Developments in Strategic Ceramic Materials

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A Collection of Papers Presented at the
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Preface

This CESP proceedings issue contains a total of 26 contributions from four Symposia, three Focused Sessions, and two special sessions that were part of the 39th International Conference on Advanced Ceramics and Composites (ICACC), in Daytona Beach, FL, January 25–30, 2015.

The wide range of topics in this issue were presented in the following Symposia and Focused Sessions: Symposium 2—Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications; Symposium 10—Virtual Materials (Computational) Design and Ceramic Genome; Symposium 11—Advanced Materials and Innovative Processing Ideas for the Industrial Root Technology; Symposium 12—Materials for Extreme Environments: Ultrahigh Temperature Ceramics and Nanolaminated Ternary Carbides and Nitrides; Focused Session 1—Geopolymers and Chemically Bonded Ceramics; Focused Session 3, Materials Diagnostics and Structural Health Monitoring of Ceramic Components and Systems; Focused Session 6, Field Assisted Sintering; the 2nd European-USA Engineering Ceramics Summit; and the 4th Annual Global Young Investigator Forum.

The editors wish to thank the symposium organizers for their time and efforts, 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 2015 ICACC program chair, Soshu Kirihara, 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 CESP issue consists of papers that were submitted and approved for the proceedings of the 39th International Conference on Advanced Ceramics and Composites (ICACC), held January 25–30, 2015 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 Engineering Ceramics Division (ECD) of The American Ceramic Society (ACerS) since 1977.

The 39th ICACC hosted more than 1,000 attendees from 40 countries and over 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 2015 conference was organized into the following 21 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	12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4	Armor Ceramics: Challenges and New Developments
Symposium 5	Next Generation Bioceramics and Biocomposites
Symposium 6	Advanced Materials and Technologies for Energy Generation and Rechargeable Energy Storage
Symposium 7	9th International Symposium on Nanostructured Materials and Nanocomposites
Symposium 8	9th International Symposium on Advanced Processing & Manufacturing Technologies for Structural & Multifunctional Materials and Systems (APMT), In Honor of Prof. Stuart Hampshire

Symposium 9	Porous Ceramics: Novel Developments and Applications
Symposium 10	Virtual Materials (Computational) Design and Ceramic Genome
Symposium 11	Advanced Materials and Innovative Processing ideas for the Industrial Root Technology
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, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials
Focused Session 2	Advanced Ceramic Materials and Processing for Photonics and Energy
Focused Session 3	Materials Diagnostics and Structural Health Monitoring of Ceramic Components and Systems
Focused Session 4	Additive Manufacturing and 3D Printing Technologies
Focused Session 5	Single Crystalline Materials for Electrical, Optical and Medical Applications
Focused Session 6	Field Assisted Sintering and Related Phenomena at High Temperatures
Special Session	2nd European Union-USA Engineering Ceramics Summit
Special Session	4th Global Young Investigators Forum

The proceedings papers from this conference are published in the below seven issues of the 2015 CESP; Volume 36, Issues 2-8, as listed below.

- Mechanical Properties and Performance of Engineering Ceramics and Composites X, CESP Volume 36, Issue 2 (includes papers from Symposium 1)
- Advances in Solid Oxide Fuel Cells and Electronic Ceramics, CESP Volume 36, Issue 3 (includes papers from Symposium 3 and Focused Session 5)
- Advances in Ceramic Armor XI, CESP Volume 36, Issue 4 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics VIII, CESP Volume 36, Issue 5 (includes papers from Symposia 5 and 9)
- Advanced Processing and Manufacturing Technologies for Nanostructured and Multifunctional Materials II, CESP Volume 36, Issue 6 (includes papers from Symposia 7 and 8 and Focused Sessions 4 and 6)
- Ceramic Materials for Energy Applications V, CESP Volume 36, Issue 7 (includes papers from Symposia 6 and 13 and Focused Session 2)
- Developments in Strategic Ceramic Materials, CESP Volume 36, Issue 8 (includes papers from Symposia 2, 10, 11, and 12; from Focused Sessions 1 and 3); the European-USA Engineering Ceramics Summit; and the 4th Annual Global Young Investigator Forum

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 Jubilee Celebration of the 40th International Conference on Advanced Ceramics and Composites (http://www.ceramics.org/daytona2016) January 24-29, 2016 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
July 2015

Geopolymers
and Chemically
Bonded Ceramics

PROPERTIES OF GRANITE POWDER REINFORCED POTASSIUM GEOPOLYMER

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Granite powder is a waste product at many quarries and stone processing plants all over the globe. This waste powder, when properly sieved into an appropriate size distribution, can be used as a suitable reinforcement for geopolymers. The goal of this design was to create a sustainable, cost-effective and reliable structural geopolymer composite utilizing resources that are easily attained worldwide. Its properties and viability as a structural material were determined through four-point flexure testing according to ASTM standards and analyzed by Weibull statistics. Its refractory properties were tested by exposing samples to various temperatures, then testing for shrinkage and flexure strengths. Heat treatment of all samples yielded cracking and warping, but the coarse granite samples maintained strengths over 2 MPa while fine samples maintained 10 MPa strengths. Scanning electron microscopy (SEM) was used to characterize the size and geometries of the granite powder, and to determine its viability as a reinforcement for potassium geopolymer.

INTRODUCTION

Geopolymers are an inorganic polymeric structural material consisting of alumina, silica and an alkali metal oxide. This study used potassium hydroxide, mixed with water and fumed silica, to create potassium waterglass. When combined with metakaolin, this mixture became liquid geopolymer precursor. This liquid can be easily poured into molds of almost any shape, and can also accommodate a multitude of reinforcement options. Geopolymers are emerging as an environmentally-friendly alternative to ordinary cements, as they produce only about 20% of the carbon dioxide compared to that produced by the manufacturing of Portland cement, an industry that is responsible for 5% of the world's carbon dioxide emission[1]. The abundance of all the materials needed to make effective geopolymers also creates the opportunity to eventually make bulk production of geopolymers cheaper than ordinary cements.

Geopolymers can be used with a wide range of reinforcements, including but not limited to metals, ceramics, and polymers[2]. Geopolymers can be used in composites with such a multitude of composites due to its ability to encapsulate many materials. This good adhesion allows for load transfer to the less expensive reinforcement, meaning cheap reinforcements can be used to simultaneously increase the flexural strength of the composite and lower its overall cost. This adhesion has been demonstrated in other studies of rock powder reinforced geopolymers[3].

The addition of a reinforcement, such as a rock powder, can reduce the geopolymer composites' overall mechanical sensitivity to dehydration. Despite this water sensitivity, geopolymers tend to maintain high flexural strengths when exposed to elevated temperatures. Potassium geopolymers have been shown to exhibit room temperature in situ flexural strengths on the MPa level after being exposed to temperatures well over 1000°C[3]. At room temperature, significant improvements to the mechanical strengths of geopolymers have been proven with the addition of reinforcement[4].

Granite powder is an extremely common material chemically composed of primarily crystalline silica and alumina. Granite is formed in the magma below the Earth's crust, and is found all over the world. When granite is processed, granite powder is produced and usually treated as waste at quarries and stone processing plants[5]. This study chose granite powder as reinforcement due to its cost, availability and environmental impact. The purpose of this study was to investigate the microstructure and mechanical properties of rock-powder reinforced geopolymers.

EXPERIMENTAL PROCEDURE

Sample Preparation

A potassium silicate solution ($K_2O\bullet 2SiO_2\bullet 11H_2O$), henceforth referred to as "potassium waterglass", was first prepared by mixing pellets of potassium hydroxide, deionized water and fumed silica with a magnetic stir rod. Once the hydroxide was dissolved, the fumed silica was slowly added until it had completely dissolved. The mixture was then allowed to mix in a fume hood for an additional 24 hours. After that time, the amount of water lost to evaporation due to heat created by the reaction was replaced.

Metakaolin was then added to the waterglass in order to create a geopolymer of chemical composition $K_2O\bullet Al_2O_3\bullet 4SiO_2\bullet 11H_2O$. The metakaolin was initially worked into the waterglass using an IKA overhead stirrer (Model RW20DZM, IKA, Wilmington, NC) with high shear blade for five minutes at about 1800 rpm. From there, the mixture was degassed on a shaker table for about 30 seconds. The mixture was then further mixed in a Thinky ARE-250 planetary mixer (Intertronics, Kidlington, Oxfordshire, UK) at 1200 rpm for 3 minutes and then 1400 rpm for another 3 minutes.

Granite powder was then introduced into the mixture using the IKA overhead mixer. For coarse granite samples, the granite was added as-received in its broad size-distributed state. For the fine granite samples, 1-2 kg of granite was mixed with water before being hand-sieved through a 90 µm mesh. This wet mixture was then heated until complete evaporation, and crushed into powder form. In both cases, granite powder was added until the mixture was unpourable (65 wt% and 55 wt% for coarse and fine granite additions, respectively).

After the powder was added to the geopolymer, the mixture was again placed on the shaker table for degassing. Vibrations from the table decreased the viscosity of the mixture, allowing it to be poured into vertical 1x1x10 cm Delrin molds. These molds were placed on the shaker table once more before being wrapped in plastic wrap and allowed to cure in an oven at 50°C for 24 hours.

Mechanical Testing

All samples were tested immediately after being removed from the curing oven. The samples were tested on an Instron Universal Testing Frame following ASTM C78/C78M-10 guidelines for four-point flexure testing. Lower supports were placed equidistant from the points of load application, with the outer span equal to 40 mm and the inner span equal to 20 mm. The displacement rate of the head was set at 0.00012 mm/sec to maintain the 1 MPa/min rate of stress increase required by the standard.

Some samples were heat-treated before undergoing flexural testing. These were placed in a Carbolite CWF 1200 Box Furnace with heating and cooling rates of 5°C/min and a 1 hour isothermal soak at the appropriate temperature. Temperatures tested included 300°C, 600°C, 900°C and 1200°C.

The granite powder for this study was K-feldspar granite powder provided by Rock Dust Local, Bridport, Vermont, USA. Its composition can be seen in Table I[6]. Details of its size distribution and geometry were determined through dry-sieving, wet-sieving, and SEM imaging (Fig 1). Difficulties with large granite sizes led to the fine powder experiment, which focused solely on granite powder less than 90 μm in size.

Table I. Granite Powder Chemical Composition[6]

	wt%	mol%
SiO_2	70.96	78.825
Al_2O_3	14.51	9.498
Na_2O	3.87	4.167
K_2O	4.49	3.181
CaO	1.39	1.654
MgO	0.75	1.242
Fe_2O_3	2.49	1.041
TiO_2	0.368	0.307
P_2O_5	0.1	0.038
MnO	0.04	0.038
LOI	1.44	

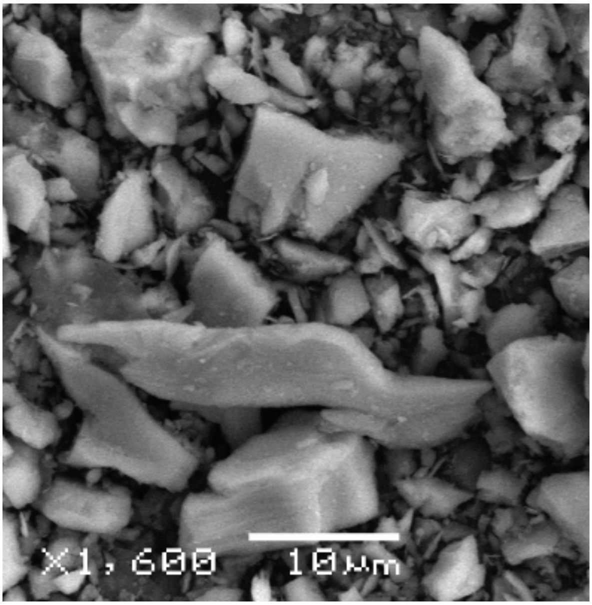

Fig 1. Scanning electron microscopy image of as-received granite powder examined under accelerating voltage of 20 kV in high vacuum mode

RESULTS AND DISCUSSION

Initial four-point flexural tests used coarse granite powder as the reinforcement. Pure K-GP was found to have an average flexural strength of about 11 MPa. However, this number was found to have a large degree of variation. Increased solids loading yielded an initial decrease in strength, before an eventual climb towards greater strength. However, the maximum amount of coarse granite that could be mixed in the K-GP (65 wt%) still did not yield strengths greater than those of pure K-GP. Upon inspection of the fracture surfaces, it became clear that large inclusions on the millimeter scale lowered the possible strengths of the composite (Fig 2).

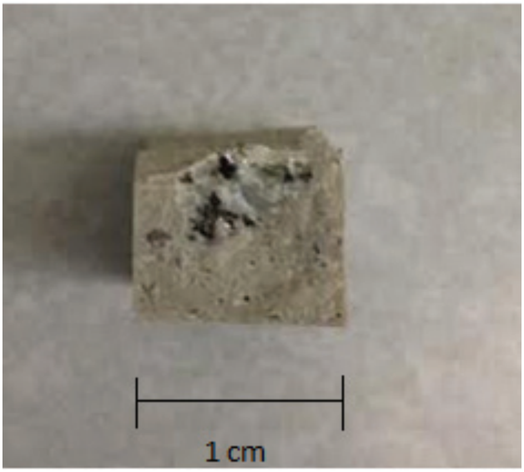

Fig 2. Fracture surface of a coarse granite powder reinforced sample. Inclusions on the millimeter scale, such as this one, might have contributed to lower strengths in the coarse powder samples

Because of this, it was decided that strengths could be improved if the coarse granite was sieved into a smaller size distribution centered around a sub-100 micrometer average.

The granite was successfully sieved through a 90 micrometer mesh by wet-sieving. Once sieved, the granite was dried and finally soft agglomerates were broken up which allowed for its mixing into K-GP. The fine granite powder solids loading was increased until it was extremely viscous, at 55 wt%. Again, increasing the solids loading initially showed a decrease in strength, but eventually came back up to levels comparable with pure K-GP. It is important to note that in both the case of coarse and fine powders, as solids loading increased, the level of variation in the sample groups decreased (Fig 3).

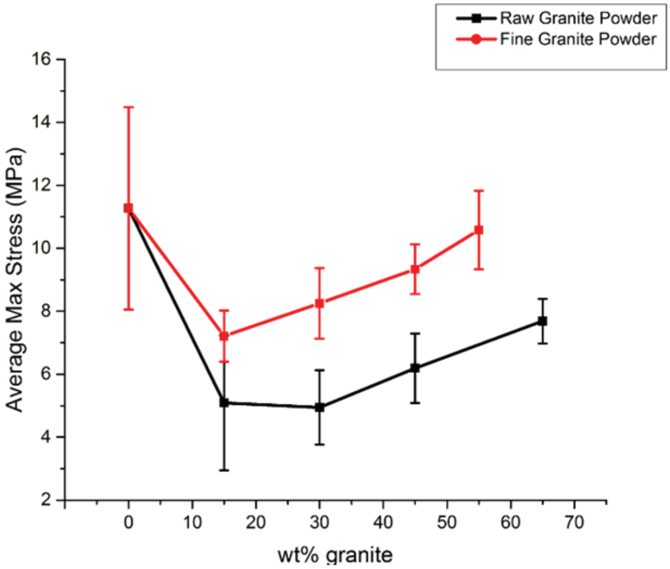

Fig 3. Average maximum stress obtained by four point flexure testing in both coarse and fine powder samples. Variation in sample data decreased with increased solids loading, and fine powder significantly increased the flexure strength compared to coarse powder.

To note the effect that heat treatment had on the samples, one sample from the maximum solids loading group of the coarse granite reinforcement was selected to be exposed to one hour of 300°C, 600°C, 900°C and 1200°C. The samples warped and cracked more and more with increasing temperature. It is speculated that the curving was due to settling of the granite powder in the sample while it was initially cured. Despite extensive cracking and warping, all four samples maintained flexural strengths of over 2 MPa (Fig. 4).

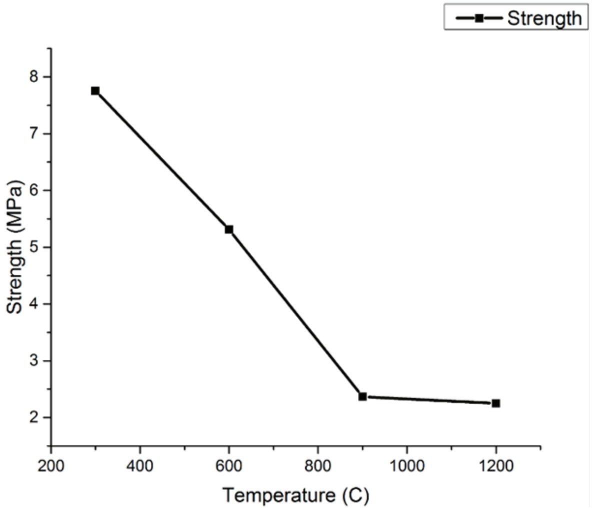

Fig 4. Flexural strength measured for coarse powder reinforced samples exposed to various temperatures.

These samples were then measured in thickness and width in order to determine shrinkage in the samples, seen in Figure 5.

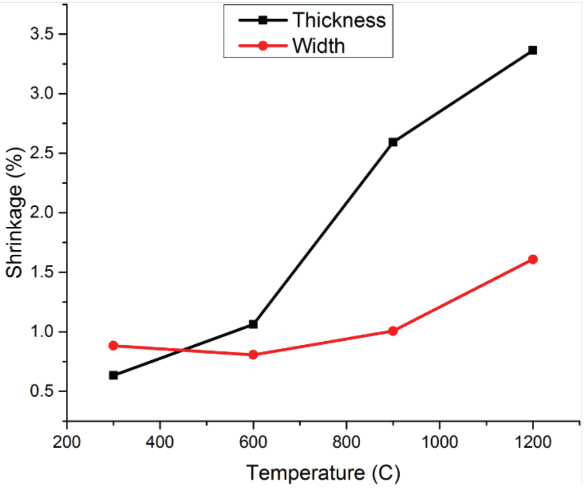

Fig. 5. Shrinkage in the thickness and width of coarse powder reinforced samples. Thickness shrank more due to the positioning of the mold during curing which led to particles settling along the thickness.

Subsequently, a more extensive study was carried out to determine strength and shrinkage for the fine powder reinforced samples. Three samples were exposed to each temperature group in this case. When compared to the strengths of the coarse samples, the fine samples were much stronger, with all three sample groups maintaining average strengths around 10 MPa (Table II).

Table II. Fine Powder, Heat-Treated Sample Strengths

	300°C	600°C	900°C	1200°C
Sample 1	15.88 MPa	10.52 MPa	9.74 MPa	11.88 MPa
Sample 2	11.18 MPa	11.91 MPa	8.56 MPa	9.02 MPa
Sample 3	11.70 MPa	8.95 MPa	10.15 MPa	
Average	12.92 MPa	10.46 MPa	9.48 MPa	10.35 MPa

Shrinkage for both coarse and fine samples never exceeded 5% (Table III).

Table III. Fine Powder Thermal Shrinkage

	300°C	600°C	900°C	1200°C
Thermal Shrinkage in Thickness (%)	0.7	1.4	3.5	5.0
Thermal Shrinkage in Width (%)	0.8	1.3	3.3	4.8

Thickness was speculated to have shrunk more than width due to settling of the powder in the curing phase. Even the highest shrinkage in these samples was an order of magnitude lower than that of pure K-GP.

CONCLUSION

The granite powder both in coarse and fine form were shown to initially decrease, then to increase the strength of potassium geopolymer. As solids loading increased, there was a noted decreased in deviation from average strengths within the sample group. Since coarse powder provided inclusions that decreased the strength of the composite, wet-sieved fine powder was used to significantly increase the sample strengths. Heat treatment of all samples yielded cracking and warping, but the coarse granite samples maintained strengths over 2 MPa and fine samples maintained 10 MPa strengths. Both coarse and fine powder reinforcement kept shrinkage at or below 5%, a whole order of magnitude lower than that of pure K-GP.

This composite was shown to provide flexural strengths competitive with pure K-GP and exceeding that of Portland cement. It also had numerous other benefits. With a high granite solids loading, the cost of mass producing this material would be significantly decreased. The presence of granite powder would also decrease the water sensitivity of K-GP. Finally, the reduced thermal shrinkage experienced by the samples in this study prove that it could also be used more successfully as a refractory material than pure K-GP.

This study will hopefully serve as evidence that simple rock powders available globally can be used as a cheap, reliable reinforcement for geopolymers. Its strengths and other properties make it a competitive material for structural and refractory purposes. Finally, its environmental benefits make it an appealing composite for a wide variety of applications.

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