



Advances in Materials Science Research

Volume
29

Maryann C. Wythers
Editor

NOVA

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ADVANCES IN MATERIALS SCIENCE RESEARCH

**ADVANCES IN MATERIALS
SCIENCE RESEARCH**

VOLUME 29

MARYANN C. WYTHERS
EDITOR



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ADVANCES IN MATERIALS SCIENCE RESEARCH

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SCIENCE RESEARCH**

VOLUME 29

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PREFACE

This book provides readers with the latest developments in materials science research. Chapter One reviews the advances achieved over the last three years by exploiting photo-induced polymerization processes for the obtainment of functional (and often nanostructured) coatings. Chapter Two analyzes superalloy machining. Chapter Three examines a mechanistic exposure of welded Ni-Mo-Cr-Fe alloys in coal gasification syngas plants for morphological and microstructural examination and corrosion mechanism study. Chapter Four discusses atomistic investigations of ion migration in electroactive polymers. Chapter Five focuses on the property and electron shift kinetics of glassy carbon electrodes, and explores biosensor technology that bred diverse trends in detecting heavy metal ions with the adoption of glassy carbon electrode. Chapter Six provides a review of studies regarding antioxidant reaction mechanisms and their electroanalytical applications in glassy carbon electrodes. Chapter Seven investigates the effect of A-site and B-site isovalent doping in Bismuth Titanate ceramics on its dielectric and ferroelectric properties. Chapter Eight concludes with the current progress in the synthesis and luminescence properties of doped Bismuth complex oxides.

Chapter 1 - This chapter reviews the very recent advances achieved over the last three years by exploiting photo-induced polymerization processes for the obtainment of functional (and often nanostructured) coatings. In fact, the high fastness of the polymerization method, together with the low energy consumption and the possibility of designing and tailoring the UV-curable formulations, allows producing smart functional coatings. These latter exhibit the peculiar features required for selected advanced applications. In particular, it is possible to obtain superhydrophobic, thermally and/or electrically conductive, anti-corrosion (nano)coatings. Furthermore, photo-

induced polymerization allows designing nanostructured thin films with high barrier properties toward different gases, as well as nanocoatings for biomedical applications. This surface approach possesses remarkable advantages, as it is able to provide any underlying substrate with the desired functional properties, without changing the structure and behavior of the bulk.

Chapter 2 - Superalloys have a chemical composition with high content of alloying elements, which are responsible for their mechanical and thermal properties; however, these features difficult the machining, leading to occurrence of some troubles during the process. Because of its high mechanical strength and low thermal conductivity, there is a concentration of heat at high temperatures, mainly on the chip-tool interface that complicates its machinability. The objective of this work is the presentation of results obtained during machining study for turning with finishing parameters of the two alloys: Nimonic 80A and Pyromet 31V. In these works were tested alloys both as hot rolled as solubilized and aged, using coated and uncoated cemented carbide tools, with flood fluid applictaion and minimal quantity lubrication (MQL). The wear mechanisms acting for both alloys, using coated tools, the most common were abrasion, attrition, chipping and hammering. While to machining with uncoated tools, the main wear mechanisms were cratering by diffusion, abrasion and oxidation action (notches). The chips shape generated during tests with Pyromet was diverse but predominantly long and it is also highlighted the presence of double chip. Only minor chips was observed with MQL technique. In tests with Nimonic, for some parameters settings it was possible to obtain short chips, but the occurrence of long chips was more frequent for tested conditions.

Chapter 3 - A mechanistic exposure experiment was performed on the commercially available and welded Haynes® HYBRID-BC1® Ni-Mo-Cr-Fe alloy samples (62wt% Ni, 22wt% Mo, 15wt% Cr, 2wt% Fe, 0.5wt% Al, 0.25wt% Mn, 0.08wt% Si, and 0.01wt% C) at coal gasification pilot plant facilities affiliated with the Institute for Advanced Engineering. The alloy samples were pre-oxidized at 400°C under stagnant air atmosphere for 24 h prior to exposure to the corrosive environment (60% CO, 28.4% H₂, 2.5% CO₂, 0.8% CH₄, 600ppm H₂S, and 110ppm carbonyl sulfide under 2.005 MPa and 170°C). Thermodynamic Ellingham-Pourbaix stability diagrams were constructed to provide insight into the mechanism of the observed corrosion behavior prevailing in the piping materials between the particulate removal unit and water scrubber of the coal gasification pilot plant. The thermodynamic inference on the corrosion mechanism was supplemented with the morphological, compositional and microstructural analyses of the exposed

samples using scanning electron microscopy, X-ray diffraction and energy-dispersive X-ray spectroscopy analyses performed on the external and cross-sectional surfaces of the recovered corrosion test samples to comprehensively examine the corrosion scale. X-ray diffraction result revealed stable corrosion products of NiO and MoNi₄ after accumulated total exposure duration of 139 h to the corrosive atmosphere. Scanning electron microscopy and energy-dispersive X-ray spectroscopy positively identified formation of rather continuous and adherent pre-oxidation corrosion products in the alloy samples although extensively peeled-off oxides were finally observed as corrosion scales on the post-exposure alloy samples, which were attributed to the combined effects of evaporation of hydrated Fe, Al, and Cr chlorides and their subsequent transformation into thin (spalled) oxides.

Chapter 4 - The work shows how atomistic methodologies can reveal the motion of ions in polymer lattices, thereby eliciting hitherto experimentally inaccessible information. In static lattice (SL) methods investigating the mechanism of the transport of the ions through conductive polymer (CP) electrodes the studies show the interaction between the host polymer and guest ionic lattices may result in ion channels, enabling the estimation of activation energies. Lattice simulations and electrostatic calculations show how K⁺ ions migrate rather freely through the square channels in polyacetylene, with higher energies for the transport of alkali cations, halogens BF₄⁻ and PF₄⁻ in polythiophene and its 3-derivatives. They also study the thermochromic and piezochromic behaviors of the latter systems.

Molecular dynamics (MD) are applied to the migration of ions in poly(3-alkylthiophene)s and to the entry of solvent into the polymer lattice. Also studied are the novel properties conferred on polythiophene by the addition of a flexible side chain in the 3 position of the thiophene rings, which may make the CP soluble. Polymers resulting from the substitutions producing an amphiphilic monolayer on a water surface and their special behavior are studied. The surface order is disrupted by changing the lateral pressure on the monolayer and also by imposing a redox charge on the thiophene rings of the polythiophene surfactant, in accordance with its CP property. The altered charge density imposes an electrical capacitance of the double layer which is related to the interfacial tension.

An MD investigation in the presence an electric field considers the migration of monovalent ions passing through an artificial channel; the channel is composed of fourteen 15-CE-5 (crown ether) rings rigidly linked in a stacked conformation. The channel, which has a narrow internal diameter, is mounted in a bilayer membrane separating two aqueous regions. The channel

system readily admits alkali metal ions but precludes entry to even the smallest anion (F^-) and to solvent molecules. The dynamics of the M^+ ions are accounted for by the axial electrostatic potential and field. The absence of channel water molecules results in the trajectories of the ion migrants being characterized by damped oscillations. By varying the groups linking the CE rings it is demonstrated that migration is favored by the rings that relax the channel's rigidity, particularly the end rings.

Functionalized polythiophene with acid $[-CH_2-O-CH_2-CH_2-SO_3^-]$ and basic $[-CH_2-O-CH_2-CH_2-N(CH_3)_3^-]$ side-chains in thiophene's 3-position are water-soluble polyelectrolytes. Since linear polymers readily form helical conformations it is supposed that polythiophenes do the same, with a pitch of 14\AA and an internal diameter of 8.2\AA . If the redox property of CPs is applied to charge the thiophene rings it is found that the axial potential is substantially altered, and the channel admits both Na^+ and Cl^- ions without the requirement of an externally imposed axial electric field.

Chapter 5 - Owing to its physical and chemical properties, glassy carbon has become an interesting and widely applied electrode material. It exhibits a rather low oxidation rate and a rather high chemical inertness which, together with very small pore sizes and a small gas and liquid permeability, make glassy carbon a convenient inert electrode. Introduction of newer methods and modification of the existing analytical method for the determination of pollutants constitute a rule in green chemistry. Nowadays, modified methods highly contribute to the development of sensors for pollutants and hazard materials. In this chapter, the characterization and electrochemical activation will be firstly summarized. Then, strategies for glassy carbon electrode surface modification were detail discussed. In the end, the recent application of modified glassy carbon electrode in heavy metal ions determination were summarized.

Chapter 6 - In this chapter, the authors show the results for electrochemical response at glassy carbon electrodes of many antioxidants. Those antioxidants have a great relevance in the agroalimentary industry. The results obtained by the authors' research group provide very important data about thermodynamic, kinetics and electroanalytical properties of natural antioxidants such as lutein, butein, morin, fisetin, eugenol and α , β , γ tocopherols. In addition, data obtained for the synthetic antioxidants such as tert-butyl hydroxyanisole and tert-butyl hydroxytoluene are also discussed. Results found for these substrates at bare glassy carbon electrodes are compared with those obtained at nanostructure modified glassy carbon electrodes such as multiwalled carbon nanotubes, electrochemically reduced

graphene oxide, and ultramicroelectrodes (carbon fiber disk and a Pt band). The main electrochemical techniques used were cyclic and square wave voltammetry. Moreover, the authors also discussed the implementation of sensitive and selective electroanalytical techniques to determine these antioxidants in real matrices of interest for the agroalimentary systems.

Chapter 7 - *BIT: Bismuth Titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$)* is one of the least complicated chemical compositions of the bismuth layer structured ferroelectrics and therefore is an ideal member to study the relationship between the defect structure and conductivity. A-site modification by an isovalent dopant reduces the vacancies formed due to Bi^{3+} volatilization and improves the electrical properties of the ceramics, apart from lowering the Curie temperature T_c . Remnant polarization of the ceramics increases with the increase in the level of the dopant. Behavior of conductivity suggests that conduction in these ceramics is a temperature dependent phenomenon. B-site modification by an isovalent dopant decreases the conductivity due to the electronic hopping between Ti^{3+} and Ti^{4+} . A marked increase in dielectric constant and remnant polarization was observed due to the B-site isovalent dopant, which causes orthorhombic distortion in the bismuth titanate lattice. Simultaneous addition of isovalent dopants at A- and B-sites of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ significantly improves its dielectric and ferroelectric properties as compared to that of pure bismuth titanate ceramic.

Chapter 8 - Bismuth-based complex oxides containing phosphate, vanadate, molybdate tungstate, etc. groups are known for structural diversity providing unique frameworks and outstanding optical, luminescence and catalytic properties. Formation of three-dimensional or layered structures is usually seen to be driven by coordination requirements of bismuth and polyvalent metals within the anionic sublattice. Taking into consideration bismuth-containing salt systems different types of BiOnpolyhedra have been described with $n = 2-8$. Considering coordination peculiarities, bismuth should be treated in a special matter due to the influence of 6s2 lone pair of electrons. Currently, there have been used three common approaches to describe crystal structures of bismuth-containing compounds. The first one represents the building block of fluorite chains $[\text{BiO}_2]$ with comparatively short Bi-O distances 2.30-2.34 Å and coordination number 4. The second one describes the highly distorted open BiOnpolyhedra with $n = 5-6$ and Bi-O distance up to 2.85 Å with localized lone pair of electrons. The third viewpoint includes additional oxygen atoms in the nearest bismuth coordination environment up to coordination number 8-9 and cut-off distances limited to 3.2 Å. In a light of structure-luminescence properties connectivity the peculiarities of rare-earth

activators as well as bismuth role itself requires additional attention as luminescent materials with high quantum yield and low possibility of concentration quenching.

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Chapter 1

RECENT ADVANCES IN UV-CURABLE FUNCTIONAL COATINGS

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ABSTRACT

This chapter reviews the very recent advances achieved over the last three years by exploiting photo-induced polymerization processes for the obtainment of functional (and often nanostructured) coatings. In fact, the high fastness of the polymerization method, together with the low energy consumption and the possibility of designing and tailoring the UV-curable formulations, allows producing smart functional coatings. These latter exhibit the peculiar features required for selected advanced applications. In particular, it is possible to obtain superhydrophobic, thermally and/or electrically conductive, anti-corrosion (nano)coatings. Furthermore, photo-induced polymerization allows designing nanostructured thin films with high barrier properties toward different gases, as well as nanocoatings for biomedical applications. This surface approach possesses remarkable advantages, as it is able to provide any underlying substrate with the desired functional properties, without changing the structure and behavior of the bulk.

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Keywords: photo-induced polymerization, UV-curable formulations, UV-cured (nano)coatings, smart functional coatings, superhydrophobic coatings, anti-corrosion coatings, anti-static coatings, electrically-conductive coatings, high barrier coatings, bio-based UV-curable coatings

INTRODUCTION

The design of high performing surface treatments on different kinds of substrates (such as plastics, metals, wood, glass, composite laminates, ...) has been a real target and a challenging issue for more than 30 years, stimulating both the academic and industrial research toward the development of new products, suitable for different application fields [1]. In fact, the possibility of changing the surface of a material without affecting its bulk features represents a significant step-foreword for the development of new systems that exhibit peculiar, functional and “smart” properties [2]. Sometimes, this modification is achieved even by mimicking the behavior of natural materials or living matter [3]. In this context, among the different suitable surface approaches, the possibility of treating any substrate with a curable organic or hybrid organic-inorganic coating represents an interesting approach. This way, it is possible to provide (multi)functional properties to the underlying material [4-6]. Despite the remarkable use of thermally-induced curing reactions [7] and the possibility of using electron beams or magnetically-induced curing reactions [8], one of the major current opportunities refers to the exploitation of photo-induced curable systems: these latter show several advantages and peculiarities as compared with the thermal approach, which will be discussed onward.

In particular, the photo-induced polymerization (i.e., the so-called UV-curing) of multifunctional reactive monomers and oligomers represents one of the fastest and more effective methods, suitable for producing highly cross-linked 3-D polymer networks. From an overall point of view, thanks to its specific benefits related to process facilities and product quality, the radiation-curing technology has found major openings in different industrial application sectors [9-15]. An overall scheme of the photopolymerization reactions is presented in Figure 1.

Several experimental parameters can influence the cure extent, hence determining the final physico-chemical and mechanical features of the obtained UV-cured networks. In particular, such properties as glass transition temperature, hardness, abrasion and scratch resistance, thermal and thermo-oxidative stability, surface tension, permeability, ..., can be strictly correlated