Nanostructured Materials and Nanotechnology VII

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Edited by
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The American Ceramic Society

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A Collection of Papers Presented at the 37th International Conference on Advanced Ceramics and Composites January 27–February 1, 2013 Daytona Beach, Florida

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Preface

This CESP issue contains papers that were presented during two symposia held during the 37th International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, Florida, January 27–February 1, 2013:

- Symposium 7: 7th International Symposium on Nanostructured Materials and Nanocomposites
- Focused Session 3: Nanomaterials for Sensing Applications: Fundamental Material Designs to Device Integration

Over 90 contributions (invited talks, oral presentations, and posters) were presented by participants from universities, research institutions, and industry, which offered interdisciplinary discussions indicating strong scientific and technological interest in the field of nanostructured systems. This issue contains 15 peer-reviewed papers cover various aspects and the latest developments related to nanoscaled materials.

The editors wish to extend their gratitude and appreciation to all the authors for their cooperation and contributions, to all the participants and session chairs for their time and efforts, and to all the reviewers for their valuable comments and suggestions. Financial support from the Engineering Ceramic Division of The American Ceramic Society (ACerS) is gratefully acknowledged. The invaluable assistance of the ACerS staff of the meetings and publication departments, instrumental in the success of the symposium, is gratefully acknowledged,

We believe that this issue will serve as a useful reference for the researchers and technologists interested in science and technology of nanostructured materials and devices.

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Introduction

This issue of the Ceramic Engineering and Science Proceedings (CESP) is one of nine issues that has been published based on manuscripts submitted and approved for the proceedings of the 37th International Conference on Advanced Ceramics and Composites (ICACC), held January 27–February 1, 2013 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society's (ACerS) Engineering Ceramics Division (ECD) since 1977.

The 37th ICACC hosted more than 1,000 attendees from 40 countries and approximately 800 presentations. The topics ranged from ceramic nanomaterials to structural reliability of ceramic components which demonstrated the linkage between materials science developments at the atomic level and macro level structural applications. Papers addressed material, model, and component development and investigated the interrelations between the processing, properties, and microstructure of ceramic materials.

The conference was organized into the following 19 symposia and sessions:

Symposium 1	Mechanical Behavior and Performance of Ceramics and Composites
Symposium 2	Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3	10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4	Armor Ceramics
Symposium 5	Next Generation Bioceramics
Symposium 6	International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution
Symposium 7	7th International Symposium on Nanostructured Materials and Nanocomposites: Development and Applications

Symposium 8	7th International Symposium on Advanced Processing & Manufacturing Technologies for Structural & Multifunctional Materials and Systems (APMT)
Symposium 9	Porous Ceramics: Novel Developments and Applications
Symposium 10	Virtual Materials (Computational) Design and Ceramic Genome
Symposium 11	Next Generation Technologies for Innovative Surface Coatings
Symposium 12	Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)
Symposium 13	Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy
Focused Session 1	Geopolymers and Chemically Bonded Ceramics
Focused Session 2	Thermal Management Materials and Technologies
Focused Session 3	Nanomaterials for Sensing Applications
Focused Session 4	Advanced Ceramic Materials and Processing for Photonics and Energy
Special Session	Engineering Ceramics Summit of the Americas
Special Session	2nd Global Young Investigators Forum

The proceedings papers from this conference are published in the below nine issues of the 2013 CESP; Volume 34, Issues 2–10:

- Mechanical Properties and Performance of Engineering Ceramics and Composites VIII, CESP Volume 34, Issue 2 (includes papers from Symposium 1)
- Advanced Ceramic Coatings and Materials for Extreme Environments III, Volume 34, Issue 3 (includes papers from Symposia 2 and 11)
- Advances in Solid Oxide Fuel Cells IX, CESP Volume 34, Issue 4 (includes papers from Symposium 3)
- Advances in Ceramic Armor IX, CESP Volume 34, Issue 5 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics VI, CESP Volume 34, Issue 6 (includes papers from Symposia 5 and 9)
- Nanostructured Materials and Nanotechnology VII, CESP Volume 34, Issue 7 (includes papers from Symposium 7 and FS3)
- Advanced Processing and Manufacturing Technologies for Structural and Multi functional Materials VII, CESP Volume 34, Issue 8 (includes papers from Symposium 8)
- Ceramic Materials for Energy Applications III, CESP Volume 34, Issue 9 (includes papers from Symposia 6, 13, and FS4)
- Developments in Strategic Materials and Computational Design IV, CESP Volume 34, Issue 10 (includes papers from Symposium 10 and 12 and from Focused Sessions 1 and 2)

The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD members. We would especially like to express our sincere thanks to the symposia organizers, session chairs, presenters and conference attendees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.

ACerS and the ECD invite you to attend the 38th International Conference on Advanced Ceramics and Composites (http://www.ceramics.org/daytona2014) January 26-31, 2014 in Daytona Beach, Florida.

To purchase additional CESP issues as well as other ceramic publications, visit the ACerS-Wiley Publications home page at www.wiley.com/go/ceramics.

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Nanostructured Materials and Nanotechnology

SOL-GEL APPROACH TO THE CALCIUM PHOSPHATE NANOCOMPOSITES

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ABSTRACT

The sol-gel chemistry route has been developed to prepare Ca-O-P gels samples. In the sol-gel process 1,2-ethanediol and EDTA were used as complexing agents. Additionally, triethanolamine and polyvinyl alcohol were used as gel network forming materials. Calcium phosphate/hydroxyapatite thin films were obtained on silicon substrate by dip-coating technique. The final nanocomposites were obtained by calcination of coatings for different time at 1000 °C. It was shown that adjustment of heating time and dip-coating conditions can be used to control the synthesis processing, phase purity and morphology of thin films. It was concluded, that the formation of calcium phosphate/hydroxyapatite composites in some cases is promoted by dipping time.

INTRODUCTION

Calcium hydroxyapatite (CHA) coatings have received considerable attention because they exhibit bone bonding capabilities, i.e. excellent biocompatibility, bioactivity and osteoconductivity).[1,2,3] CHA coatings on different substrates (Ti-6Al-4V alloy, NiTi alloy, Mg, Ti, Si, steel) are being widely used in orthopedics and dentistry.[4,5,6,7,8,9] Many preparation techniques are used currently in coating CHA onto different substrates. However, some metastable and amorphous phases appear in the CHA coating during the plasma spraying process[10,11] or pulsed laser deposition[12] which result in the low crystallinity of CHA coating. The biomimetic CHA coatings have the limitation of poor adhesion and lower growth rates.[13,14] The sol-gel and hydrothermal methods are cost effective, low temperature routes for coating hydroxyapatite on various substrates.[3,15]

Sol-gel processing also provides a convenient method for applying tricalcium phosphate (TCP) films.[16,17] Calcium phosphate ceramic is well known for its osteoinductive properties, good degradability, high hydrophilicity.[18,19,20] Calcium phosphate cements have been used in medical and dental applications for many years.[18] For example, tetracalcium phosphate is one of the major powder components of self-setting orthopedic and dental cements.[21,22] However, the low strength and high brittleness of calcium phosphate cements prohibit their use in many stress-bearing locations, which would require an improvement in mechanical properties.[23] It was shown that gelatine addition to calcium phosphate bone cement improves its mechanical properties.[24]

Calcium phosphate ceramics, which are commonly used as implants for bone reconstruction, appear to be good candidates for biocompatible drug carriers, since they can be resorbed by cells and they promote new bone formation by releasing calcium and phosphate ions.[25] Drug-loaded polymers and calcium phosphate composites were also tested as cell and drug carrier materials.[26,27] Recently calcium phosphate systems, including both hydroxyapatite and tricalcium phosphates (CHA-TCP), have attracted significant interest as drug delivery vehicles. It was demonstrated that protein loading and release behaviour of CHA-TCP can be controlled by tailoring particle size and surface area.[28] The CHA-TCP cement was suggested as carrier for different drugs, proteins and chemotherapeutic agents.[29,30] Many preparation techniques were suggested for the preparation of CHA-TCP films coating, such as microplasma spray[31], high-power ion beam ablation plasma[32], rf-magnetron sputtering[33,34] or electrochemical/hydrothermal method.[35] The sol-gel approach was used only for the preparation of biphasic CHA-TCP powders.[36,37] In this paper we report on the synthesis and characterization of CHA-TCP thin films on the silicon[33] substrate using dip-coating technique. For the preparation of stable sols a novel sol-gel synthesis approach was suggested.

EXPERIMENTAL

Aqueous sol-gel chemistry route based on phosphoric acid as the phosphorus precursor and calcium acetate monohydrate as source of calcium ions have been developed to prepare Ca-O-P gel samples. These gels were used as precursors for the deposition of $Ca_{10}(PO_4)_6(OH)_2$-$Ca_3(PO_4)_2$ (CHA-TCP) composites onto commercial silicon (Si, 1.5×1.5) substrates by dip-coating technique from the Ca-O-P gels stabilized with complexing reagents. In the sol-gel process, 2.6425 g of calcium acetate monohydrate, $Ca(CH_3COO)_2 \cdot H_2O$ (99.9 %; Fluka) was dissolved in 50 ml of distilled water under continuous stirring at 65 °C. To this solution 4.82185 g of ethylenediaminetetraacetic acid (EDTA; 99.0 %; Alfa Aesar) was added. After stirring at 60-65 °C for 1 h, 2 ml of 1,2-ethanediol (99.0 %; Alfa Aesar) and 9 ml of triethanolamine (99.0 %; Merck) were slowly poured to the solution. After stirring at 60-65 °C for 10 h, appropriate amount of phosphoric acid, H_3PO_4 (85.0 %; Reachem) was added to the above solution. Finally, 10 ml of 3% polyvinyl alcohol (PVA7200, 99.5 %; Aldrich) solution was added. The obtained solution was stirred in a beaker covered with watch glass for 2 h at the same temperature and was used for coating of silicon substrates. Dip-coating method was employed to produce sol-gel coatings.[38,39] The standard immersing (85 mm/min) and withdrawal rates (40 mm/min) for dip-coating process were applied for all the samples. The dipping procedure was repeatedly performed 5, 15 and 30 times. After evaporation of solvent the substrates were dried in an oven for 10 min at 110 °C and heated at 1000 °C for 5 h with heating rate of 1 °C/min.

For the characterization of surface properties, the X-ray powder diffraction (XRD) analysis, scanning electron microscopy (SEM), Raman spectroscopy, atomic force microscopy (AFM) and the contact angle measurements were recorded. XRD analysis was performed on a Bruker AXE D8 Focus diffractometer with a LynxEye detector using Cu K_α radiation. The measurements were recorded at the standard rate of 1.5-2θ/min. The scanning electron microscope JEOL JSM 8404 and atomic force microscope Veeco Bioscope 2 were used to study the surface morphology and microstructure of the obtained thin films. For the characterization of surface hydrophobicity of coatings, the measurements of a contact angle on dip-coating apparatus KVS Instrument CAM 100 were performed. A micro-droplet of water (volume 6 μl) was allowed to fall onto the sample from a syringe tip to produce a sessile drop. The Raman spectra were registered with confocal Raman spectrometer/microscope LabRam HR 800 using 632.8 nm laser for excitation.

RESULTS AND DISCUSSION

Fig. 1 represents the XRD patterns of films obtained from Ca-O-P gel using dip-coating technique. These results present the influence of the number of coating procedures on the crystallization of calcium phosphate coatings. As seen from Fig. 1, after first immersing, withdrawal and annealing procedure no peaks attributable to the $Ca_{10}(PO_4)_6(OH)_2$ or $Ca_3(PO_4)_2$ crystal phases are observed. The layer formed contains only amorphous materials. However, already after five dipping and annealing times the main characteristic peaks attributable to tricalcium phosphate $Ca_3(PO_4)_2$ and dicalcium diphosphate $Ca_2P_2O_7$ (DCDP) crystal phases appear in the XRD pattern. The repetition of immersing, withdrawal and annealing procedures for 15 times did not change phase composition of coating. However, such repeating increased the crystallinity of phosphates significantly since the diffraction lines became more sharp and intense. Finally, with further increasing of calcium phosphate layers up to 30, the formation of calcium hydroxyapatite is evident (diffraction lines of CHA are marked as solid rhombus).[11] The $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$ phases also remain in the sample obtained after 30 immersing and annealing procedures. Thus, suggested sol-gel chemistry