Innovative Processing and Manufacturing of Advanced Ceramics and Composites

Edited by
Zuhair A. Munir
Tatsuki Ohji
Yuji Hotta

Volume Editor
Mrityunjay Singh

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Preface

With continued discoveries and innovations, the field of materials synthesis and processing remains as it has been for many decades, a vibrant and fertile area for research and development. It comes, therefore, as no surprise that every Pac Rim conference has had considerable emphasis on this topic with many symposia devoted to various aspects of this field.

This Ceramic Transactions volume represents selected papers based on presentations in four symposia during the 8th Pacific Rim Conference on Ceramic and Glass Technology, held in Vancouver, British Columbia, May 31-June 5, 2009. The symposia and their organizers are:

Synthesis and Processing of Materials by the Spark Plasma Method, organized by Zuhair A. Munir, University of California-Davis, USA, Manshi Ohyanagi, Ryukoku University, Japan, Enrique J. Lavernia, University of California-Davis, USA, Masao Tokita, SPS SYNTEX INC, Japan, and Javier E. Garay, University of California-Riverside, USA.

Innovative Processing and Manufacturing, organized by Tatsuki Ohji, National Institute of Advanced Industrial Science and Technology (AIST), Japan, Juergen G. Heinrich, Clausthal University of Technology, Germany, Dongliang Jiang, Shanghai Institute of Ceramics, China, Takashi Goto, Tohoku University, Japan, Richard D. Sisson, Jr., Worcester Polytechnic Institute, MA, USA, and Junichi Tatami, Yokohama National University, Japan.

Advanced Powder Processing and Manufacturing Technologies, organized by Koji Watari, National Institute of Advanced Industrial Science and Technology (AIST), Japan, George V. Franks, University of Melbourne, Australia, Jianfeng Yang, Xi'an Jiaotong University, China. Guo-Jun Zhang, Shanghai Institute of Ceramics, China, Yoshio Sakka, National Institute for Materials Science, Japan, Junichi Tatami, Yokohama National University, Japan, Satoshi Tanaka, Nagaoka University of Technology, Japan, Hae Jin Hwang, Inha University, Korea, Lennart Bergstrom, Stockholm University, Sweden, Christopher B. DiAntonio, Sandia National Laboratories, USA, and Yuji Hotta, National Institute of Advanced Industrial Science and Technology (AIST), Japan.

We are grateful for the help of all of our co-organizers and for the support of the Pac Rim organizers and the American Ceramic Society. We want to especially acknowledge the help of Mr. Gregory Geiger of the Society. We also acknowledge the financial support from SPS SYNTEX, Inc. of Japan to the symposium on the Synthesis and Processing of Materials by the Spark Plasma Method.

ZUHAIR A. MUNIR, University of California-Davis, USA
TATSUKI OHJI, National Institute of Advanced Industrial Science and Technology (AIST), Japan
YUJI HOTTA, National Institute of Advanced Industrial Science and Technology (AIST), Japan

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Introduction

The 8th Pacific Rim Conference on Ceramic and Glass Technology (PACRIM 8), was the eighth in a series of international conferences that provided a forum for presentations and information exchange on the latest emerging ceramic and glass technologies. The conference series began in 1993 and has been organized in USA, Korea, Japan, China, and Canada. PACRIM 8 was held in Vancouver, British Columbia, Canada, May 31–June 5, 2009 and was organized and sponsored by The American Ceramic Society. Over the years, PACRIM conferences have established a strong reputation for the state-of-the-art presentations and information exchange on the latest emerging ceramic and glass technologies. They have facilitated global dialogue and discussion with leading world experts.

The technical program of PACRIM 8 covered wide ranging topics and identified global challenges and opportunities for various ceramic technologies. The goal of the program was also to generate important discussion on where the particular field is heading on a global scale. It provided a forum for knowledge sharing and to make new contacts with peers from different continents.

The program also consisted of meetings of the International Commission on Glass (ICG), and the Glass and Optical Materials and Basic Science divisions of The American Ceramic Society. In addition, the International Fulrath Symposium on the role of new ceramic technologies for sustainable society was also held. The technical program consisted of more than 900 presentations from 41 different countries. A selected group of peer reviewed papers have been compiled into seven volumes of The American Ceramic Society's Ceramic Transactions series (Volumes 212-218) as outlined below:

- **Innovative Processing and Manufacturing of Advanced Ceramics and Composites, Ceramic Transactions, Vol. 212,** Zuhair Munir, Tatsuki Ohji, and Koji Watari, Editors; Mrityunjay Singh, Volume Editor
  Topics in this volume include Synthesis and Processing by the Spark Plasma

Method; Novel, Green, and Strategic Processing; and Advanced Powder Processing

- **Advances in Polymer Derived Ceramics and Composites, Ceramic Transactions, Vol. 213,** Paolo Colombo and Rishi Raj, Editors; Mrityunjay Singh, Volume Editor
  This volume includes papers on polymer derived fibers, composites, functionally graded materials, coatings, nanowires, porous components, membranes, and more.
- **Nanostructured Materials and Systems, Ceramic Transactions, Vol. 214,** Sanjay Mathur and Hao Shen, Editors; Mrityunjay Singh, Volume Editor
  Includes papers on the latest developments related to synthesis, processing and manufacturing technologies of nanoscale materials and systems including one-dimensional nanostructures, nanoparticle-based composites, electrospinning of nanofibers, functional thin films, ceramic membranes, bioactive materials and self-assembled functional nanostructures and nanodevices.
- **Design, Development, and Applications of Engineering Ceramics and Composite Systems, Ceramic Transactions, Vol. 215, Dileep Singh, Dongming Zhu, and Yanchum Zhou; Mrityunjay Singh, Volume Editor**
  Includes papers on design, processing and application of a wide variety of materials ranging from SiC SiAlON, ZrO_2, fiber reinforced composites; thermal/environmental barrier coatings; functionally gradient materials; and geopolymers.
- **Advances in Multifunctional Materials and Systems, Ceramic Transactions, Vol. 216,** Jun Akedo, Hitoshi Ohsato, and Takeshi Shimada, Editors; Mrityunjay Singh, Volume Editor
  Topics dealing with advanced electroceramics including multilayer capacitors; ferroelectric memory devices; ferrite circulators and isolators; varistors; piezoelectrics; and microwave dielectrics are included.
- **Ceramics for Environmental and Energy Systems, Ceramic Transactions, Vol. 217,** Aldo Boccaccini, James Marra, Fatih Dogan, and Hua-Tay Lin, Editors; Mrityunjay Singh, Volume Editor
  This volume includes selected papers from four symposia: Glasses and Ceramics for Nuclear and Hazardous Waste Treatment; Solid Oxide Fuel Cells and Hydrogen Technology; Ceramics for Electric Energy Generation, Storage, and Distribution; and Photocatalytic Materials.
- **Advances in Bioceramics and Biotechnologies, Ceramic Transactions, Vol. 218;** Roger Narayan and Joanna McKittrick, Editors; Mrityunjay Singh, Volume Editor
  Includes selected papers from two cutting edge symposia: Nano-Biotechnology and Ceramics in Biomedical Applications and Advances in Biomineralized Ceramics, Bioceramics, and Bioinspiried Designs.

I would like to express my sincere thanks to Greg Geiger, Technical Content Manager of The American Ceramic Society for his hard work and tireless efforts in

the publication of this series. I would also like to thank all the contributors, editors, and reviewers for their efforts.

MRITYUNJAY SINGH
Volume Editor and Chairman, PACRIM-8
Ohio Aerospace Institute
Cleveland, OH (USA)

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Synthesis and Processing by the Spark Plasma Method

SIMULATION OF CONTACT RESISTANCES INFLUENCE ON TEMPERATURE DISTRIBUTION DURING SPS EXPERIMENTS

A. Cincotti[1], A.M. Locci[1,*], R. Orrù[1], G. Cao[1,2,*]

[1]Dipartimento di Ingegneria Chimica e Materiali, Unità di Ricerca del Consorzio Interuniversitario Nazionale di Scienza e Tecnologia dei Materiali (INSTM), Unità di Ricerca del Consiglio Nazionale delle Ricerche (CNR), Università degli Studi di Cagliari, Piazza d'Armi, 09123 Cagliari, Italy

[2]CRS4 – Centro di Ricerca, Sviluppo e Studi Superiori in Sardegna, Parco Scientifico e Tecnologico, POLARIS, Edificio 1, 09010 PULA (CA), Italy

* Authors to whom correspondence should be addressed

ABSTRACT

The behavior of the Spark Plasma Sintering/Synthesis (SPS) apparatus, which represents an effective tool for sintering/synthesizing advanced materials, is simulated in this work. A step-by-step heuristic procedure is proposed since several, concomitant physico-chemical phenomena, for example heat transfer and generation, electric current transport, and stress-strain mechanics along with chemical transformation and sintering, take place during SPS processes. In this work we consider the SPS behavior of specific sample configurations characterized by the absence of powders. This approach permits to determine the electric and thermal resistances experimentally evidenced in the horizontal contacts between stainless steel electrodes and graphite spacers as functions of temperature and applied mechanical load. Horizontal contact resistances between graphite elements are experimentally found to be negligible and, accordingly, they are not modeled. Model reliability is tested by comparing numerical simulations with experimental data obtained at operating conditions far from those adopted during fitting procedure of unknown parameters. The proposed model can be successfully compared from a quantitative point of view to the measured temperature, voltage once rms current, geometry are taken into account.

INTRODUCTION

SPS is an effective process for the sintering/synthesis of advanced materials like ceramics, metals, polymers and semiconductors.[1] Basically, it consists in heating up the powder sample shaped into a die inserted between two water cooled electrodes (rams) by means of a pulsed electric DC forced to pass through, while uniaxially pressing the system in order to facilitate sintering processes and guarantee electric circuit closure.

In the technical literature, SPS is considered a thermo efficient sintering process since highly dense products in relatively short times are attainable.[1-8] A volumic heating rate due to joule effect, in contrast to the conductive heat transport applied in conventional sintering systems, permits a quick temperature rise able to enhance the mass transport mechanisms responsible for sintering phenomena, thus improving consolidation rate and minimizing grain coarsening. The latter aspect leads to improved mechanical, physical and optical properties of final sintered products.[2]

While an updated review of modeling approaches adopted to simulate the behavior of SPS apparatus is reported elsewhere[1], a reliable mathematical model of SPS can be obtained in our view by separately analyzing an increasing complex system behavior in the framework of a step by step procedure, where physico-chemical phenomena, previously excluded, are gradually introduced along with their unknown model parameters. This approach allows one to independently fit the complete set of unknown parameters of the comprehensive SPS model, thus avoiding the masking effect given by the various phenomena involved in the whole process. In this work, the first step of this ideal approach is carried out by taking into account heat transfer phenomena, and current distribution. In particular,

the evaluation of the predominant electric and thermal contact resistances is carried out by comparing model results with experimental data obtained when appropriate samples characterized by the absence of powders are used. Specifically, explicit dependence of horizontal electric and thermal contact resistances on applied load and local temperature is obtained.

EXPERIMENTAL SECTION

A SPS apparatus 515S model (Sumitomo Heavy Industries Ltd., Japan) is used for the experimental runs. The power supply is a DC pulse generator which is reported to provide a maximum current and voltage equal to 1500 A and 10 V, respectively, while the mechanical load applied through an hydraulic system can be varied between 3 and 50 kN. Specifically, current pulses of 3.3 ms fixed duration are generated. Operator is free to select the pulse sequence, i.e. number of ON pulses (from 1 to 99) vs. number of OFF pulses (from 1 to 9) that represent periods of time with zero current. Typically, a 12/2 sequence is adopted (as prescribed by Sumitomo). This choice corresponds to the repetition of a sequence of 12 ON pulses followed by 2 OFF pulses for a total sequence period of 46.2 ms (i.e. 3.3x14 ms). It should be mentioned that no specifications are available regarding the measured current and voltage, i.e. average or rms values. Referring to Figure 1, the sample is inserted into a die placed between two plungers that are not in direct contact with the stainless steel rams, but spacers are typically inserted in between. From the electric point of view, the end parts of the rams are connected to an electric generator through copper bars and wires. Spacers, plungers and die are made of AT101-grade graphite (ATAL, Italy) which guarantees relatively high electric and thermal conductivities, i.e. lower power dissipation, higher heat transfer to powder specimen, and quicker cooling step. The use of graphite limits the attainable pressure level to a value less than 100 MPa, while the vacuum chamber permits to avoid chemical oxidation of graphitic elements. As it may be seen in Figure 1, the vacuum chamber is made of two coaxial cylinders both jacketed with cooling water circulation. A vacuum level down to 10 Pa is attainable with the SPS 515S model. Rams are made of stainless steel (AISI 304) and cooling water flows through them, as depicted in Figure 1, where the corresponding horizontal section a-a of the water circuit is also shown.

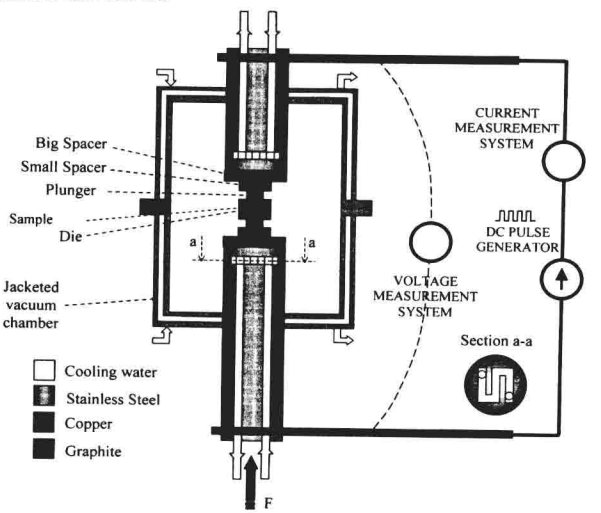


Figure 1: Schematic representation of SPS experimental set-up (not in scale).

A new data acquisition system has been designed and installed for independently measuring instantaneous (pulsed) values of electric current and voltage, from which calculating average and rms values. In particular, referring to Figure 1, an open loop Hall effect current transducer has been used (LEM HAX 2500-S, nominal primary current 2500 A rms, maximum primary current 5500 A, bandwidth 25 kHz, accuracy 1 % at nominal current) along with a voltage isolation amplifier (DATAFORTH DSCA41-09, Input range -40 to + 40 V, bandwidth 3 kHz, accuracy 0.03 % of full scale). The latter one is connected to the copper bars right close to the stainless steel electrodes. The output signals of these transducers are fed to a data acquisition board (200 kS/s, 12-Bit, 16 Analog Input Multifunction, National Instruments) connected to a PC, where a specifically designed Labview (National Instruments) virtual instrument is installed. This data acquisition system is able to collect instantaneously current and voltage measurements and calculate the corresponding average and rms values (sampling time $\tau = 0.5$ s), along with all the other variables typically measured in SPS processes (i.e. time, temperature, displacement, load, and gas pressure).

Specific sample configurations characterized by the absence of powders are considered in this work. In particular, we used the graphite cylindrical samples reported in Table I, along with the size of upper and lower stainless steel electrodes provided with SPS 515S model. Graphite samples have been inserted between rams during experimental runs. It should be noted that sample IV consists of two big spacers, two small spacers and one monolithic block in order to avoid vertical contact resistances, mimicking two plungers slid into a die.

MODELLING SECTION

Due to heat losses by radiation from lateral surfaces as well as heat removal by cooling water in axial direction, along with variations of cross sections, a 2D model for the energy balance of SPS technique is proposed, while radial symmetry is considered. Vertical symmetry cannot be assumed due to different heights of stainless steel electrodes and the corresponding cooling circuits. Although isotropic materials are considered, temperature variation in radial and axial directions induces spatial gradients of thermophysical properties like electric and thermal conductivities and coefficient of thermal expansion.

The energy balance in cylindrical coordinates (r,z) related to the stainless steel rams as well as the graphite samples depicted in Figure 1 and Table I is given by:

$$\rho_i C_{p,i} \frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\, k_i \frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(k_i \frac{\partial T}{\partial z}\right) + \frac{1}{\rho_{el,i}}\left[\left(\frac{\partial \varphi}{\partial r}\right)^2 + \left(\frac{\partial \varphi}{\partial z}\right)^2\right]; i = \begin{cases} Stainless\ Steel \\ Graphite \end{cases} \quad (1)$$

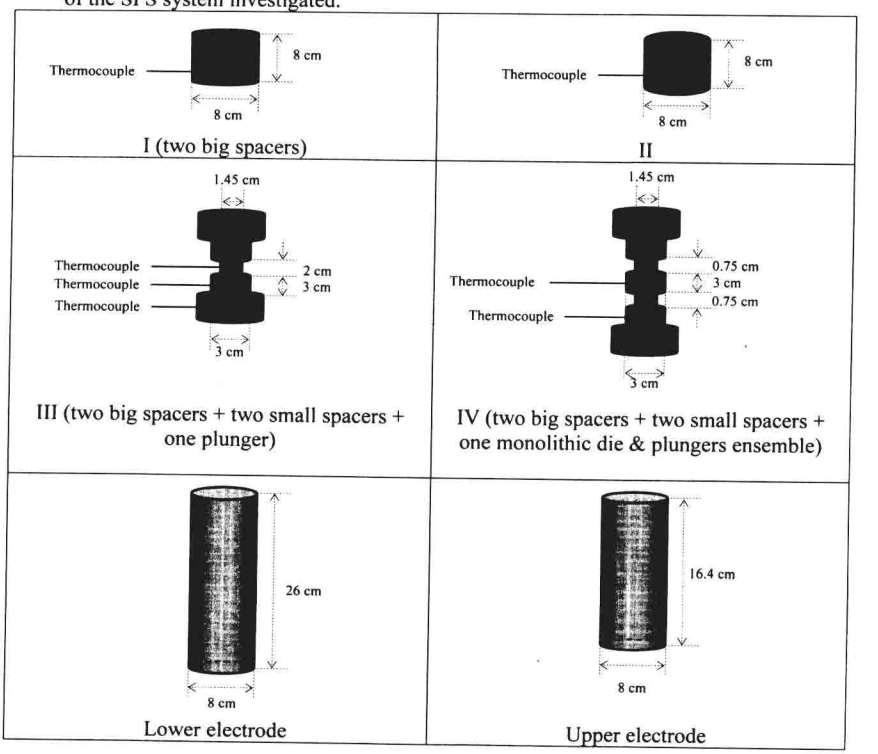
with the initial condition $T = T_0$ at $t=0$, while boundary conditions are reported in Figures 2 and 3. The meaning of the other symbols is reported in the Nomenclature Section. Only contact resistances at stainless steel-graphite interfaces are considered, with a local joule heat (q_e) due to electric contact resistance,[9] which has been equally split between the materials at the interface (i.e. $f = 0.5$ is considered when solving the model). The following steady-state conduction model:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{1}{\rho_{el,i}} r \frac{\partial \varphi}{\partial r}\right) + \frac{\partial}{\partial z}\left(\frac{1}{\rho_{el,i}} \frac{\partial \varphi}{\partial z}\right) = 0 \quad ; \quad i = \begin{cases} Stainless\ Steel \\ Graphite \end{cases} \quad (2)$$

coupled with the boundary conditions reported in Figures 2 and 3, is adopted for describing the electrical behavior inside the SPS system. Only contact resistances at stainless steel-graphite interfaces are considered, while equipotential conditions for electrode surfaces in contact with copper bars (cf.

Figure 1) have been adopted. The resistive portion of the rms voltage (φ) is given by the equation $\varphi = R\ I_{RMS}$, where resistance is determined from the measured average voltage and electric current ($R = \overline{V}/\overline{I}$). The pseudo isostatic equilibrium model adopted to simulate the mechanical behavior of SPS systems is reported elsewhere[10] for sake of brevity.

Table I: Samples configurations and dimensions (not in scale) of graphite and stainless steel elements of the SPS system investigated.



The resulting system of differential-algebraic-integral equations has been solved by FEM numerical technique. In particular, the commercial software COMSOL MULTYPHISYCS® 3.2 has been adopted (numbers of DOF and elements equal to about 25000 and 3000, respectively). Parameters used for computations are reported in Table II and Figure 4. In particular, heat transfer coefficient (h) is calculated as discussed elsewhere while heat graphite thermal conductivity determination deserves a comment, since different data are reported in the literature. In this work, $k_G(T)$ is evaluated by averaging the temperature dependences given by the two different references available in the literature consistent with the only value (100 W m^{-1} $°C^{-1}$ at 25 °C) provided by ATAL vendor for the graphite AT101. The only unknown model parameters remain therefore thermal and electric conductances, C_T and C_E, at the horizontal contacts between stainless steel electrodes and graphite spacers (cf. see

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