FIELD ASSISTED SINTERING OF LARGER SCALED CERAMIC PARTS USING ADAPTED TOOL DESIGN AND HYBRID HEATING

Martin Bram, Forschungszentrum Jülich GmbH
m.bram@fz-juelich.de
Moritz Kindelmann, Forschungszentrum Jülich GmbH
Alexander M. Laptev, Forschungszentrum Jülich GmbH
Olivier Guillon, Forschungszentrum Jülich GmbH

Key Words: FAST/SPS, hybrid heating, oxide ceramics, thermal gradients, tool design

Field Assisted Sintering/Spark Plasma Sintering (FAST/SPS) is a promising technology for the energy efficient sintering of ceramic, composite and metal powders. The combination of direct current heating and applied pressure enables high heating rates, rapid densification and offers the potential to decrease the sintering temperature significantly. FAST/SPS is of special interest for materials, which are difficult to densify by conventional methods like pressure less sintering. To establish this processing technology on industrial scale, fundamental studies are required to better understand the relationship between processing parameters, specific FAST/SPS boundary conditions and resulting material properties. A challenging task – especially for non-conductive oxide ceramics – is the decrease of thermal gradients during FAST/SPS cycles to a minimum and to suppress interface reactions with the tool material.

In the present work, a systematic study was conducted in our FAST/SPS device aiming on to homogeneously densifying commercial yttria (Y2O3) powder to discs with diameter up to 100 mm. Specific attention was laid on the formation of thermal gradients during the cycle and to investigate their influence on the resulting microstructure. Therefore, different tool set ups were used. Amongst others, carbon fiber reinforced carbon (CFC) inlays were implemented to adjust thermal conductivity of the tool. Furthermore, the effect of hybrid heating was evaluated. For this experimental series, an additional induction coil was mounted in the FAST/SPS device. For evaluating the efficiency of hybrid heating, total energy consumption of the FAST/SPS device – operated with and without induction coil – was measured.

The experimental studies were accompanied by finite element modelling to estimate the temperature distribution of non-conductive yttria sample during FAST/SPS processing. The modelling results will be correlated with the grain size distribution along the cross section of the 100 mm disc. Additionally, Vickers hardness measurements were done to investigate how thermal gradients tend to influence mechanical properties.

ELABORATION OF COMPLEX SHAPES BY SPARK PLASMA SINTERING

Antoine Van der Laan, CIRIMAT, Université de Toulouse, CNRS, Université Toulouse 3, France ; Norimat, 51 Rue de l'Innovation, 31670 Labège, France
van-der-laan@chimie.ups-tlse.fr
Romain Epherre, Norimat, 51 Rue de l'Innovation, 31670 Labège, France
Claude Estournès, CIRIMAT, Université de Toulouse, CNRS, Université Toulouse 3, France

Key Words: Spark Plasma Sintering, Complex shapes, Mobile interface, Thermo-electrical and mechanical simulation

Spark Plasma Sintering (SPS) is an efficient powder consolidation technique that allows the production of fully dense materials with a controlled microstructure. Recently a milestone has been reached by C. Manière et al. [1] on the elaboration of parts with complex shapes using SPS. This method is based on a mobile interface placed between the powder to be sintered and a sacrificial porous material, which defines a pre-form of the part to be obtained. The mobile interface enables an easy separation of the dense part and the sacrificial material after the sintering cycle. In order to industrialize this process a thorough investigation of the sintering mechanisms and the mechanical interactions between the two materials is needed.

Numerical simulation is an efficient tool to address these new challenges and allows a better understanding of the process. A fully coupled thermo-electrical and mechanical simulation of the sintering of a complex shape was developed in order to obtain a dense and near-net shape object by SPS. The model was done by finite element analysis in parallel with experimental testing to ensure the validity of the predicted results. Numerical simulation can also be used as a predictive tool in order to anticipate issues like the apparition of hot spots or local concentration of mechanical stress during SPS.

[1] : C. Manière et al. / Powder Technology 320 (2017) 340–345

FLASH SINTERING OF INJECTION MOLDED ZIRCONIA UNDER AC ELECTRIC FIELD FOR ENHANCEMENT OF OPTICAL PROPERTIES

Andre Prette, LUCIDEON
andre.prette@lucideon.com
Christopher Green, LUCIDEON
David Pearmain, LUCIDEON

Key Words: zirconia, AC, translucency, fracture toughness, flash sintering

Zirconia is a very versatile ceramic material used in many applications, from structural components to healthcare implantable parts. The majority of current flash research has been performed using uniaxial pressed samples. In our research, we looked to study a large-scale manufacturing technique to produce the samples to be sintered. Ceramic injection molding (CIM) is a known method to produce complex shaped parts with great precision and high density. The high binder content in CIM parts can cause difficulty during flash sintering, due to the high porosity left after debinding process. This can cause localization and flashover during the application of the electric field. Commercially injection molded partially stabilized zirconia (3YSZ) was chosen as it has important properties, such high fracture toughness, however, it is usually opaque due to inherent microstructure defects and grain size of the material. For many applications, zirconia, does not require a particular color or specific appearance, but in some cases for aesthetic uses, a transparent-like material is highly desirable. This paper will describe the results on flash sintering equipment design and field parameters used in order to optimize levels of translucency in zirconia disks, with high fracture toughness. The flash sintering process is shown to be repeatable, and is compared with conventionally sintered samples to assess the improvement on translucency and/or fracture toughness. It is then proposed that flash sintering is an enabling mechanism for the use of zirconia in a wider range of applications and markets, where aesthetics and toughness are required in parallel.

ELECTRICAL FIELD ASSISTED SINTERING OF YTTRIUM DOPED CERIA INVESTIGATED BY SINTER-FORGING

Chen Cao, Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Germany
c.cao@fz-juelich.de
Robert Mücke, Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Germany
Olivier Guillon, Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Germany, Jülich Aachen Research Alliance

Key Words: sinter-forging, electrical field assisted sintering, uniaxial viscosity, sintering stress, ceria

The production of traditional and advanced ceramics is an energy-intensive activity, which requires high sintering temperatures and long holding times to activate diffusional processes necessary for densification. Electric field assisted processing has the potential to significantly reduce the sintering time and temperature which are not obtainable by other methods. The role of electric fields in the densification and coarsening of oxide ceramics is still under debate. By using a sinter-forging device equipped with a versatile power source and high-resolution laser scanners, it is possible to investigate in detail field assisted sintering process by quantifying uniaxial viscosity, viscous Poisson's ratio and sintering stress of oxide ceramics. The macroscopic Joule heating effect was eliminated by using Finite-Element Simulations calibrated experimentally and by lowering the furnace temperature accordingly. In other words, the sample temperature was kept constant under the different testing conditions, enabling a correct estimation of a thermal electric field effects. The sintering parameters of the ceramic pellets were measured without / with alternating electrical field well below flash sintering conditions. Clear effect of the electrical field on both uniaxial viscosity and sintering stress were observed. Microstructures of the specimens were investigated by SEM and TEM, and correlated to the electrical properties of the samples measured by Electrochemical Impedance Spectroscopy in order to understand the interplay between grain boundaries and electric field.

ADVANTAGES OF THE METHOD OF HIGH-VOLTAGE CONSOLIDATION OF POWDER MATERIALS

Evgeny Grigoryev, ISMAN
eugengrig@mail.ru
Vladimir Goltsev, NRNU MEPhI
Natalya Ermakova, NRNU MEPhI
Andrey Osintsev, NRNU MEPhI
Aleksandr Plotnikov, NRNU MEPhI

Key Words: high-voltage electropulse consolidation, cumulative closure of interparticle pores, W-based alloys powders, plastic flow, tensile strength.

The main features of high-voltage electropulse consolidation (H-VEC) of powder materials and the unique possibilities of the method caused by them are considered. The electro-thermal processes in the H-VEC at the contacts between the powder particles and in the macroscale of the whole consolidated sample are analyzed. The results of calculations of the dynamics of closure (collapse) of interparticle pores in the consolidated material are presented. The experimental results of high voltage consolidation W-based heavy alloys are discussed and a theoretical analysis of the kinetics of compaction of powder materials is made. The results of investigation of the macro- and microstructure of consolidated materials and the stress - strain testing are presented. Compression testing showed that all tested alloys bear compressive stress at room temperature without failure. Figure 1 shows a characteristic diagram of the compressive deformation, which indicates the appearance and development of plastic deformation at the stress above 1250 MPa.

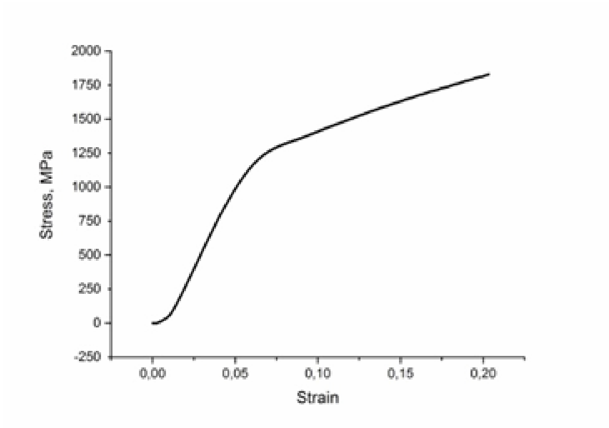


Figure 1 - Deformation curve of the heavy alloy

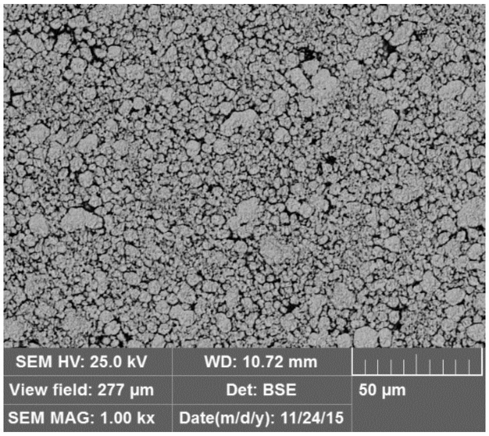


Figure 2 - Microstructure of the heavy alloy

The plasticity of the heavy tungsten alloy is one of the objectives of the current research. Microstructure of the sample obtained by a scanning electron microscope is shown in Figure 2. The high-voltage consolidation contributes to maintaining a initial fine-grained structure, more uniform distribution of iron-nickel binder and almost total absence of porosity.

The optimal modes of high voltage consolidation W-based heavy alloys on the results of tests of short cylinders according to the “Brazilian test” scheme were obtained.

Examples of the use of H-VEK and the direction of further research are considered.

FLASH SINTERING OF BETA"-ALUMINA SOLID ELECTROLYTES FOR SODIUM BATTERY APPLICATIONS

Gareth Jones, The University of Warwick, United Kingdom
gareth.jones@lucideon.com
Y. Hu, Ionotec Limited, 14 Berkeley Court, Manor Park, United Kingdom
S. Ghanizadeh, Lucideon Limited, Queens Road, Penkhull, Stoke-on-Trent, United Kingdom
D. Pearmain, Lucideon Limited, Queens Road, Penkhull, Stoke-on-Trent, United Kingdom
S.N. Heavens, Ionotec Limited, 14 Berkeley Court, Manor Park, United Kingdom
J.S. Blackburn, Ionotec Limited, 14 Berkeley Court, Manor Park, United Kingdom

S.Maclachlan, Lucideon Limited, Queens Road, Penkhull, Stoke-on-Trent, United Kingdom

The rechargeable sodium batteries, sodium sulphur (NaS) batteries and molten-salt sodium nickel chloride (Na-$NiCl_2$) are proven commercially available systems, particularly for large-scale energy storage applications and electric vehicle applications respectively. They have attractive properties such as the use of abundant low-cost raw materials, high energy and power density, high faradaic efficiency of charge/discharge, zero self-discharge rate and proven long-term durability. Conventional manufacturing of the core component, the sodium beta"-alumina solid electrolyte, requires a high sintering temperatures, ~ 1600 °C to achieve high density and good ceramic quality, which contributes significantly to battery cost, energy and time consumption in production. Flash sintering, a novel low-cost electrical field-assisted sintering technology, has been investigated for sintering beta"-alumina samples in a collaboration between Lucideon Limited and Ionotec Limited. This work will describe the preliminary results on flash sintering equipment design and prototype sodium beta"-alumina ceramics with variation of the flash-sintering process parameters, i.e. current, frequency, times (incubation, development, holding), pulse experiments, current ramp rate, the on-set furnace temperature, sample geometry (discs versus open-ended tubes), electrode materials (Ag versus Pt paints), single versus double electrode and sample homogeneity. In particular, we will report a significant step towards scale up by showing results on homogeneously-sintered, highly dense more complex geometries such as tubes and closed end tubes using refined field sintering process.

ELECTROCHEMICAL, OPTICAL AND THERMAL EFFECTS DURING FLASH SINTERING OF 8YSZ

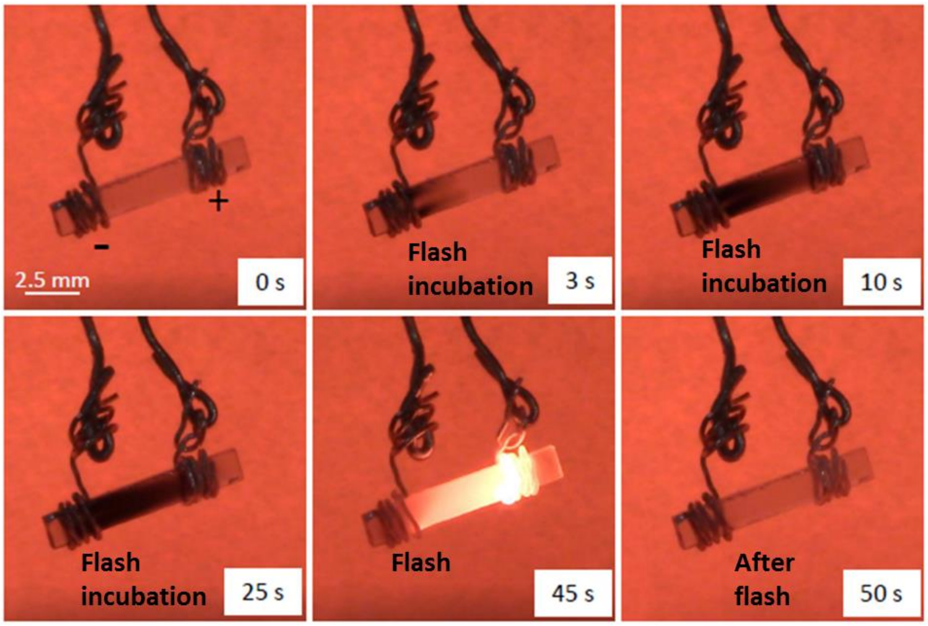
Mattia Biesuz, Queen Mary University of London
mattia.biesuz@outlook.com
Lorenzo Pinter, University of Trento
Theo Saunders, Queen Mary University of London
Jon Binner, University of Birmingham
Vincenzo Sglavo, University of Trento
Salvatore Grasso, Southwest Jiaotong University
Mike Reece, Queen Mary University of London

Key Words: Flash sintering; 8YSZ; electrochemistry; electrochemical reduction; electronic conductivity

We report on the electrochemical effects occurring during the flash sintering of 8YSZ. In-situ observations for both polycrystalline and single crystal specimens confirm electrochemical blackening/darkening during the incubation period prior to flash sintering (Figure1), even though chromatic alterations are usually visible only after the samples are cooled down in a protective atmosphere rather than in air. The phenomenon is induced by cathodic partial reduction under a DC field. When using a low frequency AC (square 0.1 – 10 Hz) field, the blackening becomes reversible and it follows the imposed polarity switching. Thermal imaging combined with sample color changes (transparent single crystals) and electrical conductivity mapping give a complete picture of the multi-physical phenomena occurring during each stage of the flash sintering event.

The partial reduction causes a modification of the electrical properties in the samples, the blackened regions (close to the cathode) are more conductive than the rest of the sample. The asymmetrical nature of the electrochemical reduction follows the field polarity causing asymmetry of temperature from anode to cathode where the positive electrode tends to overheat. The phenomena are governed by the quality of electrical contacts and treating atmosphere.

Figure 1 – Color change during flash sintering of 8YSZ single crystal.



STUDY OF THE PHASE TRANSFORAMTION INDUCED BY FLASH SINTERING IN MN2O3 AND THE INVESTIGATION OF THE ROLE OF DEFECTS IN FLASH SINTERING USING IN-SITU RAMAN SPECTROSCOPY

Shannon Murray, University of Illinois at Urbana-Champaign
semurra2@illinois.edu
Tyler Jensen, University of Illinois at Urbana-Champaign
Soumitra Sulekar, University of Illinois at Urbana-Champaign
Daniel Shoemaker, University of Illinois at Urbana-Champaign

Key Words: Flash sintering, Mn_2O_3, in-situ Raman

Flash sintering is a method to rapidly densify materials by applying an electric field at elevated temperatures [1]. Besides densification, flash sintering is also a technique for reactive sintering. A number of materials, including Al_2TiO_5, have been synthesized by flash sintering [2]. Utilizing the thermal runaway, ion migration, or defect creation resulting from the flash could allow for the synthesis of novel materials. This work has demonstrated the simplest synthesis, the transformation of one phase into another. When Mn_2O_3 is flash sintered under the appropriate experimental parameters, it transforms into Mn_3O_4 during stage III.

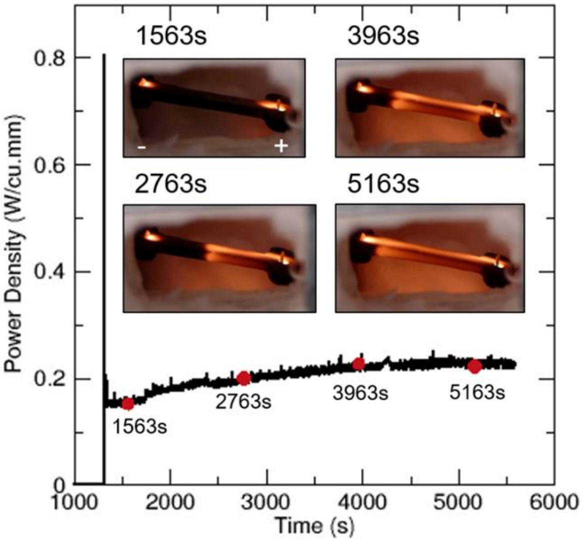


Figure 2 - Images of a 12.5 V/mm, 0.095 A/sq.mm flash. The labeled red dots on the power density plot correlate to the images. With increasing time, the glow progresses from the right (anode, +) to the left (cathode, -). The areas glowing orange are Mn_3O_4 while the black areas are Mn_2O_3.

When Mn_2O_3 is flashed above a threshold electric field (12.5 V/mm) and furnace temperature, and stage III is held for a sufficient amount of time, an orange glow progresses from anode to cathode. Figure 1 shows the progression where each image corresponds to a dot on the power density trace. During a flash, the black areas are Mn_2O_3 while the glowing orange areas are Mn_3O_4. The phase transformation only occurs when the sample is flashed using a specific electric field. At fields below 12.5 V/mm the sample remains Mn_2O_3, but at fields larger than 16.25 V/mm the sample breaks due to localized current flow.

Via flash sintering, the conversion of Mn_2O_3 to Mn_3O_4 occurs at a furnace temperature of 285°C, far lower than 950°C, the temperature required by conventional methods [3]. Additionally, once the sample begins to flash, external heat from the furnace is no longer needed and the phase propagation occurs while the furnace is off.

After stage II, Mn_3O_4 has formed at both electrodes of the Mn_2O_3 pellet. Since Mn_2O_3 is an electronic conductor, it is possible the flash forms oxygen vacancies at the anode which cannot propagate to the cathode since there is no ionic transport [4]. Switching the polarity of the electrodes and flashing an Mn_2O_3 pellet a second time does not change the direction of phase propagation, so the first flash must induce a change in the material that is not overcome by the second.

Studies have demonstrated flash sintering produces anomalous defects, but no in-situ studies of defects have been performed [5]. In-situ Raman spectroscopy is capable of such experiments and, in this work, a custom furnace with a window was built for this purpose and the in-situ setup was proven to provide reliable Raman data. Mn_2O_3 does not produce a Raman signal with enough intensity for in-situ measurements, but more suitable materials such as $SrTiO_3$ may help answer the question of what role defects play in flash sintering.

[1] M. Cologna et al., J. Am. Ceram. Soc., vol. 93, no. 11, pp. 3556–3559, 2010.
[2] S. K. Jha et al., J. Eur. Ceram. Soc., vol. 36, no. 3, pp. 733–739, 2016.
[3] D. M. Tinsley et al., J. Thermal Anal., vol. 3, pp. 43–48, 1971.
[4] M. Biesuz et al., Materials (Basel)., vol. 11, no. 7, 1214, 2018.
[5] E. K. Akdogan et al., J. Appl. Phys., vol. 113, no. 23, 233503, 2013.

INCREASE IN HARDNESS FOR FLASH SINTERED CERAMICS

David Kok, University of California, Irvine
dkok@uci.edu
Rishi Raj, University of Colorado, Boulder
Martha Mecartney, University of California, Irvine

Key Words: Flash Sintering, Hardness, Alumina, Spinel, 8YSZ

A study of the hardness values of flash sintered multiphase ceramics was carried out to determine the effect of flash sintering on mechanical property. A three-phase ceramic of equal volume percent of Al_2O_3, $MgAl_2O_4$, and 8YSZ was compared to single phase Al_2O_3, $MgAl_2O_4$, and 8YSZ. Samples were flash sintered with an isothermal furnace temperature of 1450°C, a field of 680 V/cm, and a current limit set to $50 mA/mm^2$. Control samples were made by conventional sintering and two-step sinter forging. Vickers hardness tests were conducted to evaluate hardness as a function of process parameters. Initial results revel an increase of hardness for flash sintered samples compared to conventional sintered and two-step sinter-forged samples. The two-step sinter-forged samples and flash sintered three-phase samples had similar grain sizes and density, and the increase in hardness is hypothesized to be a result of increase point defects resulting from flash sintering.

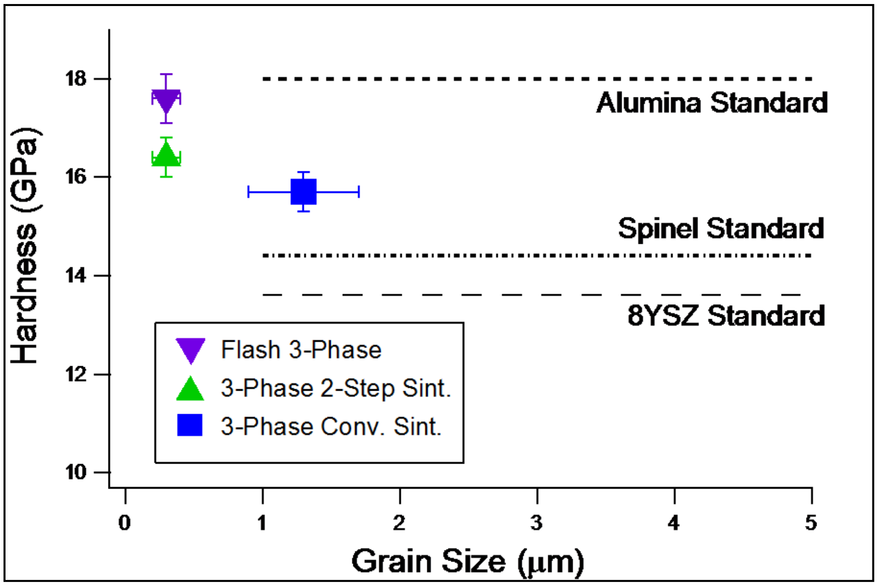


Figure 3 – Hardness values of flash versus conventionally sintered samples

IN-SITU X-RAY CHARACTERIZATION OF PHASE EVOLUTION DURING SOLID-STATE REACTIONS OF MULTICOMPONENT SYSTEMS

Sanjit Ghose, NSLS-II, Brookhaven National Laboratory, Upton, USA
sghose@bnl.gov

Key Words: synchrotron, x-ray, x-ray diffraction (XRD), pair distribution function (PDF), phase transformation, reactive flash sintering

The discovery of new solid inorganic materials cuts across their synthesis, nanostructure and properties. They cover both structural and functional materials and have potential impact in a wide range of technologies. Understanding the synthesis pathways of these solid-state materials is a prerequisite in correlating chemistry and nanostructure to properties.

Advanced processing and synthesis methods such as High Temperature Flux, Electrical Flash Sintering and Microwave Synthesis, require probing the time resolved state of materials, in order to understand the kinetics and structure of intermediate phases. This need is addressed by fast in-situ atomic level x-ray characterization techniques such as X-ray Diffraction (XRD) and X-ray Pair Distribution Function (PDF), which have been implemented at the 3rd generation synchrotron sources around the world.

In this presentation I will be discussing how XRD and PDF tools are used to study the synthesis mechanisms and evolution of crystal compositional phases for the ceramic and battery materials. Providing a few examples, I will describe the technical aspects of the tools, the capabilities for sample environments and results from the XPD beamline at the NSLS-II synchrotron radiation source of Brookhaven National Laboratory. This presentation will not only provide information on the topics discussed but also open up new ideas to look at new materials with different prospective.

SOLUTE–DRAG VS. SOLUTE-ACCELERATION DURING MICROSTRUCTURAL EVOLUTION OF ALUMINA

Wayne D. Kaplan, Technion, Israel Institute of Technology
kaplan@technion.ac.il
Ruth Moshe, Technion, Israel Institute of Technology
Rachel Marder, Technion, Israel Institute of Technology

Key Words: Mobility, Alumina, Adsorption, Solubility, Grain Boundaries.

The role of dopants in processing ceramics has been an important issue for many years, especially given the contradicting reports of retarded or accelerated grain growth by key dopants and impurities. To fully understand these effects in terms of solute segregation versus enhanced grain boundary (GB) mobility due to liquid phase formation, an effort has been made to quantify the high temperature (1600°C) solubility limit of Mg, Ca, and Si in alumina. Using these values, samples doped below the solubility limit with Mg, or Ca, or C, or co-doped with Mg and Ca were prepared at concentrations which were measured using fully standardized wavelength dispersive spectroscopy. Measurements of GB mobility as a function of measured dopant concentration below the solubility limit has shown that Mg and carbon indeed retard GB mobility by solute-drag. However, Ca impurities increase the GB mobility of alumina at dopant values below the solubility limit (i.e. without forming liquid phases at the grain boundaries or triple junctions). The segregating dopants are associated with 2-D structural and compositional transitions at the GBs, and possible changes in the mechanism of GB migration. This presentation will review recent GB mobility measurements and the concept of 2-D GB transitions and their potential role on the mechanism of GB motion.

DIELECTRIC BEHAVIOR OF FLASH SINTERED KNN

Ricardo Serrazina, CICECO-UA
serrazina@ua.pt
Ana M.O.R. Senos, CICECO-UA
Luis Pereira, FCT-NOVA
Paula M. Vilarinho, CICECO-UA

Key Words: FLASH, KNN, Lead-free piezoceramics, Dielectrics.

The market for lead-based piezoceramics, mainly ($Pb_{1-x}Zr_xTiO_3$, PZT) - based materials, is higher than $100 billion per year. Due to lead-toxicity, the demand for lead-free piezoceramics is increasing. Potassium Sodium Niobate solid solutions, namely $K_{0.5}Na_{0.5}NbO_3$, KNN, is currently one of the most promising materials for electromechanical applications. However, monophasic conventionally sintered KNN is hard to obtain, due to alkali evaporation during sintering (T > 1100 ºC, t > 2h). Within this context, there is an increasing interest in sustainable sintering techniques, as FLASH, to decrease both sintering time and temperature, avoiding alkali vaporization. However, FLASH applied to bulk ceramics, frequently produces inhomogeneous specimens.

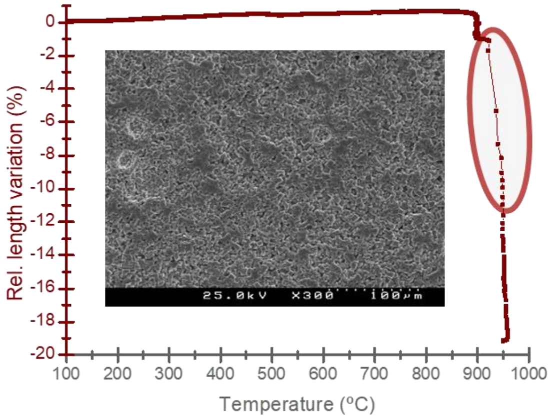


Figure 4 – Variation of length with temperature of FLASH sintered KNN, after a 2 h isothermal step. SEM micrograph showing the uniformly dense microstructure.

In this work, we propose an experimental approach that allows the production of homogeneous, highly dense, KNN. In this method, the use of FLASH sintering contributed to reduce KNN sintering temperature for more than 200 ºC and the cycle time in ~3h. Uniform densification was achieved by using an isothermal step before the application of the electric field. Scanning Electron Microscopy (SEM) and Specific Surface Area (SSA) measurements were performed to characterize the pre-FLASH sintering microstructure.

Interestingly, and for the first time, we show that FLASH sintered KNN behave very closely to conventionally sintered materials, in terms of permittivity as a function of temperature, with a Curie temperature of FLASH sintered KNN very close to 420 ºC. Moreover, despite some leakage currents, FLASH sintered KNN can be polarized and its ferroelectric characteristic determined.

Acknowledgments:

This work is financed by Portugal 2020 through European Regional Development Fund (ERDF), in the frame of Operational Competitiveness and Internationalization Programme (POCI), in the scope of the project “FLASH sintering of lead free functional oxides towards sustainable processing of materials for energy and related applications- FLASH”, POCI-01-0247-FEDER-029078, and in the scope of the project CICECO- Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), cofinanced by national funds through the FCT/MEC

FORMATION OF DEFECT-ENRICHED PHASES FAR FROM EQUILIBRIUM AS A FLASH SINTERING MECHANISM

Malte Jongmanns, Department of Physics, University of Duisburg-Essen, D-47057 Duisburg, Germany
Malte.Jongmanns@uni-due.de
Dietrich E. Wolf, Department of Physics, University of Duisburg-Essen, D-47057 Duisburg, Germany

Key Words: flash sintering, defect generation, Frenkel defects, phonons, molecular dynamics

Flash sintering is a non-equilibrium phenomenon that manifests itself in rapid densification of green bodies, non-linear rise in the electrical conductivity and light emitted by electroluminescence. The underlying physics of this combination of phenomena remains puzzling. Flash sintering experiments in poly- and single-crystal ceramics imply the formation of phases far from equilibrium. These phases are considered to be enriched by Frenkel defects which separate into charge neutral vacancies and interstitials as well as electron-hole pairs, explaining the unique observations of flash sintering. We hypothesize that these crystal defects are being generated due to a fast proliferation of short-wavelength lattice vibrations. This hypothesis is supported by recent experiments, where the Debye-temperature was found to be a lower bound for the onset of the flash.

In this talk, we will show by means of Molecular Dynamics simulations of single crystal aluminum, that a non-equilibrium state enriched by Frenkel pairs can be induced by excitation of short-wavelength lattice vibrations with a high rate. We find that Frenkel interstitials are only created above the Debye temperature, but much below the melting point. The molar concentration of the Frenkel pairs is far above equilibrium. While these results were found for Al, we discuss the universality of this mechanism on the example of rutile TiO_2. First simulation results indicate, that Frenkel pairs are also generated in TiO_2, where oxygen atoms take interstitial lattice sites.

DEEP LEARNING OF CVD GROWTH AND PHASE-TRANSITION PATHWAYS IN LAYERED MATERIALS

Rajiv Kalia, Rajiv Kalia, University of Southern California, USA
rkalia@usc.edu

Electrical and optoelectronic properties of two-dimensional (2D) transition metal dichalcogenides (TMDCs) can be tuned by exploiting their polymorphism. Here, polymorphism in TMDCs and their growth by chemical vapor deposition (CVD) are examined using deep generative models namely, the variational autoencoder (VAE) and Restricted Boltzmann Machine (RBM), trained with molecular dynamics (MD) simulation data. The VAE correctly identifies pathways connecting the semiconducting (2H) and metallic (1T) phases via novel intermediate structures called a and *b*□in $MoWSe_2$ alloy. These intermediate structures are similar to those observed in a 2D MoS_2 by scanning transmission electron microscopy. Structures generated solely by VAE are combined to form novel $MoWSe_2$ devices with *a* and *b* interfaces. Quantum simulations based on density functional theory show that interfaces synthesized by VAE are stable and the devices with those interfaces are suitable for novel nanoelectronics applications. A novel deterministic RBM algorithm is used to identify 2H and 1T phases and defects in reactive MD simulations of the synthesis of a MoS_2 monolayer by CVD. Applications of the deterministic RBM approach to modeling of experimental data will also be presented.

* This work was supported as a part of the Computational Materials Sciences Program funded by the U.S Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC0014607.

MODELING OF JOULE HEATING IN KNN FLASH SINTERING

Ricardo Serrazina, CICECO-UA
serrazina@ua.pt
Julian Dean, University of Sheffield
Ian M. Reaney, University of Sheffield
Ana M.O.R. Senos, CICECO-UA
Luis Pereira, FCT-NOVA
Paula M. Vilarinho, CICECO-UA

Key Words: FLASH, KNN, TEM, FEM, Joule Heating.

In this work, we propose the use of FLASH sintering as an alternative technique to densify Potassium Sodium Niobate, $K_{0.5}Na_{0.5}NbO_3$, KNN, a piezoceramic with relevant promising applications and a possible viable substitute of lead zirconate titanate based compositions ($Pb_{1-x}Zr_xTiO_3$, PZT). We aim to increase this material performance by densifying KNN ceramics without secondary phase segregation. Furthermore, FLASH will contribute to a more sustainable processing of piezoelectrics as lead-free ceramics at reduced sintering temperature and time.

Our results show that KNN can be FLASH sintered at temperatures as low as 300 ºC, when special sintering atmosphere conditions are considered. Moreover, no secondary phases are segregated, and, highly dense areas can be found. We show that particle amorphization and sliding, as consequence of Joule Heating, are the main mechanisms contributing for KNN FLASH sintering. Transmission Electron Microscopy, TEM, of FLASH sintered KNN ceramics revealed that GBs are amorphous and contain segregated contaminations. It was concluded that Joule heating contributed to reach very high local heating rates up to also high temperatures, causing particle surface melting, amorphization and sliding. In addition, the characteristic cuboid shape of KNN particles allowed to correlate the particle contact geometry with the final microstructure. As shown in fig.1, sharp contacts, as vertex or edges, can even penetrate the faces of the neighbor's cuboid and the amount of produced liquid phase was observed to be dependent on the type of particle contact, decreasing by the following order: vertex-vertex > vertex-face > edge-face > face-face.

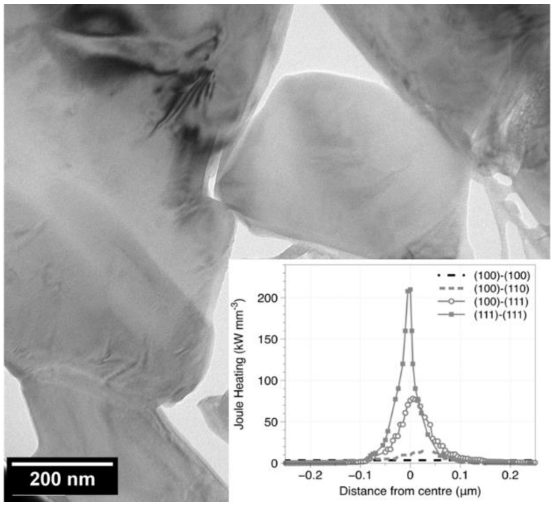


Figure 5 – TEM micrograph of FLASH sintered KNN, with amorphized GBs and penetration of sharp edge trough neighbor face. Overlapped calculated Joule heating for the four considered possible particle contacts.

Finite element modeling, FEM, was used as a tool to model the microstructure of particle contacts and calculate the current density and Joule heating. A coherent relation between the model and TEM experimental observations was found. In the vertex-vertex configuration, an excess of Joule heating that is 250x higher than that in the face-face configuration was found, which can explain the particle penetrations.

Acknowledgments:
This work is financed by Portugal 2020 through European Regional Development Fund (ERDF), in the frame of Operational Competitiveness and Internationalization Programme (POCI), in the scope of the project "FLASH sintering of lead free functional oxides towards sustainable processing of materials for energy and related applications- FLASH", POCI-01-0247-FEDER-029078, and in the scope of the project CICECO- Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), cofinanced by national funds through the FCT/MEC

THERMAL RUNAWAY, DYNAMIC STABILITY AND PROCESS CONTROL IN FLASH SINTERING

João Gustavo Pereira da Silva, Forschungszentrum Jülich
joao.silva@fz-juelich.de
Chen Cao, Forschungszentrum Jülich
Tarini Mishra, Forschungszentrum Jülich
Robert Mücke, Forschungszentrum Jülich
Olivier Guillon, Forschungszentrum Jülich

Key Words: Flash Sintering, Modeling, Joule Heating.

Flash sintering is an innovative sintering method in which a critical combination of electrical field and temperature triggers a sudden densification in seconds. Due to the nature of the process, the flash sintering conditions lead to a non-linear conductivity surge followed by current control. This work tries to answer some questions related to process control during flash sintering by using a dynamic system model-based approach. An explicit solution for the folding points in the voltage control mode is presented (Figure 1). The analytical model uses a dynamic bifurcation approach which explains why the current control mode always leads to a steady state, due to the unicity of the solution to the equations, and why different modes of flash sintering such as current-controlled or power-controlled lead to a more uniform process. The model is validated with experiments in Cerium Oxide doped with Gadolinium and Yttrium.

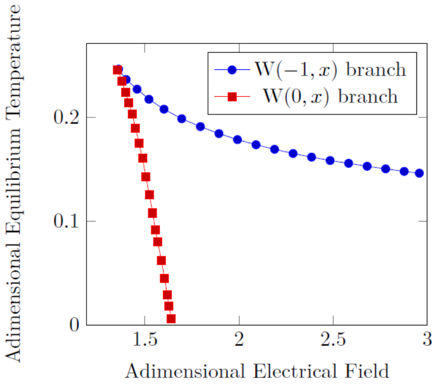


Figure 1. Branches of the folding point of the equilibrium surface.

KINETICS OF LIQUID-ASSISTED DENSIFICATION DURING FLASH SINTERING OF CERAMIC NANOPARTICLES

Rachman Chaim, Department of Materials Science and Engineering
Technion – Israel Institute of Technology, Israel
rchaim@technion.ac.il

Key Words: Flash sintering; liquid-assisted sintering; ceramics; electro-osmosis; nanocrystalline

The recent liquid film capillary mechanism [1, 2] proposed for the rapid densification during the flash sintering was consistent energetically with the dissipated power during the process. Following this mechanism, melting of contacts with high electric resistance will induce high attractive capillary forces. Wetting of a solid substrate by its own melt is termed homologous wetting with zero wetting (dihedral) angle. Therefore, wetting and spreading of the melt on its own substrate is extremely fast. Here we will show that particle surface softening / melting and the following transient processes associated with it namely local melt wetting and spreading, particle rearrangement, melts solidification, are also kinetically compatible with the flash process and its duration.
We analyzed the liquid-assisted densification kinetics of ceramic nanoparticles during flash sintering in terms of wetting and melt spreading, from the nanoparticle contacts, affected by the local electric field and capillary forces. Homologous wetting and spreading of the melt from the particle contacts reveal wetting velocities of $0.3 \cdot 10^{-6}$ $m \cdot s^{-1}$ and 1 $m \cdot s^{-1}$ induced by the electric field and the capillary forces, respectively. The ultrafast densification kinetics by particle rearrangement is consistent with the enhanced diffusion and calculated wetting velocities. Epitaxial solidification of the melt after particle rearrangement is energetically favorable, and its tendency depends on the melt viscosity.

1. R. Chaim, Materials 9 (2016) 280.
2. R. Chaim, C. Estournes, J. Mater. Sci. 53 (2018) 6378-6389.

IMPEDANCE CHARACTERIZATION OF CALCIA-STABILISED ZIRCONIA AS A FUNCTION OF APPLIED FIELD

Julia Ramírez González, The University of Sheffield
jramirezgonzalez1@sheffield.ac.uk
Anthony R. West, The University of Sheffield

Key Words: Calcia-stabilised zirconia, impedance spectroscopy, electric field effect, oxygen partial pressure.

Cubic stabilised-zirconias are well-known oxide ion conductors. They are used as solid electrolytes in oxygen sensors and in solid oxide fuel cells (SOFCs). However, it has been demonstrated recently that electronic conduction can be introduced into yttria-stabilised zirconia (YSZ), under the application of either (i) a small *dc* bias or (ii) for YSZ compositions with higher yttria content, by an increase in oxygen partial pressure (pO_2) [1]. Such electronic conduction will have implications for materials that are to be used as ionically-conducting but electrically-insulating components in fuel cells and sensors.

A drop in resistance is a characteristic feature of flash sintering (FS), especially during the flash process [2] but the role of electronic conductivity in stage (I), prior to flash, is not well understood. In order to gain further understanding of the sensitivity of materials to an electrical field and the conditions under which electronic conduction may be introduced, the electrical properties of calcia-stabilised zirconia (CSZ) ceramics were studied under the application of a *dc* bias and with different pO_2. Three electrical components were identified: bulk, grain boundary and, sample-electrode interphase, Figure 1. It was noticed that the resistance of the three components decreased in the presence of an electric field and also, with change in pO_2. A more extensive set of results will be presented and evaluated.

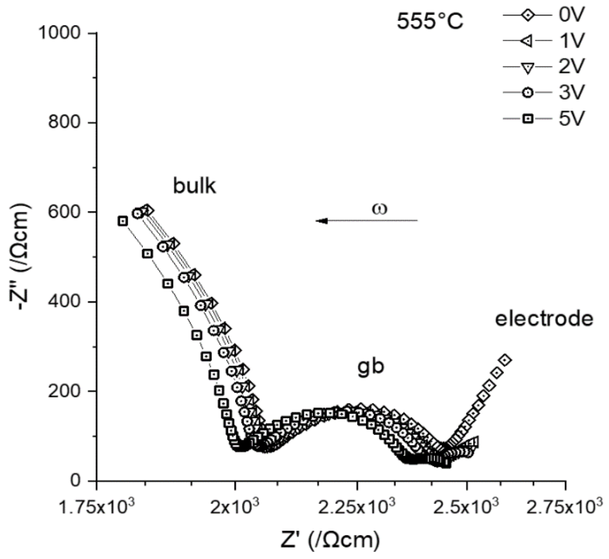


Figure 6 – Impedance complex plane of CSZ under the application of a dc bias.

References

[1] M. Jovani, H. Beltran-Mir, E. Cordoncillo, and A. R. West, “Atmosphere- and Voltage-Dependent Electronic Conductivity of Oxide-Ion-Conducting $Zr_{1-x}Y_xO_{2-x/2}$ Ceramics*", Inorganic Chemistry*, 56 [12] 7081-7088 (2017)

[2] M. Yu, S. Grasso, R. Mckinnon, T. Saunders, and M. J. Reece, “Review of flash sintering: materials, mechanisms and modelling", *Advances in Applied Ceramics*, 116 [1] 24-60 (2017)

HIGH TEMPERATURE TENSILE BEHAVIOR OF ZIRCONIA CERAMICS UNDER DC CURRENT

Koji MORITA, National Institute for Materials Science (NIMS)
MORITA.Koji@nims.go.jp
Hidehiro YOSHIDA, National Institute for Materials Science (NIMS)
Byung-Nam KIM, National Institute for Materials Science (NIMS)
Keijiro HIRAGA, National Institute for Materials Science (NIMS)
Yoshio SAKKA, National Institute for Materials Science (NIMS)

Key Words: Current effect, High temperature tensile deformation, Zirconia, Oxygen vacancy.

These Flash sintering phenomena, which occurs by applying DC current directly to ceramic powder compacts, has been the subject of many paper of ceramic sintering. This is because the flash event can succeed to lower the sintering temperature/time of several ceramic powders. On the other hand, Conrad and his colleagues examined the effect of electric fields on the high temperature tensile properties of 3Y-TZP and confirmed that the fields can lower the tensile flow stresses of 3Y-TZP enough to attain superplasticity. The enhanced deformation was explained by suppressed grain growth due to the electric bias effect. However, the mechanism/phenomena of the flash event are still unclear. In order to clarify the effect of electric current on high temperature deformation, therefore, the present study was carried out to examine the tensile behavior of polycrystalline zirconia ceramics under the several temperature and electric field/current conditions.

By applying the DC electric power higher than a critical value E_c, the flash event similar to that of powder sintering occurs even in dense zirconia ceramics. At around 1000 °C, for example, the E_c value is about 100 - 200 mW/mm^3, which is slightly larger than those reported in the powder compacts. For lower than E_c, the applied electric current increases sample temperature depending on the applied value, but does not enhance the rate of deformation. For higher than E_c, on the other hand, the electric current enhances the rate of the deformation to about several times as compared with that of without current conditions. The enhanced deformation cannot be interpreted only by the increment of sample temperatures and is likely to occur by the flash event. After the deformation under the electric current conditions, the tested sample shows slight gray color even under air condition. This suggests that the enhanced deformation would be related to oxygen vacancy formation. In the presentation, we will discuss the detailed current effect obtained at wide range testing conditions.

DENSIFICATION AND GRAIN GROWTH KINETICS OF 3MOL% Y_2O_3 STABILIZED ZIRCONIA DURING FLASH SINTERING

Ke Ren, Northwestern Polytechnical University, P. R. China
renke@mail.nwpu.edu.cn
Yiguang Wang, Beijing Institute of Technology, P. R. China

Key Words: flash sintering, densification kinetics, grain growth kinetics, oxygen vacancies, electrostatic interaction.

Flash sintering is an attractive technique that is capable of rapidly sintering ceramics, although its densification and microstructure evolution mechanism is arguable. Studies involving the kinetics of flash sintering are crucial in providing insights into the ultrafast densification process. Hence in the present study, a 3mol% Y_2O_3 stabilized zirconia (3YSZ) was used as a model compound for determining flash sintering densification and grain growth kinetics.

The densification kinetics of flash sintering was carried out at 900 ^{o}C, the dynamic linear shrinkage, the power dissipation and the evaluated temperature based on black-radiation model of 3YSZ sample was displayed as a function of electric field application time. Activation energy for the flash densification process was determined based on the conventional densification theory. Results indicated that injected oxygen vacancies at the incubation stage had a direct influence on the densification activation energy. In contrast, the densification during the flash sintering stage appeared to be dominated by the migration of oxygen vacancies under an electric field. This was inferred upon by the comparison of activation energies for the densification and conduction processes. Based on this finding, we propose that flash densification results from the movement of oxygen vacancies to form different charged defects that have an electrostatic interaction between them.

The grain growth kinetics on dense 3YSZ during steady stage of flash sintering was investigated using the grain size as a marker of microstructure evolution. In contrast to conventionally annealed specimen, the grain boundary mobility was enhanced by almost two orders of magnitude with the applied electric current, revealing that joule heating alone was not sufficient to account for the experimental results. Instead, activation energy for grain growth decreased significantly due to electro-sintering. Systematic characterization of graded microstructure further indicated that local oxygen vacancies and specimen temperature were responsible for a grain size transition. Based on electrochemical reaction involved in flash sintering, grain size reduction at the cathode was proposed to be attributed to the local rearrangement of lattice cations and generated oxygen ions.

DEFORMATION MECHANISMS OF FLASH SINTERED YTTRIA STABILIZED ZIRCONIA VIA IN-SITU MICROMECHANICAL TESTING

Jaehun Cho, School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA
Cho299@purdue.edu
Qiang Li, School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA
Jin Li, School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA
Han Wang, School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA
Zhe Fan, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA
Sichuang Xue, School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA
Suryanarayana Karra, School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA
Haiyan Wang, School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA
Troy B. Holland, Department of Mechanical Engineering, Colorado State University, Fort Collins, USA
Amiya K. Mukherjee, Department of Chemical Engineering & Materials Science, University of California, USA
R. Edwin García, School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA
Xinghang Zhang, School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA

Key Words: Flash sintering, deformation mechanisms, in-situ microcompression, dislocation, strain rate jump test

Flash sintering has been applied to sintering a variety of ceramic materials. However, the mechanical behavior of flash-sintered ceramics is less well understood. In this study, the deformation mechanisms of flash-sintered yttria stabilized zirconia (YSZ) were investigated via in-situ microcompression test at temperatures of 25 to 650ºC. The flash sintered YSZ exhibits high fracture strain due to transformation induced toughening below the test temperatures of 400ºC. At higher temperatures, crack nucleation and propagation are significantly retarded, and no more catastrophic failures are observed. Strain rate jump tests were also performed at elevated temperature (450 ~ 650ºC) to investigate the temperature dependent deformation mechanisms. The activation energy for deformation and its implication are discussed.

LOW TEMPERATURE AND HIGH STRAIN RATE SUPERPLASTIC FLOW IN STRUCTURAL OXIDE CERAMICS INDUCED BY FLASH EVENT

Hidehiro Yoshida, The University of Tokyo.
hyoshida@material.t.u-tokoy.ac.jp
Yamato Sasaki, Tokyo University of Science
Takahisa Yamamoto, Nagoya University

Key Words: Superplasticity, ZrO_2, Flash event, Diffusion, Grain growth

High-strength oxide ceramics are known to be brittle, with limited plastic deformability, even at high temperatures above 1000°C. However, structural ceramics with grain sizes of 1 μm or less can exhibit superplasticity, i.e., tensile elongation exceeding 100% via grain boundary sliding (GBS). Because deformation by GBS requires diffusion of atoms (ions) as a stress-relaxation process, a short accommodation length, i.e. a small grain size is critical for achieving superplasticity in ceramics. Superplastic forming is currently employed as a manufacturing technology for metals and alloys, typically at operation temperatures <1000°C and strain rates $>10^{-3}$ s^{-1}. In contrast, in typical superplastic ceramics such as Y_2O_3-stabilized tetragonal ZrO_2 polycrystals (TZP), superplastic deformation only occurs at higher temperatures (>1400°C) and lower strain rates ($<10^{-4}$ s^{-1}), though an average grain size of superplastic TZP is usually in a range of 0.3-0.5 μm. Some of nano-grained ceramic composites have been shown to exhibit superplasticity at higher strain rates, but only at higher temperatures beyond 1600°C. In order to reduce the superplastic temperature and to increase the deformation speed, an approach other than grain-size refinement is required to activate GBS in structural ceramics.

The application of a strong electric field during sintering is known to enhance densification in ceramics by accelerating diffusion mass transport. The use of flash sintering, in which a material is directly exposed to heat and a strong electrical field beyond threshold values, enables rapid sintering to achieve a fully dense sample at significantly lower furnace temperatures than conventional sintering. Field-assisted sintering and flash sintering have been used for fast manufacturing of TZP and other ceramic materials. The rapid densification during flash sintering is a result of accelerated self-diffusion and is accompanied by a non-linear increase in the electric conductivity of the material. Electron energy-loss spectrometry revealed the existence of extrinsic oxygen anion vacancies in flash-sintered Y_2O_3 and TZP, suggesting that flash sintering proceeds via the generation of atomic defects under the strong electric field. In addition, it has been pointed out that grain growth in Y_2O_3-stabilized ZrO_2 is accelerated by an electric current as well as by reduction in N_2+5%H_2 atmosphere. Thus, one can expect that the application of a strong field could also facilitate high-temperature mass-transport phenomena, such as GBS.

We demonstrate in this paper that by employing flash event under a strong DC field higher than 50 $V \cdot cm^{-1}$, conventional TZP ceramics can exhibit superplastic deformation with an elongation to failure of >150%, at a lower furnace temperature of 800°C and a higher strain rate of 2×10^{-3} s^{-1} compared to previous methods. The flash event can also enhance bending deformation as well as tensile deformation. The flow stress-strain rate relationship indicated that the enhancement in the plastic flow of TZP resulted not only from increased specimen temperature due to Joule heating but also from accelerated diffusion by electric field and/or current. The field/current effect was equivalent to increase in temperature of about 200ºC.

THE ONSET OF FLASH SINTERING 8YSZ

Jinling Liu, Southwest Jiaotong University
liujinling@swjtu.edu.cn
Dianguang Liu, Southwest Jiaotong University
Yiguang Wang, Beijing Institute of Technology

Key Words: Flash sintering; YSZ; conductivity; joule heating; electrochemical reactions.

The abrupt conductivity surge of 8YSZ was achieved with applied electric field and temperature after a short incubation time during flash sintering, and accompanying fast mass transport when using green bodies. Joule heating was proposed to explain the onset of flash sintering due to the enhanced conductivity of ceramics at high temperature, however, we observed that the black front is moved from cathode to the anode side during the incubation stage in 8YSZ, and the onset is triggered when the black front almost reach the anode, but still keep a narrow gap from the electrode. It believed the association of charged oxygen vacancies with electrons induced the flash event, then the reaction of electrons and charged oxygen vacancies to form uncharged oxygen vacancy near the anode side sustained the steady state.

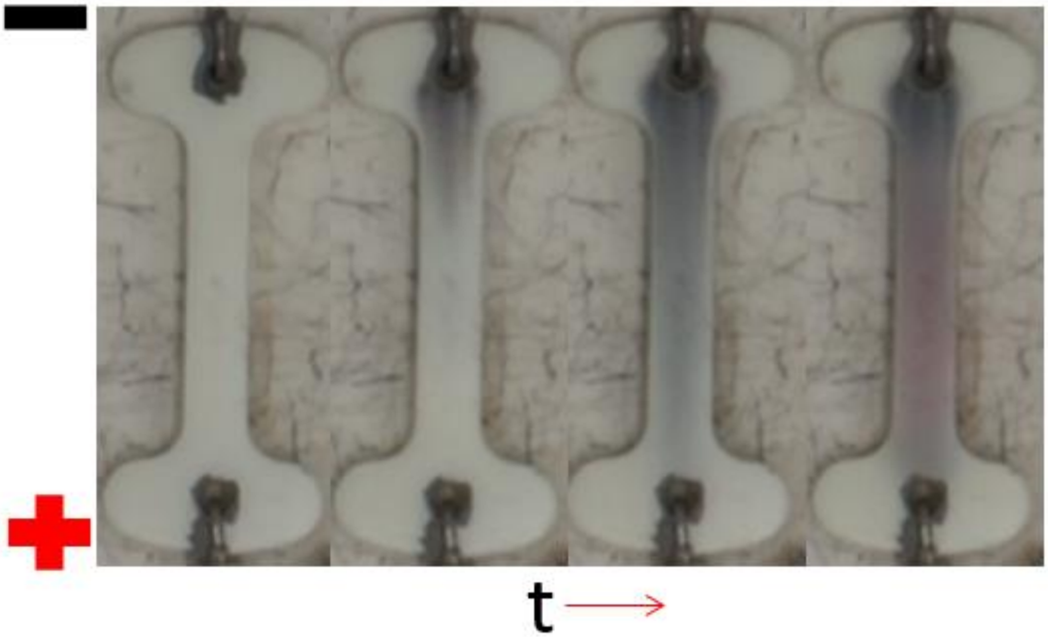


Figure 7 – The onset of flash sintering 8YSZ at 400V, 425 °C.

COMPARISON OF THE ELECTRICAL AND STRUCTURAL CHARACTERISTICS OF FLASH SINTERED YTTRIA-STABILIZED ZIRCONIA

Carolyn A. Grimley, North Carolina State University
cajensen@ncsu.edu
Andre L. G. Prette, Lucideon
Elizabeth C. Dickey, North Carolina State University

Key Words: Flash sintering, yttria-stabilized zirconia, defects, grain boundaries, impedance spectroscopy

One of the primary conundrums in the study of field-assisted sintering techniques is distinguishing between the effects of Joule heating and the athermal electric field on both the sintering process and properties of the sintered material. This is particularly true in the case of flash sintering, in which accurate and spatially differentiated temperature measurement is difficult, complicating the removal of baseline Joule heating. While high heating rates have been linked to rapid consolidation in the absence of an electric field[1], the field is assumed to affect defect behavior during sintering and produce effects on the resulting microstructural and electrical characteristics[2,3]. Studying these residual properties and their relationship to flash sintering processing parameters lends insight into the degree and nature of the field contribution during flash sintering.

We present a study using impedance spectroscopy and microstructural analysis to characterize flash sintered 8 mol % yttria-stabilized zirconia (YSZ). Samples were produced using a controllable AC flash system and parameters including frequency, current ramp rate, and electrode composition were varied. Results are contextualized within the growing understanding of the thermal characteristics of flash[4-6] as well as the effect of electric fields on cation[7] and grain boundary mobility[8] to understand the implications of observations like enhanced bulk conductivity, sensitivity of grain boundary conductivity to various processing parameters, and the temporal development of grain size. This work provides a useful perspective to the flash sintering literature with combined analysis of electrical properties and microstructure. Moreover, flash sintering via a combination of AC fields with controlled current ramps is demonstrated to be an effective route to producing more homogeneously sintered materials.

References

1 García, D. E., Seidel, J., Janssen, R. & Claussen, N. Fast firing of alumina. Journal of the European Ceramic Society 15, 935-938, doi:https://doi.org/10.1016/0955-2219(95)00071-2 (1995).
2 Charalambous, H. et al. Inhomogeneous reduction and its relation to grain growth of titania during flash sintering. Scripta Materialia 155, 37-40, doi:https://doi.org/10.1016/j.scriptamat.2018.06.017 (2018).
3 Carvalho, S., Muccillo, E. & Muccillo, R. Electrical Behavior and Microstructural Features of Electric Field-Assisted and Conventionally Sintered 3 mol% Yttria-Stabilized Zirconia. Ceramics 1, 2 (2018).
4 Todd, R. I., Zapata-Solvas, E., Bonilla, R. S., Sneddon, T. & Wilshaw, P. R. Electrical characteristics of flash sintering: thermal runaway of Joule heating. Journal of the European Ceramic Society 35, 1865-1877, doi:http://dx.doi.org/10.1016/j.jeurceramsoc.2014.12.022 (2015).
5 Charalambous, H., Jha , S. K., Christian, K. H., Lay, R. T. & Tsakalakos, T. Flash Sintering using Controlled Current Ramp. Journal of the European Ceramic Society 38, 3689 - 3693, doi:https://doi.org/10.1016/j.jeurceramsoc.2018.04.003 (2018).
6 Charalambous, H. et al. In situ measurement of temperature and reduction of rutile titania using energy dispersive x-ray diffraction. Journal of the European Ceramic Society 38, 5503-5511, doi:https://doi.org/10.1016/j.jeurceramsoc.2018.08.032 (2018).
7 Dong, Y., Qi, L., Li, J. & Chen, I.-W. Electron Localization Enhances Cation Diffusion in Zirconia and Ceria: A First-Principles Study. arXiv preprint arXiv:1808.05196 (2018).
8 Orrù, R., Licheri, R., Locci, A. M., Cincotti, A. & Cao, G. Consolidation/synthesis of materials by electric current activated/assisted sintering. Materials Science and Engineering: R: Reports 63, 127-287, doi:https://doi.org/10.1016/j.mser.2008.09.003 (2009).

STUDY OF FLASH PHENOMENA ON SINGLE CRYSTALS OF CUBIC 8 MOL% YTTRIA STABILIZED ZIRCONIA

Devinder Yadav, Department of Metallurgical and Materials Engineering, Indian Institute of Technology Patna, India; Materials Science and Engineering Program, Department of Mechanical Engineering, University of Colorado Boulder, USA
devinder@iitp.ac.in

Key Words: Flash sintering; Single crystal; Cubic zirconia; Thermal properties.

Flash sintering has recently emerged as a low energy technique for ultra-rapid densification of ceramics at remarkably low temperatures. Dense polycrystals also exhibit the flash phenomena; of course, they do not sinter. We carried out the flash experiments on single crystals of cubic zirconia and measured the temperature for the onset of flash as a function of electric field. The results were compared with flash sintering experiments on powders of cubic zirconia. The single crystals flash at lower temperatures and lower electric fields compared to that with the powders samples. The results indicate that particle-particle interface and grain boundaries are not necessary for instigating flash and that flash is more likely a matrix effect. The flash onset in single crystals occurs at similar values of the power density as the powder samples, and the values of power density, at the flash onset lies in the same range as in several oxides. The activation energy for specific conductivity, at the flash transition, was lower than for oxygen ion diffusion in zirconia. With the flash experiments at very high electric fields, on the dense polycrystals, we found that the temperature for the onset of flash decreased with the electric field and the lower bound temperature was the materials Debye temperature. The results does indicate that non-linear lattice vibrations instigate flash.

ELECTRIC FIELD INDUCED SOFTENING OF GLASS: WHAT CAN IT TELL ABOUT THE MECHANISM OF FLASH SINTERING?

Himanshu Jain, Institute for Functional Materials and Devices, Lehigh University, Bethlehem, USA
h.jain@lehigh.edu

Key Words: Glass softening, dielectric polarization, depletion layer, flash phenomena, inhomogeneous heating

Electric field induced softening (EFIS) of glass is a recently discovered phenomenon, which was inspired by dramatic effects of electric field on sintering of ceramic powders. It represents the effect of DC or AC electric field on the softening of glass that is heated at a constant rate under fixed compressive load. As shown in Fig. 1(a), the application of applied voltage reduces the softening temperature, and the softening transition becomes significantly sharper when voltage is above a critical value.[1] Remarkably, this behavior is similar to that reported for flash sintering, as seen in Fig. 1(b).[2] In both types of experiments, emission of white light is observed when the sample is in the vicinity of sharp transition. The power density at the onset of EFIS and flash sintering is comparable at ~1W/cm^2. Neither phenomena can be explained as Joule heating of a homogeneous solid. Notwithstanding these empirical similarities, we note that flash sintering of powders of varying properties is a far more complex phenomenon than heating of a clear, homogeneous, ion conducting silicate glass. As a result, EFIS is relatively well understood, while there are several diverging explanations of flash sintering that has been investigated much more extensively. The EFIS is understood to result from the following sequence of events: polarization of the sample from ion displacement under the application of electric field as in electro-thermal poling, formation of an alkali ion depletion layer, development of large internal electric fields across this layer, electrolysis and charge injection followed by dielectric breakdown, and very high localized heating near the anode, ultimately leading to thermal runaway and softening throughout the sample. Building on this understanding, in this presentation we will explore the question: how can EFIS help discern the various mechanisms of flash sintering, and compare their validity?

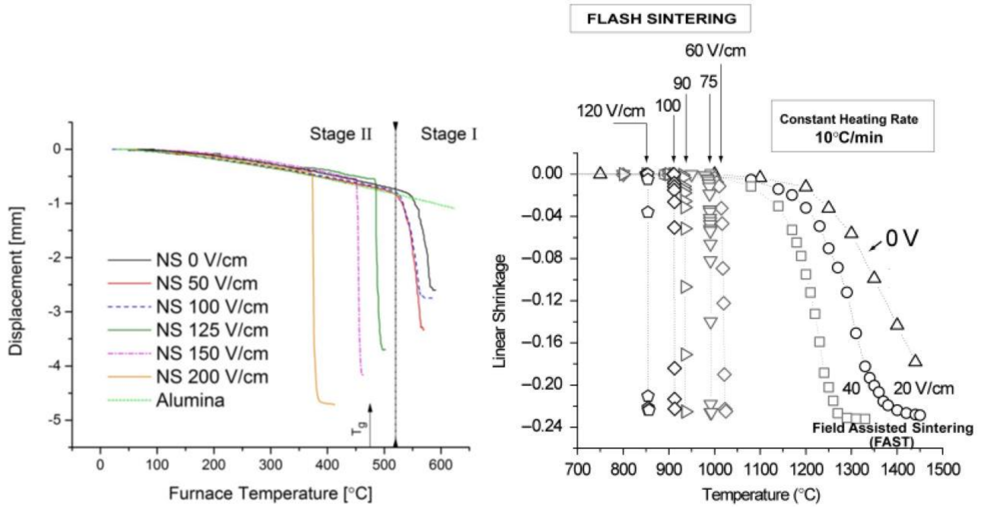


Fig. 1(a) (Left). Displacement vs. furnace temperature of sodium silicate (NS) glass at various applied electric fields with a constant heating rate of 10°C/min. The lines from right to left correspond to 0 V/cm to 200 V/cm. The monotonic dashed line is for reference alumina. Fig. 1(b) (Right). Sintering of yttria-stabilized zirconia (3YSZ) under varying dc electrical fields. Flash sintering occurs for fields > 40 V/cm.

References

[1] C. McLaren, W. Heffner, R. Tessarollo, R. Raj, H. Jain, Electric field-induced softening of alkali silicate glasses, Appl. Phys. Lett. 107 (2015) 184101. doi:10.1063/1.4934945.
[2] M. Cologna, B. Rashkova, R. Raj, Flash Sintering of Nanograin Zirconia in <5 s at 850°C, J. Am. Ceram. Soc. 93 (2010) 3556–3559. doi:10.1111/j.1551-2916.2010.04089.x

REACTION FLASH SINTERING FOR PRODUCING HIGH QUALITY FUNCTIONAL CERAMICS WITHIN SECONDS

Luis A. Perez-Maqueda, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain
maqueda@cica.es
Eva Gil-González, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain
Antonio Perejon, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain
Pedro E. Sánchez-Jimenez, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain
Rishi Raj, Department of Mechanical Engineering, University of Colorado at Boulder, USA

Key Words: Reaction FLASH sintering, multiferroic ceramics, BiFeO3, electrical properties.

For ceramic materials, it has been recently shown in literature that applying a small electric field and a small DC current through a sample produces sudden sintering (within seconds) at relatively low temperatures. This method is known as Flash Sintering and it has been applied to number of materials. In this work it is shown that both chemical reaction and sintering can be combined into a single flash sintering experiments. This new approach is known as Reaction Flash Sintering. To demonstrate the feasibility of this method, a multiferroic material, BiFeO3, is prepared from a stoichiometric mixture of Bi2O3 and Fe2O3 oxides. Thus, in a single process, dense nanostructured BiFeO3 ceramics are obtained by applying an electric field of 50 V cm-1 and with a current limit of 35 mA mm-2 within seconds at a furnace temperature of about 625 °C. The resulting materials were pure-phase perovskites without any evidence of secondary phases, sillenite or mullite, that are commonly present in materials prepared by conventional procedures. Moreover, samples were electrically insulating, as measured by complex impedance spectroscopy.

It is shown here that the synthesis of pure single-phase ceramics of complex oxides from stoichiometric mixtures of single oxides is possible by reaction flash sintering, even for materials difficult to prepare by conventional procedures. This discovery is a breakthrough in materials preparation.

CHARGED GRAIN BOUNDARIES AND THE MICROSTRUCTURAL EVOLUTION OF IONIC CERAMICS

R. Edwin García, Purdue University
redwing@purdue.edu
KSN Vikrant, Purdue University
Wolfgang Reinheimer, Purdue University

Key Words: charged grain boundaries; grain boundary electrochemical transitions; electrochemical grain boundary drag; abnormal grain growth;

The macroscopic properties of polycrystalline ionic ceramics are determined by the doping levels, point defects, and their interaction with the microstructure, as they are specified via processing and the target application. Here, the starting powders react, densify, and coarsen into microstructurally tailored grain topologies that are aimed to enhance (but sometimes limit) the performance of the device that are part of. The extent of these interactions varies with grain size, crystallographic orientation, and misorientation distribution, as well as applied fields, such as stress or electric fields. In order to understand the grain boundary characteristics, including their electrochemical properties and the driving forces that control grain coarsening, a thermodynamically consistent diffuse interface theory has been developed. The theory naturally incorporates the effects of grain boundary drag as imposed by the interfacially accumulated charged defects on the grain growth of polycrystalline ceramics. Applications to materials such as YSZ, GCO, and STO (and comparisons against experimental results) are presented.

ENHANCED IONIC CONDUCTIVITY OF 8 MOL% YTTRIA STABILISED ZIRCONIA BY FLASH SINTERING

Xavier Vendrell, Department of Materials Science and Engineering, University of Sheffield, UK
x.vendrell@sheffield.ac.uk
Devinder Yadav, Department of Metallurgical and Materials Engineering, Indian Institute of Technology Patna, India
Rishi Raj, Department of Mechanical Engineering, University of Colorado Boulder, US
Anthony R. West, Department of Materials Science and Engineering, University of Sheffield, UK

Key Words: Flash-sintering, 8YSZ, ionic conductivity.

The high conductivity of O^{2-} ions in YSZ has led to its selection as the preferred electrolyte in many solid oxide fuel cell and oxygen sensor applications[1] because of its good chemical and structural stability under the temperature and environmental conditions in operational fuel cells[2]. The addition of yttria to zirconia increases the concentration of oxygen ion vacancies, as the principal mechanism of charge compensation on replacement of Zr^{4+} by Y^{3+} leads to enhanced ionic transport in the electrolyte. The highest conductivity is obtained in the cubic phase of zirconia containing 8-10 mol% Y_2O_3.
There is much current interest in flash sintering as a novel, rapid sintering method which has evolved from initial studies on YSZ[3]. It was reported[4] that partially-stabilized, tetragonal YSZ ceramics of composition 3 mol% Y_2O_3, prepared by both conventional sintering and field-assisted flash sintering, developed similar microstructures. Impedance measurements showed the presence of grain and grain boundary components and at a given temperature of 300 °C, the conductivities of flash-sintered samples were 2 to 3 times higher than those of conventionally-sintered samples. This increase appeared to be not due to microstructural effects or changes; it was presumed, but not confirmed, that the conductivity increase was ionic. It has been suggested that flash sintering generates defect concentrations far above equilibrium values[5], some of which may be retained after flash. The increased conductivities were attributed to increased carrier (oxygen vacancy) concentration, although the mechanism by which these extra carriers were created was unclear. Experimental measurements of residual lattice expansion after flash were attributed to the creation of a high concentration of oxygen Frenkel defects during flash; first principles calculations showed that oxygen-related defects may be produced in much higher concentration than Zr-related defects[6].

In the present work, the ionic conductivity of flash-sintered, polycrystalline 8 mol% yttria stabilized zirconia (8YSZ) is investigated. Flash sintering was carried out at a furnace temperature of 850 °C with an electric field of 100 V cm^{-1} to initiate flash, the current density limit was varied between 60 and 100 mA mm^{-2}. Post-flash impedance spectroscopy measurements over the range 215–900 °C showed that both bulk and grain boundary conductivities had increased with the increased current density limit which was set prior to flash. The conductivity increases post-flash were ionic, not electronic, although electronic conductivity probably occurred, in addition to ionic conductivity, during flash and were not attributable to sample densification or microstructural changes. The higher ionic conductivities are attributed to a change in YSZ defect structure that led to an increased concentration of mobile charge carriers.

[1] N.Q. Minh, Ceramic Fuel Cells, J. Am. Ceram. Soc. 76 (1993) 563–588.
[2] B. Butz, R. Schneider, D. Gerthsen, M. Schowalter, A. Rosenauer, Decomposition of 8.5 mol.% Y_2O_3-doped zirconia and its contribution to the degradation of ionic conductivity, Acta Mater. 57 (2009) 5480–5490.
[3] M. Cologna, A.L.G. Prette, R. Raj, Flash-Sintering of Cubic Yttria-Stabilized Zirconia at 750°C for Possible Use in SOFC Manufacturing, J. Am. Ceram. Soc. 94 (2011) 316–319.
[4] J.C. M'Peko, J.S.C. Francis, R. Raj, Impedance spectroscopy and dielectric properties of flash versus conventionally sintered yttria-doped zirconia electroceramics viewed at the microstructural level, J. Am. Ceram. Soc. 96 (2013).
[5] R. Raj, M. Cologna, J.S.C. Francis, Influence of externally imposed and internally generated electrical fields on grain growth, diffusional creep, sintering and related phenomena in ceramics, J. Am. Ceram. Soc. 94 (2011) 1941–1965.
[6] J.M. Lebrun, C.S. Hellberg, S.K. Jha, W.M. Kriven, A. Steveson, K.C. Seymour, N. Bernstein, S.C. Erwin, R. Raj, In-situ measurements of lattice expansion related to defect generation during flash sintering, J. Am. Ceram. Soc. 100 (2017) 4965–4970.

* Current address: Institute of Energy Technologies, Department of Chemical Engineering, Universitat Politècnica de Catalunya, Barcelona 08019, Spain

LOCAL STRUCTURE AND KINETICS OF DEFECT ACCUMULATION IN TITANIA FLASH EVENTS

Daniel P. Shoemaker, University of Illinois, USA
dpshoema@illinois.edu
Soumitra S. Sulekar, University of Illinois, USA
Shannon E. Murray, University of Illinois, USA
Prashant S. Murray, University of Illinois, USA

Key Words: Flash sintering, point defects, X-ray scattering, in-situ analysis, pair distribution function analysis

Understanding and utilizing flash sintering as a processing technique requires disentangling the short-lived thermal effects that occur as a result of Joule heating from the more sluggish changes in the microstructure, such as defect formation, which can change over longer time scales and persist in the finished material. Adding to the challenge is the fact that typical in-situ analysis techniques, such as those built upon Bragg diffraction, are poorly suited to examine changes aside from lattice parameters since the coarsening behavior makes the time evolution of peak intensities highly variable. We find that local structure analysis via Fourier transformation of high-*Q* data to the pair distribution function leads to increased stability in the models that can be refined to X-ray scattering data. Careful examination of the lattice expansion, atomic displacement parameters, and site occupancies reveal behavior in TiO_2 that is invisible to Bragg-only analysis. Most importantly, the defect behavior is seen to be markedly different in TiO_2 than in zirconia, with quantitative signatures of defect-related phenomena that persist over long time scales. These results indicate that the integration over large Q-ranges makes PDF measurements quite robust in the face of grain reorientation during flash events, and a suitable setup at the XPD beamline at NSLS-II is in place. We will discuss how careful analysis of on-off experiments helps to disentangle defect signatures, which can then be integrated into models that explain the power versus time evolution in flashed samples.

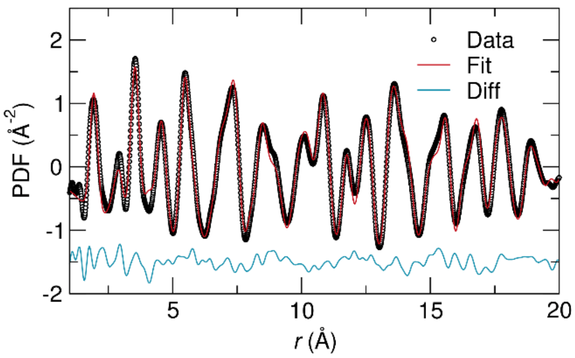


Figure 1. Representative fit to the X-ray pair distribution function of TiO_2 in an in-situ flash setup with Q_{max} = 20 Å^{-1}.

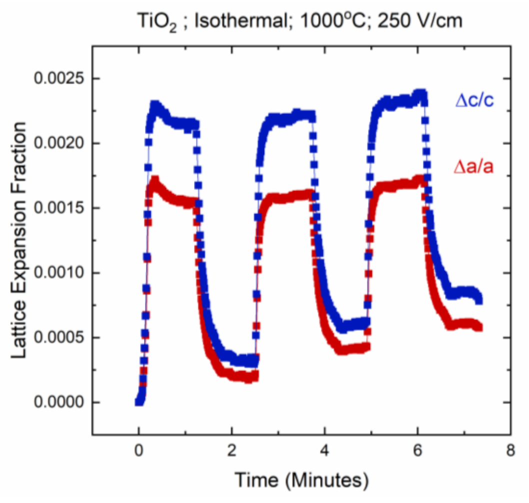


Figure 2. Changes in lattice parameters of titania over three cycles of an on-off experiment. Anisotropic expansion is seen during the on cycle as well as during the off cycle.

MIXED IONIC ELECTRONIC CONDUCTIVITY AND FLASH SINTERING

Ilan Riess, Technion, Israel
riess@technion.ac.il

In this contribution, we present and discuss similarities and differences between two phenomena connected to creation and transport of point defects. One is flash sintering (FS) on which this conference is focused on and the other is switching in some non-volatile memory devices. The explanation of flash sintering (FS) is based on the understanding that the solids being sintered contain point defects, both mobile ions and quasi free conducting electrons i.e. that they are mixed-ionic-electronic-conductors (MIECs). We shall refer specifically to oxide MIECs. The explanation also requires understanding how these MIECs respond to temperature changes, to changes in the oxygen chemical potential (or oxygen partial pressure) and how chemical diffusion can take place. The oxygen chemical potential can be fixed by the ambient or by polarization under an electric current applied on polarizing electrode. To present those properties we address a specific memory system which has much in common with FS, show the similarity where it exists and point at the differences.

The memory system is constructed of one single nano grain (crystallite), which is an insulator at room temperature, placed between two metal electrodes, subjected to a high electrical field. The temperature exhibits runaway, very similar to FS, the current increasing rapidly after an incubation period. The increase in the current of a few orders of magnitude is facilitated by both the increase in temperature and the reduction of the oxide. In this single grain system, the I-V relations are not linear (Ohmic) but rather super linear, while in FS they may be ohmic changing only due to the temperature increase.

The key difference between this system and FS is by the absence of grain boundaries within the bulk and no need for densification and grain growth. Yet not only electrical current but also material transport take place in the single grain system under an applied electric field. Heat losses in the single grain system are due to conduction of electrode and in FS mainly by radiation. Due to the small size of the system the incubation starts at room temperature despite the insulating nature of the grains, however the electrical field is of the order of 10^6 V/cm. The response time is very short and can be as low as 1 ns.

The region of high vacancy concentration in the single grain system and in FS during the transient step (II) can be either near the anode or the cathode. It is only under conditions close to steady state of step III that the vacancies concentrate near the cathode.

When the single crystal is replaced by a polycrystalline solid, mobile ions that are injected into it under an applied voltage form a percolation pattern with one branch reaching the opposite electrode, accompanied by a few shorter branches. This is reminiscent of possible percolation path during FS.

We shall discuss also the interaction of water vapor with oxides and the possible impact on surface as well as bulk conductivity.

METASTABLE NANOMATERIALS AND NANOCOMPOSITES OBTAINED BY HIGH PRESSURE TORSION POWDER CONSOLIDATION

Stefan Wurster, Erich Schmid Institute of Materials Science of the Austrian Academy of Sciences
stefan.wurster@oeaw.ac.at
Martin Stückler, Erich Schmid Institute of Materials Science of the Austrian Academy of Sciences
Lukas Weissitsch, Erich Schmid Institute of Materials Science of the Austrian Academy of Sciences
Reinhard Pippan, Erich Schmid Institute of Materials Science of the Austrian Academy of Sciences
Andrea Bachmaier, Erich Schmid Institute of Materials Science of the Austrian Academy of Sciences

Key Words: Severe Plastic Deformation, High Pressure Torsion, Nanocrystalline, Supersaturated Solid Solutions, Mechanical and Functional Properties.

Nanostructuring can dramatically improve the mechanical and functional properties of metallic materials and composites and to achieve the goal of a nanostructured bulk material innovative techniques have to be used.

High Pressure Torsion (HPT), a method of Severe Plastic Deformation (SPD) is a novel processing route for powder consolidation, featuring a complete absence of a sintering treatment – bulk samples are the direct result of the SPD process. HPT further shows two advantages: First, the starting material (powder mixtures) can be processed at any concentration. Even immiscible compositions were successfully processed for different systems (e.g. Cu-Fe, Cu-Co). Second, the severe deformation gives rise to supersaturated solid solutions (“far from equilibrium”) yielding interesting material properties, different from the pure or alloyed elements’ ones.

These supersaturated solid solutions, upon adequate annealing, show phase separations yielding nanoscaled composites. This gives a tool in one’s hands to systematically tune certain material properties. The nanostructures that were formed in such a way show high strength and ductility but also interesting functional properties. To give an example, annealing of above mentioned binary systems changes their magnetic properties regarding coercivity, remanence and magnetoresistance.

Thus, combining the right choice of processed powders (composition, size, shape), HPT-processing parameters (applied strain, processing temperatures) and subsequent annealing treatment (time, temperature) results in desired, tailored microstructures of optimized properties.

This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 757333)

SOME OBSERVATIONS ON THE RESPONSE OF OXIDES TO AN APPLIED FIELD

Anthony West, University of Sheffield, Dept of Materials Science & Engineering, Sheffield, S1 3JD UK
a.r.west@sheffield.ac.

Key words: Flash sintering, dielectric breakdown, redox-active oxygen, n-p transition, luminescence

Oxygen atoms in ionic oxides are stabilized as the oxide ion, O^{2-} by the high lattice energy of the resulting crystal structures. In the gas phase, by contrast, the O^{2-} ion has a positive enthalpy of formation and is spontaneously unstable to ionization. This talk will consider the conditions under which oxide ions in crystal lattices can ionize and the consequences for a diverse range of phenomena such as: flash sintering, memristive switching, involvement of redox-active anions in the operation of Li and Na battery cathodes and the dielectric breakdown of insulators. Depending on circumstances, an applied field may lead to enhanced n-type or p-type conductivity associated with the lattice oxygens, especially in the early stages of flash sintering, followed by the creation of a p-n junction and the luminescence characteristic of flash phenomena.

ULTRA-RAPID MICROWAVE SINTERING OF CERAMICS AND POWDER METALS

Kirill Rybakov, Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia
rybakov@ipfran.ru
Yury Bykov, Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia
Anatoly Eremeev, Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia
Sergei Egorov, Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia
Vladislav Kholoptsev, Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia
Ivan Plotnikov, Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia
Andrei Sorokin, Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia

Key Words: microwave sintering, millimeter waves, gyrotron

Over the recent years, we have demonstrated ultra-rapid microwave sintering of different ceramic materials, including Al_2O_3, ZrO_2, Y_2O_3, $MgAl_2O_4$, and Yb:$(LaO)_2O_3$, using a gyrotron system operating at a frequency of 24 GHz with an output microwave power of up to 6 kW [1-3]. The ceramic pellets were sintered to 98-99.5 % of the theoretical density with the duration of the high-temperature sintering stage not exceeding several minutes. We have shown that the absorbed microwave power required for the ultra-rapid sintering regimes is on the order of 10...100 W/cm^3, i.e., the same order of magnitude as the power of Joule heating required for the dc current-assisted flash sintering [4]. The ultra-rapid sintering is associated with the thermal instability that is characteristic of the volumetric heating processes regardless of the specific nature of the volumetric heat source. We have proposed a mechanism of ultra-rapid sintering which involves softening or melting of grain boundaries and propagation of a densification front from the core to the periphery of the sample [2,3].

In this paper we report the recent results that support these findings. A faster-than-Arrhenius growth of conductivity was observed in the *in situ* measurements of the dc conductivity in the microwave heated Yb:$(LaY)_2O_3$ samples. A low dc voltage was applied to the platinum electrodes imposed on the samples; the Joule heating of the samples by the dc current was negligible. A sharp increase in the current and a deviation from the Arrhenius dependence of the conductivity took place at a threshold temperature of about 1150 °C. Since the Arrhenius dependence of conductivity on temperature is characteristic of the dielectrics in the solid state, the deviation from this dependence observed at high levels of the absorbed microwave power suggests that the phase state of the material is changed, and a highly electrically conductive, (quasi-) liquid phase is formed in the sample.

In the experiments on the optical dilatometry of the Al_2O_3 samples using a recently developed system based on an infrared camera we have demonstrated that the shape of the dilatation curves obtained in the ultra-rapid microwave sintering regimes is different. Starting at the threshold temperature corresponding to the sharp increase in the effective conductivity, the dilatation rate exhibits a pronounced surge, in contrast to the steady decrease observed in the processes carried out at lower levels of microwave power.

We have also demonstrated by simulation that microwave ultra-rapid sintering can be implemented not only with ceramic materials, but also with powder metals. Although the conductivity of metals does not increase with temperature and therefore the thermal instability is not possible, the effective dielectric and magnetic properties of metal powders with poor electrical connectivity between the particles can be responsible for resonance phenomena during microwave heating [5]. The resonances give rise to enhanced microwave absorption in the powder compact and result in rapid densification. Fast automatic regulation of intensity and/or frequency of microwave radiation is necessary for the successful implementation of rapid sintering of metal powders and metal-ceramic composite materials.

This work was supported by Russian Science Foundation, grant # 17-19-01530.

[1] Yu.V. Bykov et al, J. Am. Ceram. Soc. 98 (2015) 3518-3524
[2] Yu.V. Bykov et al, Materials. 9 (2016) 684
[3] Yu.V. Bykov et al, Technical Physics. 63 (2018) 391-397
[4] R. Raj, J. Am. Ceram. Soc. 99 (2016) 3226-3232
[5] K.I. Rybakov, M.N. Buyanova, Scripta Mater. 149 (2018) 108-111

EFFECTIVE COLLOIDAL PROCESSING FOR DENSIFICATION BEFORE SPS

Tohru S. Suzuki, National Institute for Materials Science
suzuki.tohru@nims.go.jp
Toshiyuki Nishimura, National Institute for Materials Science
Byung-Nam Kim, National Institute for Materials Science
Kazuto Matsui, Shibaura Institute of Technology
Hajime Kiyono, Shibaura Institute of Technology

Key Words: Slurry, Particle dispersion, Slip casting, Packing density, Ceramics.

In conventional dry processing, fine particles tend to agglomerate spontaneously due to Van der Waals attractive forces. Since the agglomeration of particles forms large residual pores in green bodies, elevated temperatures are necessary for densification. Colloidal processing is a very effective technique for controlling the pore size distribution in green compacts before sintering. The green compacts having small residual pores with a narrow size distribution is expected to enhance the densification at low sintering temperature during SPS. We already reported that colloidal processing for controlling the packing structure in green compact is effective for densification in SPS in the case of SiC. A commercially available SiC (6H) powder with the average particle size of 0.55 μm was used as the starting materials. When using the dry processing for consolidation, the density of the sample sintered by SPS in a vacuum atmosphere at 1950°C was 92% of the theoretical value. Aqueous suspensions with dispersed particles were prepared by adjusting pH and consolidated by slip casting to prepare the dense green compacts. The relative density of SiC prepared by SPS was increased with increasing temperature and reached more than 97% at 1950°C as shown in Fig. 1. In this presentation, this processing was applied to fabrication of transparent alumina. Commercially available Al_2O_3 powder with the average particle size of 0.4 μm was used as the starting materials. Suspensions with 30 vol% solid were consolidated by slip casting. The green compacts before sintering were further densified by cold isostatic pressing at 392 MPa for 10 min and calcined at 500°C for 1 h in air in order to burn off the dispersant. Final sintering was carried out at 1150°C under a uniaxial pressure of 100 MPa using an SPS. After rapid heating to 600°C, the temperature was raised from 600°C to 1150°C using a heating rate of 5°C/min. After holding samples at the sintering temperature for 10 min and then subsequently annealing them at 1000°C for 10 min, we obtained a sintered disk with a diameter of 25 mm and a thickness of 2 mm. Fig. 2(a) shows the photograph of the sample from the green compact prepared by slip casting, Fig2(b) is the sample densified by SPS from the as-received powder directly. The transparency of the sample prepared by slip casting is clearer than that of the sample by SPS from the as-received powder directly.

The control of the packing density is effective for densification during SPS. Furthermore, orientation of the c-axis in alumina by a magnetic field during slip casting is more effective for enhancing the transparency.

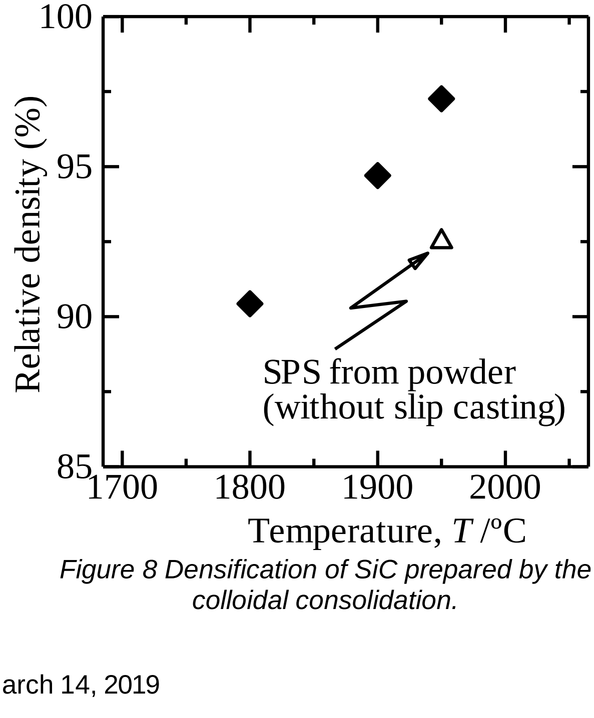


Figure 8 Densification of SiC prepared by the colloidal consolidation.

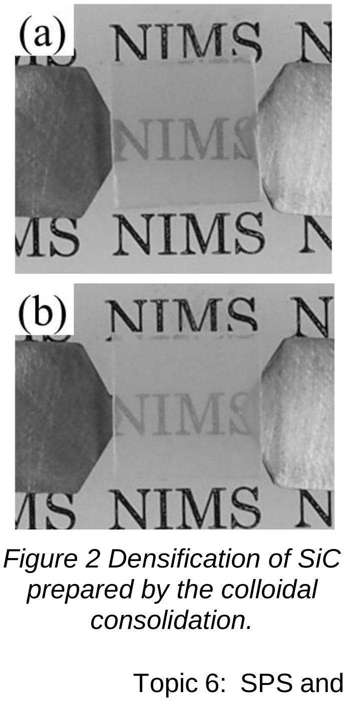


Figure 2 Densification of SiC prepared by the colloidal consolidation.

THE ROLE OF DEFECTS IN MICROWAVE-ASSISTED SYNTHESIS OF CUBIC ZRO_2

Nathan Nakamura, Department of Mechanical Engineering, Carnegie Mellon University
nnakamur@andrew.cmu.edu
Elizabeth Culbertson, Department of Applied Physics & Applied Mathematics, Columbia University
Han Wang, Department of Materials Engineering, Purdue University
Haiyan Wang, Department of Materials Engineering, Purdue University
C. Stephen Hellberg, U.S. Naval Research Laboratory
Simon J. L. Billinge, Department of Applied Physics & Applied Mathematics, Columbia University
B. Reeja Jayan, Department of Mechanical Engineering, Carnegie Mellon University

Key Words: Microwave radiation, phase stability, defects, oxygen vacancies, pair distribution function

Microwave radiation (MWR) is capable of inducing rapid, low-temperature crystallization and potential non-equilibrium phase formation in ceramic oxide materials.[1] However, the mechanisms by which MWR influences phase transitions and atomic ordering are not well understood. Theories to explain the influence of MWR range from purely thermal effects (e.g., rapid heating rate) to purely MWR-driven, non-thermal effects (e.g., enhanced defect generation).[2] To take full advantage of the opportunities provided by field-assisted methods, it is necessary to understand the underlying mechanisms. One limiting factor in determining how MWR affects phase formation has been the ability to effectively characterize the effects of an applied field on both long range (crystalline) and short range (amorphous/disordered) atomic order. Here, we utilize synchrotron x-ray pair distribution function (PDF) analysis, coupled with molecular dynamics (MD) and density functional theory (DFT) to explore the role of MWR-induced defects and local atomic disorder on low-temperature cubic phase formation in ZrO_2 thin films. PDF analysis is an experimental technique capable of quantitatively characterizing both local and long range atomic order, and thus can characterize the effects of MWR on atomic structure beyond the capabilities of conventional x-ray diffraction. We find the application of MWR can stabilize cubic ZrO_2 at temperatures as low as 225°C, about 2000°C lower than conventionally required. Our PDF analysis suggests that distortions in the local atomic structure may be responsible for the stabilization of the cubic phase, and these distortions are consistent with increased oxygen vacancy formation (Fig. 1). Interestingly, higher MWR power levels and faster heating rates do not correspond to more crystalline phase formation, suggesting that thermal effects may not be the sole driving force. To further explore the idea of MWR-induced, defect-mediated phase transitions, we utilize MD and DFT simulations to investigate how oxygen vacancy concentrations affect the relative phase stability of various ZrO_2 polymorphs, and compare the resultant simulated structures with our experimental PDF data. Through analysis of both crystalline phase formation and local atomic order, we investigate how defects and local atomic distortions are influenced by MWR exposure, and how these structural effects can impact low-temperature phase transitions.

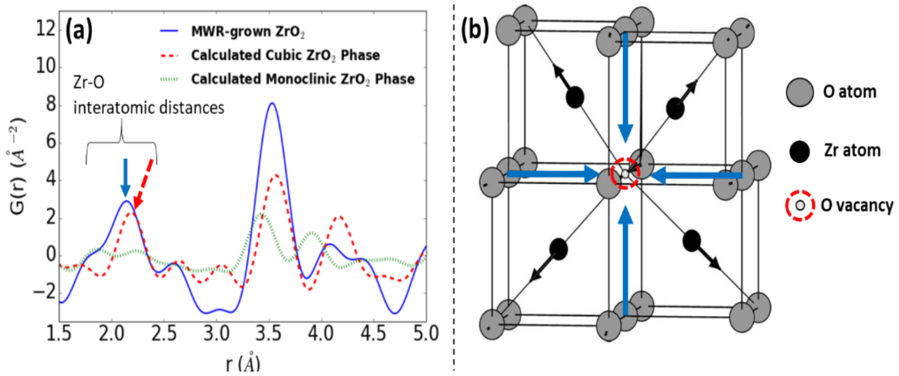


Figure 1 – (a) Experimental PDF data from an MWR-grown film (solid) compared with calculated PDFs from an ideal cubic (dashed) and monoclinic (dotted) structure. PDF peaks correspond directly to interatomic distances. The shift in the Zr-O nearest neighbor peak to shorter average interatomic distances observed in our experimental data relative to the cubic phase indicates structural relaxations consistent with oxygen vacancy formation. (b) Structural relaxations around an oxygen vacancy in cubic ZrO_2, modified from Ref.3

1. Baghbanzadeh et. al., Angew. Chem. Int. Ed. 50, 11312-11359 (2011)
2. Jha et. al., J. Am. Ceram. Soc. 102, 5-31 (2018)
3. Fabris et. al., Acta Materialia 50, 5171-5178 (2002)

ELECTRIC FIELD ASSISTED DENSIFICATION OF 10 MOL. % GADOLINIUM DOPED CERIA (GDC 10)

Tarini Prasad Mishra, Forschungszentrum Jülich GmbH
t.mishra@fz-juelich.de
Dr. Rubens Roberto Ingraci Neto, University of Colorado Boulder
PD Dr. Martin Bram, Forschungszentrum Jülich GmbH
Prof. Dr. Olivier Guillon, Forschungszentrum Jülich GmbH
Prof. Rishi Raj, University of Colorado Boulder

Key Words: Flash sintering, Electric field assisted sintering, Gadolinium doped Ceria, current controlled flash, processing map

Ceria based materials are widely studied due to their good chemical stability as compared to perovskites, mixed ionic and electronic conductivity and catalytic properties in redox processes. These unique properties make them attractive for applications in electro-chemical devices like electrolytes, diffusion barrier layers in solid oxide cells and/or oxygen ion conducting membranes. Gadolinium Doped Ceria (GDC) is one of the promising materials of this class of materials. However, GDC shows low densification behavior if sintered in air, requiring high temperature (i.e., 1400 – 1600 °C) and long dwelling time (2 – 6 hours) to densify. As an alternative to conventional sintering, flash sintering has been shown to be an effective method of sintering for many kinds of ceramics including mixed ionic and electronic conductors.

In this work, $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (i.e. GDC10, gadolinium-doped ceria, with Gd 10 mol. %) has been used for conducting a related flash sintering study under the influence of electric field and current. Constant heating rate (voltage-to-current control) flash sintering experiments has been conducted for GDC 10 material to study the effect of electrical field on the onset behavior of flash. Results of this study hint on that Debye temperature is the lower bound temperature required for initiating the flash event. This experimental finding is supporting other similar findings for 8YSZ and 3YSZ materials.

An alternative way of flash sintering has been introduced for GDC 10 material. In conventional (voltage-to-current control) flash sintering experiment, a defined electric field is applied to the sample, and after the flash event the power supply switches from the voltage control to current control. In the alternative method, the current is controlled from the beginning of the experiment and increased at a defined rate. Using a constant current rate, the densification of the material can be better controlled than in conventional flash sintering and the microstructure can be tuned. To study the effect of current rate on the densification behavior of the GDC material, current controlled flash sintering at 8 different current rates was carried out. The experimental findings suggest that the final relative density of the sample depends on the current density rather than on the current rate. Moreover, the microstructure of the current rate flash sinter samples seems to be homogenous throughout the sample.

From different flash sintering experiments, a processing map for the GDC 10 material as a function of electrical field and current density is developed. The processing map is helpful in optimizing the sintering parameters by avoiding the failed zone.

SOME STRATEGIES TO (CO)-SINTER REFRACTORY FUNCTIONAL OXIDES AT LOW TEMPERATURE BY SPARK PLASMA SINTERING

Catherine Elissalde, CNRS, Univ. Bordeaux, ICMCB, Pessac, France
catherine.elissalde@icmcb.cnrs.fr
U-Chan Chung, CNRS, Univ. Bordeaux, ICMCB, Pessac, France
Maria-Isabel Rua-Taborda, Univ. Bx, IMS, Talence - CNRS, Univ. Bordeaux, ICMCB, Pessac. France
Mario Maglione, CNRS, Univ. Bordeaux, ICMCB, Pessac, France
Graziella.Goglio, CNRS, Univ. Bordeaux, ICMCB, Pessac, France
Hélène Debéda, Univ. Bordeaux, IMS, Talence, France
Michaël Josse, CNRS, Univ. Bordeaux, ICMCB, Pessac, France
Jérôme Majimel, CNRS, Univ. Bordeaux, ICMCB, Pessac, France
Matthew Suchomel, CNRS, Univ. Bordeaux, ICMCB, Pessac, France
Claude Estournès, CIRIMAT, CNRS INPT UPS, Univ. Paul-Sabatier, Toulouse, France

Key Words: Low temperature SPS, Interfaces, Functional oxides, Piezoelectrics, Zirconia

The sintering at high temperatures (1000-1400°C) of refractory oxides widely used in electronic devices, raises several issues related to defects, chemistry, microstructure and interface control. Reducing sintering temperatures below 900°C is a major challenge in particular when high relative densities, optimal microstructure and the control of reactivity at interfaces (grain boundaries, multi-materials) are mandatory. In this context, we propose to highlight some strategies focused on interfaces and phases control through two different illustrations of our recent works. The first one is focused on Micro-Electromechanical System (MEMS) energy harvesters (EH) using piezoelectric materials[1]. We will show the potentiality of SPS to co-sinter in one step and below 900°C complex devices such as screen-printed $PbZrTiO_3$ in sandwich between two gold electrodes and supported on a stainless steel substrate. Here, the sintering aids in the pastes should be removed if possible or adapted for good adhesion, and delamination and bending of the multilayer EH must be avoided. We also intent to get rid of the annealing process after the SPS sintering. The second illustration reports on the ambitious goal to sinter zirconia ceramics at temperatures below 400°C. Recently, the exploration of non-equilibrium sintering, through transient liquid phase, hydrated precursors, or by using solvent assisted sintering, Flash sintering and Spark Plasma Sintering has been investigated to sinter ZnO and thermodynamically unstable materials at very low temperature [2-5]. Here, our approach is based on the use of specific precursors and deals with the control of transient non-equilibrium phases to find the driving force to establish the most favorable pathway for enhanced densification.

[1]. M. I. Rua-Taborda, O. Santawitee, A. Phongphut, B. Chayasombat, C. Thanachayanont, S. Prichanont, C. Elissalde, J. Bernard, H. Debéda, "Printed PZT Thick Films Implemented for Functionalized Gas Sensors", Key Engineering Materials, 777,158, 2018
[2].B. Dargatz, J. Gonzalez Julian, M. Bram, P. Jakes, A. Besmehn, L. Schade, R. Röder, C. Ronning and O. Guillon, “FAST/SPS sintering of nanocrystalline zinc oxide—Part I: Enhanced densification and formation of hydrogen-related defects in presence of adsorbed water, J. Eur. Ceram Soc. 36, 1207, 2016
[3]. S. Funahashi, J. Guo, H. Guo, K. Wang, A. L. Baker, K. Shiratsuyu, and C. A. Randall, "Demonstration of the cold sintering process study for the densification and grain growth of ZnO ceramics," Journal of the American Ceramic Society, 100, 546, 2017.
[4]. Luo J., “The scientific questions and technological opportunities of Flash sintering: from a case study of ZnO to others ceramics”, Scripta Mater., 146, 260, 2018
[5]. T. Herisson de Beauvoir, A Sangregorio, I. Cornu, C. Elissalde and M. Josse, “Cool-SPS: an opportunity for low temperature sintering of thermodynamically fragile materials” J. Mater. Chem. C, 6, 2229, 2018

COOL-SPS: PULLING DOWN THE TEMPERATURE, PUSHING UP THE REACTIVITY

Michaël Josse, Université de Bordeaux, CNRS, ICMCB, France
Michael.josse@u-bordeaux.fr
Thomas Hérisson de Beauvoir, Université de Bordeaux, CNRS, ICMCB, France
U-Chan Chung Seu, Université de Bordeaux, CNRS, ICMCB, France
Dominique Michau, Université de Bordeaux, CNRS, ICMCB, France
Cathy Elissalde, Université de Bordeaux, CNRS, ICMCB, France
Flora Molinari, Université de Bordeaux, CNRS, ICMCB, France
Liza El Khoury, Université de Bordeaux, CNRS, ICMCB, France
Subhransu Bhoi, Université de Bordeaux, CNRS, ICMCB, France
Mathieu Marchivie, Université de Bordeaux, CNRS, ICMCB, France

Key Words: Cool-SPS ; Low Temperature Sintering ; Chemical Reactivity ; Thermodynamically Fragile Materials ; Sustainable Materials and Processes

The use of materials, especially in the field of electronics, but also for catalysis, health (…), requires the control of their shaping (dense or porous materials, spherical or anisotropic particles…). This objective is frequently reached through the preparation of ceramics by conventional, high temperature sintering. Spark Plasma Sintering (SPS) is a particularly efficient densification method, initially dedicated to refractory materials, that is now extremely versatile and allows for the elaboration of nanostructured and/or transparent ceramics, among many other applications.

The recent acquisition of a proof of concept concerning the sintering of fragile ferroic materials by Cool-SPS [1,2,3] has allowed for the exploration of the opportunities associated with Cool-SPS efficiency at low temperature (typically T<400°C). Among the opportunities explored, that this communication intend to cover, are:

- The efficiency of Cool-SPS at very low temperatures, 100°C and below
- The sintering of hydrates [2]
- The synthesis and/or reactive sintering using Cool-SPS
- The diversification of the class of materials sinterable by Cool-SPS (*e.g.* Molecular Materials…)

The input from these exploratory studies will also be investigated, in an attempt to get a better insight on the sintering mechanism at play with Cool-SPS, which was found remarkably complex in the case of $MnSO_4$ [2]. An attempt will also be made to discuss the opportunity represented by Cool-SPS to develop more sustainable materials and processes, essentially through energy efficiency.

In the end, this communication aims at illustrating (see figure below) the remarkable efficiency of Cool-SPS, the large fields it opens for exploratory research centered on fragile materials, and its complementarity with others (low-)temperature sintering methods that may prove crucial for the understanding and optimization of sintering methods and strategies.

[1] T. Hérisson de Beauvoir et al, J. Mater. Chem. C., 2018, 6, 2229
[2] T. Hérisson de Beauvoir et al, J. Eur. Ceram. Soc., 2018, 38(11),3867
[3] T. Hérisson de Beauvoir et al, Ceramics International, https://doi.org/10.1016/j.ceramint.2018.12.103

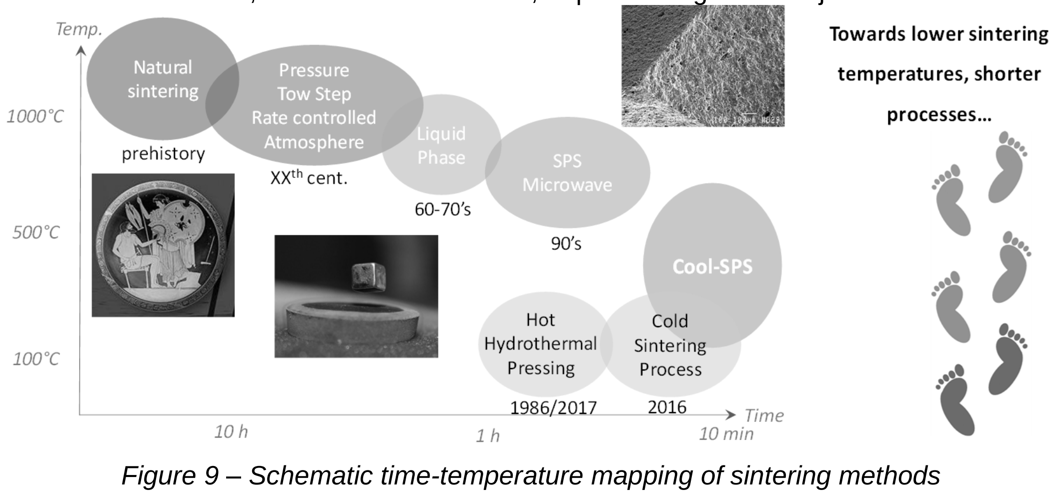


Figure 9 – Schematic time-temperature mapping of sintering methods

GRAIN GROWTH BEHAVIOR DURING SPARK PLASMA SINTERING OF CERAMICS

Byung-Nam Kim, National Institute for Materials Science, Japan
kim.byung-nam@nims.go.jp
Koji Morita, National Institute for Materials Science, Japan
Hidehiro Yoshida, National Institute for Materials Science, Japan

Key Words: Spark plasma sintering, Ceramics, Grain boundary sliding, Defects, Dynamic grain growth.

During sintering, most of densification process proceeds in the intermediate stage where channel-like open pores and large isolated pores shrink by the movement of particles or grains towards the pores. The grain rearrangement without significant shape change, one of the characteristics of sintering, is a result of the grain-boundary sliding which is the most important mechanism for high-temperature deformation, such as superplastic deformation. The grain-boundary sliding is an essential process during densification.

During spark plasma sintering of alumina, the effects of heating rate, pressure and loading schedule on the grain size were examined. Usually, high heating rates results in small grain sizes because of short heating time. However, when alumina was densified at low temperatures, high heating rates accelerated grain growth, though the total heating time was reduced. The grain growth rate after full densification was also accelerated for high heating rates. The accelerated grain growth might result from the generation of defects during densification. The densification in the intermediate stage of sintering includes the deformation of powder particles, and the deformation occurs mainly by grain-boundary sliding or grain re-arrangement. The defects generated during grain-boundary sliding may enhance the grain-boundary mobility and accelerate the grain growth rate, that is the dynamic grain growth. It is considered, therefore, that the high deformation rate at high heating rates accelerated grain growth during sintering.

The accelerated grain growth also appeared for high-pressure sintering. The grain size after sintering increased with the applied pressure. High pressures lowered the deformation temperature and increased the deformation rate. As a result, the high deformation rate during heating may generate defects and enhance the grain-boundary mobility. Lastly, the loading schedule during heating also affected the deformation and the grain growth. Applying pressure at low temperatures or at high rates may generate more defects and resultantly accelerate the grain growth. These unusual grain growth behaviors during spark plasma sintering are explained by using a concept of dynamic grain growth [1]. Hence, one of our conclusions is that the deformation of grain-boundary sliding plays an important role in both densification and grain growth during sintering.

[1] BN Kim et al., Scripta Mater., 80 (2014) 29.

DENSIFICATION OF NdFeB MAGNETS PROCESSED BY ELECTRO-DISCHARGE SINTERING – MICROSTRUCTURE, MAGNETIC, AND MECHANICAL PROPERTIES

Lennart Leich, Ruhr Universität Bochum, Institut für Werkstoffe, Lehrstuhl Werkstofftechnik
lennart.leich@rub.de
Arne Röttger, Ruhr Universität Bochum, Institut für Werkstoffe, Lehrstuhl Werkstofftechnik
Martin Krengel, WILO SE
Werner Theisen, Ruhr Universität Bochum, Institut für Werkstoffe, Lehrstuhl Werkstofftechnik

Key Words: Nanocrystalline NdFeB magnets, Electro-Discharge Sintering, processing

In this work, the densification process of nanocrystalline NdFeB powder by electro-discharge sintering (EDS) was investigated. The EDS technique is used as a fast and energy-saving compaction process for metal powders. In contrast to the spark plasma sintering (SPS) process, EDS has not received much attention during recent years. SPS is a low voltage, direct current, pulsed current-activated, and pressure-assisted sintering process. Whereas EDS is also pressure-assisted, but uses electrical energy discharged from capacitors to densify conductive powders. During EDS a large current is discharged within 5 ms from capacitors into a pre-compacted loose powder, thus resulting in complete compaction.

In this study, we investigate the microstructure, magnetic, and mechanical properties of the compacted, hard magnetic NdFeB specimens under variation of the energy E_{EDS} and compression load p_{EDS}. For all specimens, the intrinsic coercivity $H_{c,J}$ decreases on increasing the discharge energy. However, the compaction load has apparently no influence on the coercivity $H_{c,J}$, whereas the residual induction B_r decreases only with increasing discharge energy. An increase in the compression load p_{EDS} causes an increase in the specimens' density and thus promotes residual induction B_r.

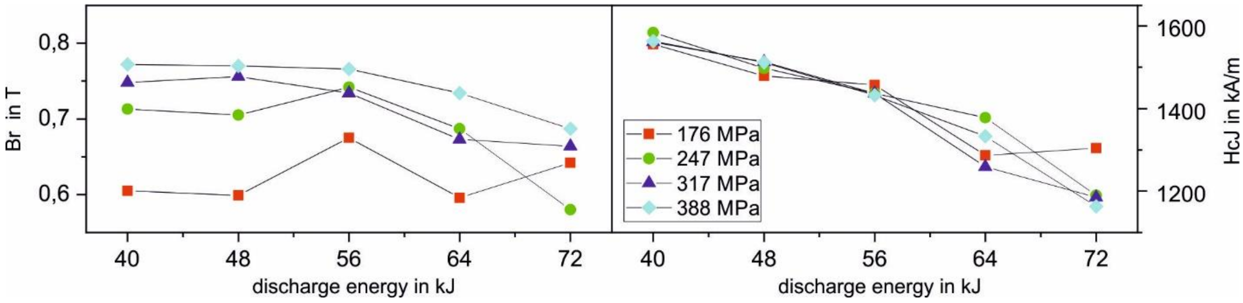


Figure 10: Energy product $(BH)_{max}$, remanence B_r, and coercivity $H_{c,J}$ with varying discharge energy E_{EDS} and compression load p_{EDS}.

The applied EDS parameters led to the formation of three different microstructures (insufficiently densified zone, fully densified zone, and remelted zone) along the cross-section of the EDS-densified specimens. Volume fractions of the three different microstructures that form during the EDS process determine the resulting mechanical and magnetic properties of the specimens.

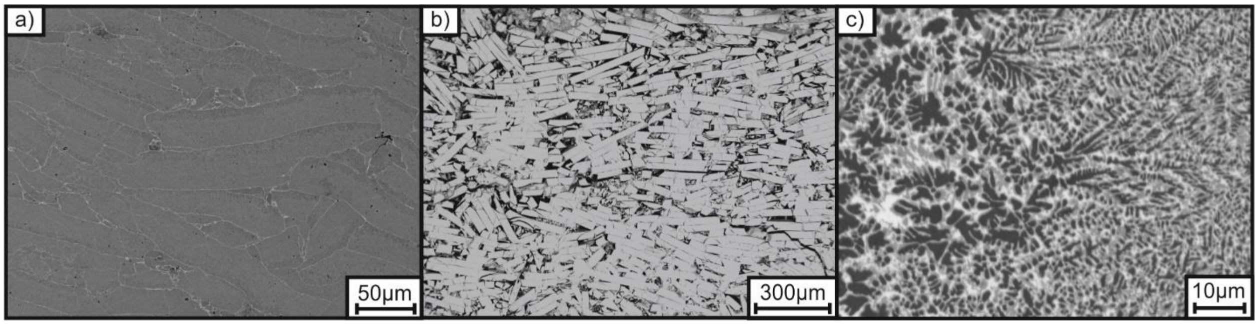


Figure 11: Three different microstructures in EDS-compacted NdFeB specimens: a) fully compacted zones, b) insufficiently compacted zones and c) remelted zones.

ELECTRICAL-FIELD ASSISTED FLASH JOINING OF CERAMIC OXIDE-CERAMIC OXIDE AND CERAMIC OXIDE-METAL

Yiguang Wang, Beijing Institute of Technology, P.R. China
Junbo Xia, Northwestern Polytechnical University, P. R. China
Ke Ren, Northwestern Polytechnical University, P. R. China

Key Words: electric-field assisted, flash joining, ceramic oxides, alloys, defects chemistry.

Joining of ceramic oxides to themselves or to metal plays crucial role in extending their applications. A variety of joining techniques have been developed in the last decades, which are generally divided into liquid-state bonding (LSB) and solid-state bonding (SSB). However, these methods are restricted due to their high joining temperature and long dwelling time, and more importantly the low use temperature. Inspired by the recently developed flash sintering technique, where the green body is fully densified in seconds at temperatures far below the traditional sintering temperatures, we herein demonstrated a novel electrical field-induced flash-bonding technique for the joining of ceramic oxides-ceramic oxides and ceramic oxides-metal.

For the ceramic oxides-ceramic oxides bonding, zirconia ceramic (ZrO_2) was selected for its outstanding mechanical property and extensive application. Zirconia ceramic was flash joined at temperatures as low as 600 ^oC in ca.1s by applying an electrical field above threshold. The bend strength of the joint was 78% of the parent material, and the strength was further increased to 95% of the parent material when the joining temperature was elevated to 900 ^oC. More importantly, the joint strength formed in optimized joining time could be equivalent to the parent material. Ultrafast superplastic deformation of the faying surfaces and the subsequent flash mass transport under the applied electrical field were proposed as the underlying mechanism.

For the ceramic oxides-alloys system, the Ni based and Ti based alloy were chosen for their ultrahigh strength and widely application in the areas of aerospace. ZrO_2 was strongly bonded to the alloys within 30 seconds assisted by the critical electrical field at temperatures from 700 ^oC to 800 ^oC. The shear strength of joined samples were greatly affected by the applied current density, holding time and the bonding temperature, as well as the direction of the field, and reached 133 MPa and 67 MPa for the ZrO_2-Ni alloy and ZrO_2-Ti alloy system. Moreover, the resultant joint can be readily de-bonded by reversing the field. The electrical field-induced internal reaction between the ceramic and metal was proposed as the mechanism for the reversible and ultrafast bonding.

FLASH SINTERING OF ARMOR MATERIALS: CHALLENGES AND OPPORTUNITIES

Andrew Rosenberger, ORAU
andrew.rosenberger3.ctr@mail.mil
Raymond Brennan, ARL
Michael Kornecki, SURVICE
Selva Vennila Raju, ORAU
Aubrey Fry, ORISE

Key Words: Flash, borides, carbides, armor, densification

Flash sintering has been found to enable rapid densification of a wide range of ceramics at lower processing temperatures and shorter times than conventional sintering. This is of particular interest for materials that are difficult to conventionally sinter, including those used in ceramic armor systems, such as B_4C, SiC, and B_6O. However, the driving mechanisms behind flash sintering are still hotly debated, and the interactions between the processing parameters and the materials being sintered are only in the early stages of being explored. Furthermore, there has been little documented effort to flash sinter these materials and characterize the process. The Army Research Laboratory strategy for research on flash and field-enhanced sintering of ceramics is described, with particular focus on the challenges and opportunities for sintering boron carbide and other relevant armor materials. The design of a scalable flash sintering apparatus and the observed effects of various process parameters such as contact mechanism, atmosphere, current/voltage profile, and part shape as they relate to flash and densification behavior are discussed.

This research was supported in part by an appointment to the Postgraduate Research Participation Program at the U.S. Army Research Laboratory administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and USARL.

Research was sponsored by the Army Research Laboratory and was accomplished under Cooperative Agreement Number W911NF-16-2-0050-P0003. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Laboratory or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein.

The research reported in this document was performed in connection with contract/instrument W911QX-16-D-0014 with the U.S. Army Research Laboratory. The views and conclusions contained in this document are those of SURVICE Engineering and the U.S. Army Research Laboratory. Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon.

EFFECT OF THE ADDITION OF DOPED-COBALT ON THE PROPERTIES OF RECYCLED TUNGSTEN CARBIDE POWDER SINTERED BY SPS

Alexandre Mégret, University of Mons
alexandre.megret@umons.ac.be
Véronique Vitry, University of Mons
Fabienne Delaunois, University of Mons

Key Words: tungsten carbide, SPS, recycled powder

A key issue that has appeared in the last twenty years is the availability of certain materials. Cobalt is considered as a critical raw material since it is massively used in batteries for electrical cars [1]. Cobalt is also the usual binder in cemented carbides because it gives excellent hardness to toughness ratio at the tungsten carbide parts. There is a tendency to replace cobalt by other binders such nickel or iron [2] but cobalt remains the best one. Recycling old WC parts is a solution to limit the use of raw cobalt powder and to keep the benefits of the cobalt as metallic binder in cemented carbides.

The recycled powder has been provided by the company Höganäs S.A. Belgium. It contains 7.5 wt% cobalt with an average WC particle size about 45 µm. The as-received powder has a very low sinterability [3]. To enhance the sintering processes, the powder has been milled with the addition of cobalt beforehand doped with 20 wt% Cr_3C_2 [4]. Two powders have been prepared: WC-10(Co+Cr_3C_2) and WC-15(Co+Cr_3C_2).

The powders have been sintered with two sintering technologies: vacuum sintering (VS) and spark plasma sintering (SPS). In vacuum sintering, the samples have been heated with 4°C/min to reach 1400°C for 1h. In SPS, the samples have been heated with 150°C/min to reach 1200°C for 10 min. The pressure applied during SPS was 50 MPa.

The density of the samples was characterized before the samples were mounted into resin and polished. The microstructure before and after etching was evaluated, as well as the mechanical properties (hardness and toughness). X-rays diffraction was used to characterize the crystallites growth appearing during the sintering and the prospective change in phases.

The results show that the mechanical properties are 10% higher for SPS than for VS. It is explained by the smaller crystallite size and the higher density. No disturbing phases, such the brittle eta-phase or graphite was found in the XRD patterns.

Acknowledgments
The authors would like to thank the company Höganäs for providing the powder and the Belgian Ceramic Research Center (BCRC) for the SPS experiments.

References

[1] CDI, “Cobalt Development Institute.” [Online]. Available: https://www.cobaltinstitute.org/.
[2] T. W. Penrice, “Alternative binders for hard metals,” J. Mater. Shap. Technol., vol. 5, no. 1, pp. 35–39, 1987.
[3] A. Mégret, A. Thuault, C. Broeckmann, S. K. Sistla, V. Vitry, and F. Delaunois, “Frittage des carbures de tungstène-cobalt recylés [Sintering of recycled tungsten-cobalt carbides],” in MATERIAUX 2018, 2018.
[4] V. I. Stanciu, V. Vitry, and F. Delaunois, “Effect of doped binder on the microstructure of a WC-Co composite,” in Euro PM2018 Congress & Exhibition, 2018.

ANOMALOUS TWINNING IN AZ 31 MAGNESIUM ALLOY DURING ELECTRICALLY ASSISTED FORMING

Franz Körkemeyer, Institut für Werkstoffkunde (Materials Science), Leibniz-Universität Hannover
koerkemeyer@iw.uni-hannover.de
Gregory Gerstein, Institut für Werkstoffkunde (Materials Science), Leibniz-Universität Hannover
Andrej Dalinger, Institut für Werkstoffkunde (Materials Science), Leibniz-Universität Hannover
Stefan Zaefferer, Max-Planck Institut für Eisenforschung, Düsseldorf
Abhishek Tripathi, Max-Planck Institut für Eisenforschung, Düsseldorf

Key Words: Electroplastic effect; magnesium alloy; microstructure; twinning; EBSD

The electro plastic effect (EPE) occurs in materials exposed to high electric currents, on the order of 10^2 to 10^4 A mm^{-2}, during elastic or plastic deformation. Current pulses with durations of about 10^{-3} s are usually used to limit resistive heating of the sample. As a result, a reduction the macroscopic of flow stress and enhanced ductility is observed, The EPE may therefore be exploited to support the deformation of inherently brittle materials. The underlying microscopic mechanisms enabling the flow stress reduction and increase in ductility are still unresolved. Besides the obvious contribution of Joule heating, various mechanisms of electron - dislocation interactions, resulting in increased dislocation mobility or changed dislocation density, have been proposed.

In the present study, the EPE was investigated using samples of extruded pure magnesium and AZ 31 Mg alloy, which were subjected to one or ten current pulses with a current density of 700 A mm^{-2} and 1 ms duration while subjected to constant compressive strain below the yield point. During the experiments the mechanical response of the sample to the current impulse, a drop of stress, the occurrence of residual plastic strain and hardening of the sample, was observed. The magnitude of the observed reduction in stress depends on the relative orientations of texture and current direction. In the case of multiple pulses, the first current pulse led to a significantly larger drop than the subsequent pulses. Reference experiments using hot air and inductive heating were conducted, in which samples were subjected to identical strains and similar temperature profiles. A similar softening could not be observed. The subsequent optical and EBSD microstructural observations, using appropriate metallographical preparation techniques, revealed unusual twinning in the samples subjected to current pulses.

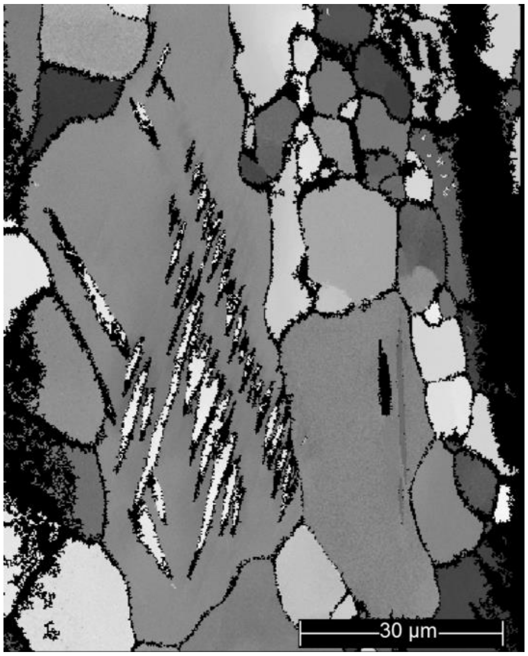


Figure 12- EBSD Map of AZ 31 subjected to one 700 A / mm² current impulse exhibiting columnar twin formation

Figure 1 shows twinning in samples subjected to one current pulse. The resulting twins are arranged in columns roughly in line with the direction of current flow. These twins exhibit wide, “sail-shaped” center sections and long, narrow “tails”. With subsequent pulses, these tails connect the individual columns until the grain is completely twinned. At that point further twinning as a result from the electrical pulse is no longer possible, resulting in a reduced macroscopic stress drop. Furthermore, twin formation is also observed along some grain boundaries. In contrast to the reference experiments, these twins do not propagate across grain boundaries.

This confirms that grain boundaries play an important role in explaining the EPE due to their different electrical properties compared to the bulk material. The formation of columns of twins in their shear plane in the interior of the sample indicate the capability of the current to activate twinning in more homogeneous regions of the sample. Twinning, along with enhanced dislocation mobility, has to be considered a micromechanism, of the electroplastic effect in magnesium. The interactions of increased dislocation mobility, possible generation of dislocations resulting from the current pulse and twinning have yet to be studied in further detail.

EVIDENCE OF LOCALIZED, INCIPIENT MELTING DURING FIELD-ASSISTED SINTERING OF OXIDE DISPERSION STRENGTHENED, NANOCRYSTALLINE METALS

Sean Fudger, US Army Research Laboratory – Aberdeen Proving Ground, MD USA
sean.j.fudger.civ@mail.mil
Chris Haines, US Army Research Laboratory – Aberdeen Proving Ground, MD USA
Thomas Luckenbaugh, Bowhead Total Enterprise Solutions, LLC, Alexandria, VA USA
Efrain Hernandez, US Army Research Laboratory – Aberdeen Proving Ground, MD USA
Billy Hornbuckle, US Army Research Laboratory – Aberdeen Proving Ground, MD USA
Anthony Roberts, US Army Research Laboratory – Aberdeen Proving Ground, MD USA
Anit Giri, US Army Research Laboratory – Aberdeen Proving Ground, MD USA
Kris Darling, US Army Research Laboratory – Aberdeen Proving Ground, MD USA

Key Words: Nanocrystalline, ODS, Incipient Melting, Metals

Oxide-dispersion-strengthened (ODS) nanostructured FeNiZr alloys were produced via high energy mechanical alloying and subsequently consolidated via the field assisted sintering technique (FAST). Processing parameters of temperature, pressure, and dwell time were altered in an effort to achieve full densification and optimize the mechanical performance. Indications of incipient melting were observed via optical and scanning electron microscopy (SEM) at processing temperatures as low as 700 °C. This temperature is less than half of the homologous temperature of the FeNiZr alloy or any of its constituents. This suggests substantially higher temperatures are achieved locally within the powder compact as a result of Joule heating during consolidation. Additional evaluation with X-ray diffraction was performed to identify the implications of this incipient melting on mechanical properties.

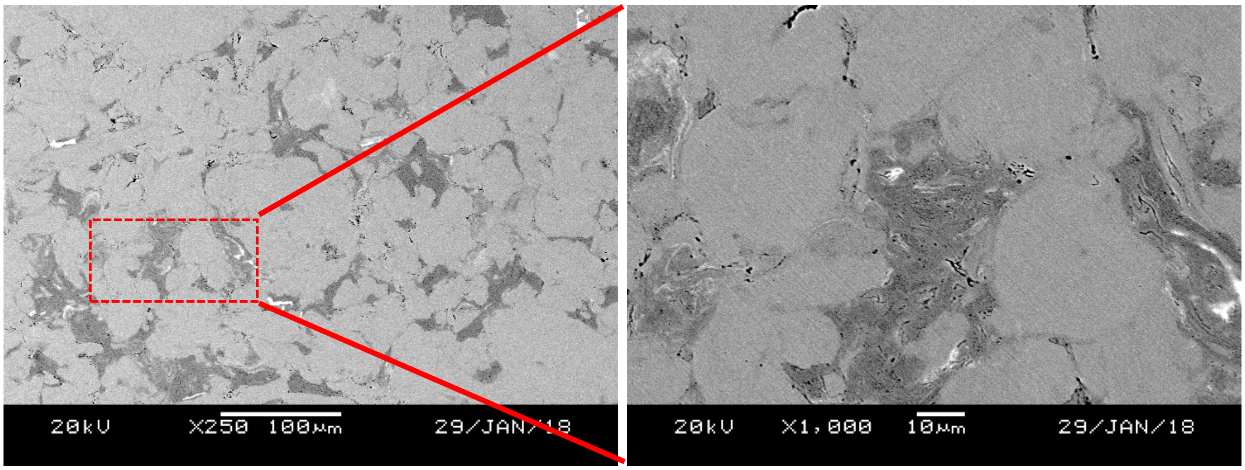


Fig. 1 Fe$_{91}$Ni$_8$Zr$_1$ consolidated via FAST at 700 °C, 100MPa, 30 minute dwell.

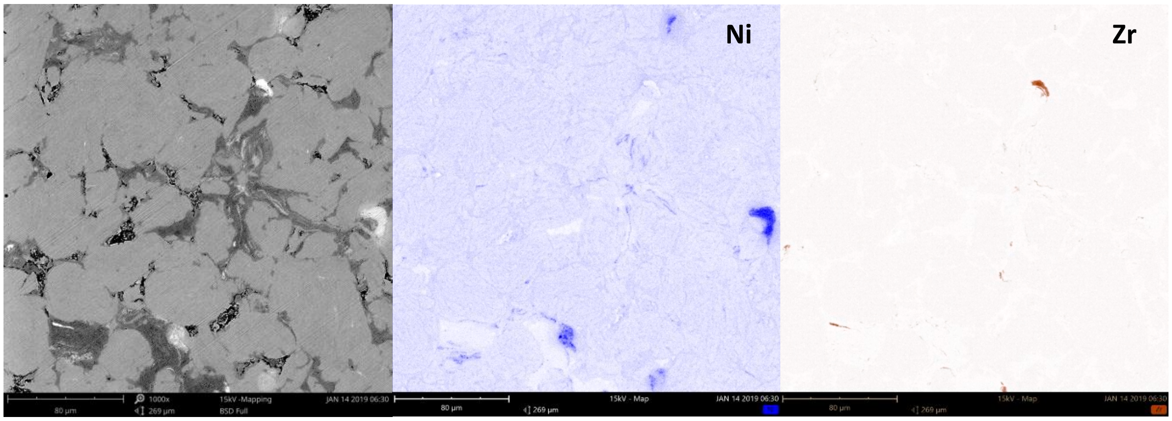


Fig. 2 EDS mapping showing evidence of Ni and Zr pooling and segregation at the grain boundaries.

TRIGGERING THE CATALYTIC ACTIVITY OF SrTiO3-Based Ceramics By Flash Sintering

Simone Mascotto, University of Hamburg, Germany
simone.mascotto@chemie.uni-hamburg.de
Bugra Kayaalp, University of Hamburg, Germany
Kurt Klauke, University of Hamburg, Germany
Mattia Biesuz, University of Trento, Italy
Alessandro Iannaci, University of Trento, Italy
Vincenzo M. Sglavo, University of Trento, Italy
Massimiliano D'Arienzo, University of Milano-Bicocca, Italy
Siwon, Lee, KAIST, Republic of Korea
WooChul Jung, KAIST, Republic of Korea

Key Words: A-site deficiency; charge carriers; confinement; methane oxidation; catalysis

Confinement of charge carriers in nanoscopic systems has revealed to be an effective strategy to confer ceramic materials unconventional conductive properties by exploiting particle size effects and interfaces characteristics[1]. Strontium titanate ($SrTiO_3$) is a piezoelectric oxide that requires to be doped by acceptor species (e.g. Fe substitution of Ti centers) in order to acquire fair chemical reactivity[2].

In the present work, we show how chemically inert $SrTiO_3$ and $La_{0.1}Sr_{0.9}TiO_3$ ceramics can be turned into active materials by improving the concentration and reactivity of the ionic species using electric-field-assisted treatments[3]. Flash sintering is a novel, sustainable consolidation technology able to massively reduce the process time and cost with respect to conventional treatments, by applying an external electric field to a ceramic sample upon heating. $SrTiO_3$-based nanoparticles of 50 nm were prepared by a green hydrothermal synthesis and treated under air using flash and conventional sintering methods. The consolidation in presence of an electric field arrested the grain growth, retained the specific surface area and enhanced the concentration of Sr vacancies and O^- species. Moreover, the confinement of such ionic defects in mesoscopic particles contributed to a significant improvement of the charge carrier mobility, but to a general decrease of the total conductivity. The effect of these electric-field-induced properties was tested with respect to the total catalytic oxidation of methane, used as high temperature, exemplary test. Flash sintered materials exhibited more than 95% of methane conversion at 800 °C, with performance over 3 times higher than for the conventionally treated material and other donor-doped perovskites.

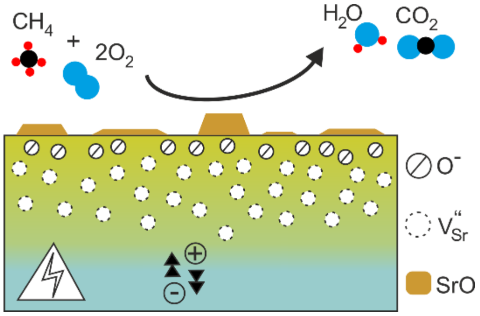


Figure 13 – Illustration of the peculiar defect nature of flash sintered $SrTiO_3$-based materials.

The employment of field-assisted processing technologies can be therefore considered as an attractive forward-looking strategy for the development of functional ceramics with innovative properties by exploiting the confinement effect of charge carriers in mesoscopic systems.

References:

[1] P. Lupetin, G. Gregori, J. Maier, Angew. Chemie - Int. Ed. 2010, 49, 10123–10126.
[2] B. Kayaalp, S. Lee, K. Klauke, S. Jongsu, L. Nodari, A. Kornowski, WC. Jung, S. Mascotto, under revision 2018.
[3] B. Kayaalp, K. Klauke, M. Biesuz, A. Iannaci, V. M. Sglavo, M. D'Arienzo, S. Lee, WC. Jung, S. Mascotto, under revision 2018.

ATMOSPHERE ASSISTED FLASH SINTERING OF KNN

Ana M.O.R. Senos, CICECO-UA
anamor@ua.pt
Ricardo Serrazina, CICECO-UA
Luis Pereira, FCT-NOVA
Paula M. Vilarinho, CICECO-UA

Key Words: Atmosphere-assisted FLASH, KNN, Low temperature sintering.

The use of FLASH alternative sintering technique allows a significant decrease in sintering time and temperature, contributing to the sustainable processing of high sintering temperature piezoelectrics. This is the case of potassium sodium niobate, $K_{0.5}Na_{0.5}NbO_3$ (KNN), a relevant lead-free piezoelectric, which, due to alkali evaporation, is difficult to produce by conventional sintering, at T > 1100 ºC.

In this work, KNN was FLASH sintered and the sintering atmosphere and powder humidity effect on the consolidation process was investigated. Different atmospheres were tested (from reducing to oxidizing and dry to wet) and the FLASH temperature, T_F, was accessed. We have observed that T_F is highly dependent on the sintering atmosphere and it can be as low as 270 ºC, if a reducing atmosphere is used. KNN powder conductivity was accessed for the different atmospheres as a function of the temperature during FLASH, as depicted in fig. 1. Humidified KNN powders were successfully FLASH sintered. The FLASH sintered KNN ceramics were structurally and microstructurally characterized (XRD, SEM and TEM). Electric and dielectric responses were accessed as a mean to explain the FLASH sintering dependence on atmospheres and humidity.

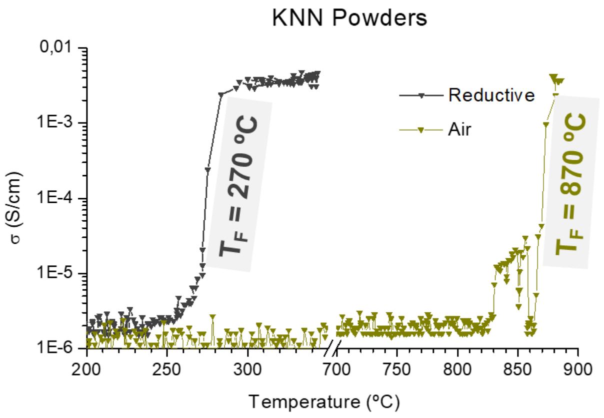


Figure 14 – KNN logarithmic conductivity dependence with temperature, for two different atmospheres: air and reducing. An inset for FLASH temperature is presented for each curve.

Acknowledgments:

This work is financed by Portugal 2020 through European Regional Development Fund (ERDF), in the frame of Operational Competitiveness and Internationalization Programme (POCI), in the scope of the project “FLASH sintering of lead free functional oxides towards sustainable processing of materials for energy and related applications- FLASH”, POCI-01-0247-FEDER-029078, and in the scope of the project CICECO- Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), cofinanced by national funds through the FCT/MEC

NEW AND ONGOING RESEARCH ACTIVITIES IN BOULDER

Rishi Raj, University of Colorado, USA
Rishi.Raj@Colorado.edu