

Developments in Strategic Materials and Computational Design IV

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Edited by

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Volume Editors

Soshu Kirihara and Sujanto Widjaja



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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

Contributions from two Symposia, two Focused Sessions, and the Annual Global Young Investigator Forum that were part of the 36th International Conference on Advanced Ceramics and Composites (ICACC), in Daytona Beach, FL, January 27–February 1, 2013 are presented in this volume. The broad range of topics is captured by the Symposia and Focused Session titles, which are listed as follows: Focused Session 1—Geopolymers and Chemically Bonded Ceramics; Focused Session 2—Thermal Management Materials and Technologies; Symposium 10—Virtual Materials (Computational) Design and Ceramic Genome; and, Symposium 12—Materials for Extreme Environments: Ultrahigh Temperature Ceramics and Nanolaminated Ternary Carbides and Nitrides.

This was the 11th consecutive year for the topic covered by Focused Session 1 concerning Geopolymers and Chemically Bonded Ceramics. As in years past, it continued to attract attention from international researchers as well as new application domains. Twelve papers are included in this year's proceedings. The studies focus on processing as well as the associated microstructural and mechanical properties in relevant environments. Such studies are critical in the pursuit of sustainable and environmentally friendly ceramic composites. Focus Session 2 emphasizes new materials and the associated technologies related to thermal management. The topic includes innovations in ceramic or carbon based materials tailored for either high conductivity applications (e.g., graphite foams) or insulation (e.g., ceramic aerogels); heat transfer nanofluids; thermal energy storage devices; phase change materials; and a slew of technologies that are required for system integration. One paper is included here addressing the relatively new application of high conductivity graphite foams for thermal energy storage.

Symposium 10 is dedicated to the modeling of ceramics and composites. This includes property prediction, innovative simulation methods, modeling defects and diffusion in ceramics as well as the study of virtual materials with the aim of further optimizing the behavior to facilitate the design of new ceramics and composites with tailored properties. Nine papers are available within this volume discussing

subjects such as stochastic crystal growth, crack modeling, numerical assessment of self-healing composites, multi-scale modeling of CMCs, and laminate property predictions using 3D unit cells. Symposium 12 addresses the many facets related to materials for extreme environments. This includes the relationship between material structures and properties, structural stability under extreme environments, novel characterization methods, and life predictions. Four papers from this symposium are included within this collection. Lastly, a single study is included from the Second Annual Global Young Investigators Forum. The paper is focused on the dielectric and piezoelectric properties of a novel PZT ceramic.

The editors wish to thank the symposium organizers for their time and labor, the authors and presenters for their contributions; and the reviewers for their valuable comments and suggestions. In addition, acknowledgments are due to the officers of the Engineering Ceramics Division of The American Ceramic Society and the 2013 ICACC program chair, Dr. Sujanto Widjaja, for their support. It is the hope that this volume becomes a useful resource for academic, governmental, and industrial efforts.

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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 Multifunctional 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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Volume Editors
August 2013

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Geopolymers and Chemically Bonded Ceramics

IMPORTANCE OF METAKAOLIN IMPURITIES FOR GEOPOLYMER BASED SYNTHESIS

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ABSTRACT

Geopolymers are the object of numerous studies because of their low environmental impact. The synthesis of these geomaterials is achieved by the alkaline activation of aluminosilicates. Alkaline activation is typically accomplished by the activation of potassium or sodium silicate. Since these alkaline silicate solutions are relatively expensive. It is imperative to understand all of the phenomena and reactions involved during geopolymer synthesis. We thus attempted to study the role played by siliceous species in the alkaline silicate solutions.

During the setting of the materials, the reactive mixture forms at least two phases: (i) a solid phase and (ii) a gelified liquid which recovered it. The quantity of gel varies with the Si/Al, Si/K and Si/H₂O molar ratios. Several exchanges take place at the gel-solid interface and involve composition and pH variations. Moreover, the nature and the number of networks depend on the alkaline solution used.

1. INTRODUCTION

The alkaline silicate solutions (waterglass) necessary for the synthesis of geopolymer materials are solutions containing a dissolved glass with an aspect similar to water. Alkaline silicate solutions are widely used in the industry as binders, emulsifying agents, deflocculants or in the paper industry. These sodium or potassium-based solutions, present complex structures, composed of diverse monomeric and polymeric species [1,2,3]. Their composition evolves according to various variables, such as the value of pH [4] or the SiO₂/M₂O molar ratio (where M=Na or K). These parameters allow control of the various species in the mixture which confer variable properties of the solutions, in particular in terms of reactivity. Important differences are also noted between potassium and sodium elements; these differences can be at the origin of variations, both in terms of structure and stability, within geopolymer materials.

Several studies were recently realized in these alkaline silicate solutions [5] and on their role during geopolymer formation [6,7,8]. These various studies allowed highlighting the existence of two phases within the consolidated material [7]: a geopolymer phase and a gel phase, present in more or less high quantity according to the source of silica used during the manufacture of the alkaline silicate solution. Indeed, the use of sand as a substitute for the amorphous silica leads to a decrease of the Si / Al ratio and of the quantity of geopolymeric phase [7].

The consolidation of the material is then possible thanks to the important presence of gel but leads to a decrease in the mechanical properties. These materials, synthesized from a commercial metakaolin, also contain impurities initially present in the raw material (e.g. anatase, muscovite, quartz).

The objective of this study is to understand the role played by the siliceous species from the activation solution during the formation of geopolymers. Hence, the role of the alkaline silicate solution was studied by comparing a commercial solution with a laboratory prepared solution with the same Si / K molar ratio. To eliminate the effect of impurities within the consolidated materials, a high purity metakaolin (99 %) was used for both activating solutions.

II. EXPERIMENTAL PART

1. Sample preparation

Geopolymer materials were synthesized according to two ways as described by Figure 1.

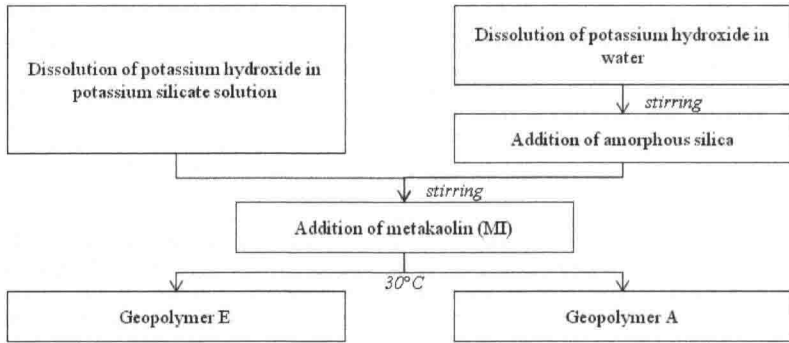


Figure 1 : Synthesis protocol of geopolymer compounds.

In the case of geopolymers E [9], potassium hydroxide pellets (85.7 % of purity) were dissolved in some potassium silicate solution supplied by the Chemical Labs company (Si / K=1.7; density of 1.20 g / cm³). Dehydroxylated kaolinite MI (98.8 % of purity) supplied by IMERYS France is added to this preparation under stirring. This metakaolin has been calcined at 750°C during 5 hours (S_{BET} = 8 m².g⁻¹). The reactive mixture is then placed in a polystyrene cylindrical mould at room temperature. The characteristics of the raw materials are presented in Table 1.

In the case of geopolymers A [6], the KOH pellets were first dissolved in water at room temperature to form an alkaline solution (pH=14). An amorphous silica, being very fine and highly reactive (denoted S; purity of 99.9%) and supplied by SIGMA ALDRICH was dissolved in the alkaline solution. The continuation of the protocol is similar to what was previously described. Nomenclatures and molar ratios are presented in the Table 2.

Table 1 Characteristics and nomenclature of raw materials used.

Nature	Amorphous silica	Metakaolin MI
Nomenclature	S	MI
d ₅₀ (µm)	0.14	7.54
BET value (m ² /g)	202	~ 7
Chemical analysis (wt. %)	99.9 SiO ₂	50 SiO ₂ 50Al ₂ O ₃

Table 2 Nomenclature and compositions of compounds.

Sample	Used metakaolin	Si/Al	Si/K	Si/H ₂ O
A	MI	1.40	2.10	0.30
E	MI	1.40	2.10	0.23

2. Characterization

X-ray patterns were performed from powder samples after crushing at 63 μm , and obtained using a Bruker-AXS D 5005 apparatus from 5 to 70° (2 theta). The device is equipped with a cobalt anode ($\lambda = 1.79026 \text{ \AA}$). The acquisition time is 1 second, and the step is 0.02° (2 theta). XRD patterns were analyzed using EVA software.

The FTIR spectra were obtained using a Thermo Fisher Scientific 380 infrared spectrometer (Nicolet). The IR spectra were gathered over a wave number range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . The atmospheric CO₂ contribution was removed with a straight line between 2400 and 2280 cm^{-1} . To follow the evolution of the involved bonds within the sample in time, a computer algorithm was used to acquire a spectrum every 10 minutes for 13 hours, producing 64 scans. To allow comparisons of the various spectra, the spectra were corrected with the baseline and then normalized. The characterization of the powders and gels was also conducted by FTIR.

Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were performed on a SDT Q600 apparatus from TA Instruments in an atmosphere of flowing dry air (100 mL/min) in platinum crucibles. Signals were measured with Pt/Pt-10%Rh thermocouples. Some milligrams of material are placed in a platinum crucible and the analysis is made from 30 °C to 800 °C, at 10 °C / min.

The chemical analyses were obtained by XRF investigations using a XMET 5500 X from Oxford. Samples are analyzed from pressed pellet.

III. RESULTS AND DISCUSSION

1. Synthesis of materials

In the way to study the influence of the alkaline solution only one sort of metakaolin highly pure (MI metakaolin) was used. Therefore, the influence of the impurities was eliminated. It was chosen to maintain constant the Si / K and Si / H₂O ratios, what leads to a decrease in the Si / Al ratio from 1.62 to 1.40 compared to the previous study from an other type of metakaolin raw material [10]. Whatever the composition, (i) a consolidated geopolymer-like material was synthesized, and (ii) a demixing brought in the reactive mixture from the first hour after the synthesis: a fine coat of transparent liquid appeared slowly at the surface. The polycondensation phase is effective in 6 at 10 hours. The viscosity of the supernatant liquid increased until to form a gel, 5 to 8 days after the synthesis. Afterward, the supernatant phase will be named "gel" and the solid phase "solid". As an example, the reactive mixture E gave a sample consisting of the "solid E" recovered from the "gel E". The same results were observed for A samples.

According to previous results the variations of the various molar ratios during the substitution of the other metakaolin by the MI metakaolin led to the formation of a more important quantity of gel on the solids surface. This increase seemed to be inversely proportional to the Si / H₂O ratio leading to an extension of the gelation time. The quantity of gel formed also increased with the Si/Al ratio. This observation highlighted the role of the aluminum as a networking agent. The variation of these molar