temperature for (1 h and 20 min) of cooling. Their tests were analyzed using visual inspection, XRD calculation of mass transition, and an analyzed by SEM / EDS. The coated sample showed decrease of mass by 25.41 percent and 67.02 percent compare with the uncoated sample, respectively.

Rasha Hamed Ahmed conducted (2021)[19] studied preparation of Aluminum Nanoparticles and the effect of Laser by Laser Ablation Method Aluminum nanoparticles by Nd-YAG pulsed laser ablation at a wavelength of 1064 nm at 6 Hz and 250 pulses.. A pure aluminum metal target was immersed in ethanol and the nanoparticles were removed using five different laser energies ranging from (400-800) mj. The effect of the laser energy difference on the optical properties of aluminum nanoparticles was examined. The optical properties were tesed using UV spectroscopy for both the absorption and transmittance spectrum according to the change of laser power. The transmittance changes with the wavelength and laser energy and the best pulsed laser energy works to excise these particles.

Emma White et al. (2022)[20], studied Influence of surface treatment on the metal dusting behavior of alloy 699 XA, Metal dusting attack is a serious problem in processing industries using carbonaceous gases and high temperatures. Ni-based alloy 699 XA was recently developed as an alloy for these types of environments with high resistance against metal dusting. In this study, different surface treatments of this chromium- and aluminum-rich alloy are shown to have an important influence on the metal dusting onset behavior. It was found that surface treatments that are traditionally considered to be helpful for fatigue performance, for example, shot peening, and pickling were detrimental to the metal dusting performance of alloy 699 XA. Additionally, the shot peening surface treatment promoted Fe surface contamination, resulting in a negative impact on the metal dusting pitting resistance of the alloy. Deformation accompanied by apparent BCC α-Cr precipitation in the bulk microstructure, but a comparison with cold-rolled materials shows that the surface treatment dominates the metal dusting resistance.

1-3 Aim of the study

1- The aim of the present work is to characterize the aluminum nano particles prepared by the pulsed laser ablation technique and use them in an anticorrosion application.

2- Study the structural properties for aluminum nanoparticles (Al NPs) prepared by X-Ray diffraction.

3- Study the optical properties and know the absorbance of Al NPs using ultraviolet-visible spectrometer (Uv-Vis) as well as the infrared spectrometer (FTIR) to know the locations of bonds.

4- Studying the dynamic of light scattering and the structural properties by field emission scanning electron microscope (FESEM) to know the shape and size of the Al NPs.

5- Test the hardness and the corrosion rates of iron in saline water media (1%, 2% and 3%) under acidic aqueous media (pH=l, pH=2, pH=3), both at different temperatures (30,40,50 °C).