FINAL REPORT

Project Title:	
FUNDAMENTALS OF SPARK-PLASMA SINTERING: MATERIAL PROCESSING FOR ENERGY APPLICATIONS FUNDAMENTALS OF SPARK-PLASMA SINTERING: RAPID AND ULTRA-RAPID MATERIALS CONSOLIDATION AND JOINING (RENEWAL) FIELD-ASSISTED SINTERING: THERMAL AND NON-THERMAL FACTORS OF CONTROLLED NON-EQUILIBRIUM (RENEWAL)	
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EXECUTIVE SUMMARY

This project was focused on the development of the general theory of spark-plasma sintering (SPS) taking into account the role of both thermal and non-thermal factors in the acceleration of SPS mass transport. SPS is a particular kind of field-assisted sintering, which provides potentially revolutionary capabilities to the processing of materials into configurations previously unattainable. This approach significantly improves the processing time- and quality-wise. It carries the potential of maintaining the nano and sub-micron structure in nano-powder-based materials after consolidation. SPS gains particular prominence in connection with its exceptional potential of rapid and ultra-rapid processing of very hard-to-deform materials, which would typically require lengthy consolidation times at significantly elevated temperatures under conditions of conventional powder pressing or sintering.

The achievement of the ultimate goal of the formulation of the general theory of spark plasma sintering required the identification of the contributions of all the thermal and non-thermal factors in the enhancement of mass transport under SPS processing conditions. As our research indicated, this enhancement is mostly reduced to the creation of the conditions of controlled non-equilibrium, which is especially important in ultra-rapid field-assisted sintering techniques.

Thus, the main project objective was the analysis of the SPS physical basis at multiple scales specifically exploring the role of electric current in the acceleration of mass transport and with an emphasis on the conditions of controlled non-equilibrium.

PARTICIPANTS

1. Participant: Dr. Eugene Olevsky
Project Role: Principal Investigator/Project Director
Contribution to the Project: Overall management of the Project.

2. Participant: Mr. Geuntak Lee
Project Role: Graduate Student (Research Assistant)
Contribution to the Project: Ph.D. Student G. Lee: participated on the optimization of SPS of monocarbides and mononitrides; participates in the development of new constitutive models of SPS.

3. Participant: Mr. Xialu Wei
Project Role: Graduate Student (Research Assistant)
Contribution to the Project: Ph.D. Student X. Wei: participated in the modeling, simulation, and experimentation on spark-plasma sintering; currently is concentrated on the SPS net-shaping.

4. Participant: Ms. Diletta Giuntini
Project Role: Graduate Student (Research Assistant)
Contribution to the Project: Ph.D. Student D. Giuntini participated in the modeling, simulation, and experimentation on spark-plasma sintering; she was focused on the optimization of SPS tooling.

5. Participant: Mr. Wei Li
Project Role: Graduate Student (Research Assistant)
Contribution to the Project: Ph.D. Student W. Li participated in the modeling, simulation, and experimentation on spark-plasma sintering; he was focused on the development of new SPS constitutive models.

6. Participant: Mr. Steven Rolfing
Project Role: Graduate Student (Research Assistant)
Contribution to the Project: M.S. Student Steven Rolfing: participated in the experimentation on flash SPS; has successfully graduated.

7. Participant: Mr. Jack Rechtin
Project Role: Graduate Student (Research Assistant)
Contribution to the Project: Jack Rechtin was an MS Student who participated in the experiments on spark plasma sintering of all-solid-state lithium-ion batteries.

8. Participant: Ms. Shirley Chan
Project Role: Graduate Student (Research Assistant)
Contribution to the Project: S. Chan was an MS Student who participated in the determination of sintering constitutive parameters.

9. Participant: Dr. Elisabeth Torresani
Project Role: Postdoctoral scholar
Contribution to the Project: Dr. Elisabeth Torresani participated in the modeling and experimentation of spark plasma sintering processes.

10. Participant: Dr. Charles Maniere
Project Role: Postdoctoral scholar
Contribution to the Project: Dr. Charles Maniere: participated in the development of constitutive models and finite- element codes for modeling of field-assisted sintering.

11. Participant: Dr. Jose Alvarado-Contreras
Project Role: Postdoctoral scholar
Contribution to the Project: Dr. J. Alvarado-Contreras participated in the development of finite-element codes for modeling of sintering.

12. Participant: Dr. Andrey Maximenko
Project Role: Visiting Scholar
Contribution to the Project: Dr. A. Maximenko: participated in the development of constitutive models of spark- plasma sintering.

13. Participant: Dr. Yingchun Shan
Project Role: Visiting Scholar
Contribution to the Project: Dr. Y. Shan participated in the studies on SPS of transparent ceramic materials.

COLLABORATING ORGANIZATIONS

1. Partner: General Atomics Co.
Contribution to the Project: General Atomics collaborated on optimization of SPS of nuclear engineering – related powder components (fuel and reactor components.)

2. Partner: University of California, San Diego.
Contribution to the Project: Ph.D. Students have been supervised in the framework of the Joint SDSU-UCSD Doctoral Program in Engineering Sciences.

3. Partner: University of New Mexico
Contribution to the Project: UNM affiliates collaborated on SPS-joining technique.

ACCOMPLISHMENTS

1. What are the major goals of the project?

The achievement of the ultimate goal of the formulation of the general theory of spark plasma sintering requires the identification of the contributions of all the thermal and non-thermal factors in the enhancement of mass transport under spark-plasma sintering (SPS) processing conditions. As our research indicates, this enhancement is mostly reduced to the creation of the conditions of controlled non-equilibrium, which is especially important in ultra-rapid field-assisted sintering techniques.
The main project objective was the analysis of the SPS physical basis at multiple scales specifically exploring the role of electric current in the acceleration of mass transport and with an emphasis on the conditions of controlled non-equilibrium.

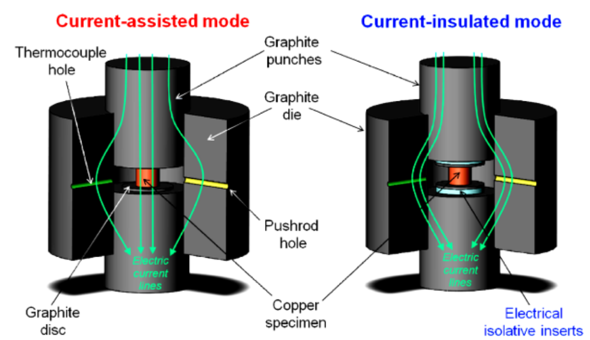
2. What was accomplished under these goals?

The main project objective was the analysis of the spark plasma sintering physical basis at multiple scales specifically exploring the role of electric current in the acceleration of mass transport and with an emphasis on ultra-rapid materials consolidation and joining. Thereby the project specifically addressed the following issues: (I) The development of a new constitutive model for spark-plasma sintering, taking into account the role of electric current in the acceleration of mass transport. (II) The development of a comprehensive multi-scale SPS modeling framework incorporating the elaborated SPS-specific constitutive model. (III) The development of a new Flash Hot Pressing (Flash SPS) processing technique. (IV) Exploring SPS capabilities for joining (including direct seamless bonding) of ceramic and metallic materials.
The fundamental aspects of this research program were focused on the development of the theory of

SPS die-punch set-up: photo (left); CAD model (middle); and 3D FE modeling of SPS processing (right).

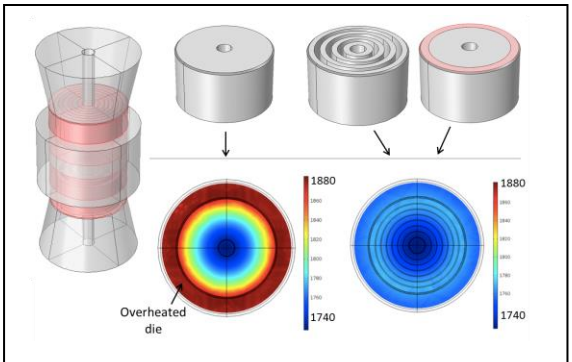
spark-plasma sintering (SPS) of powder components. SPS is a rapidly emerging powder consolidation technique capable of producing highly dense materials with a significant potential for grain size retention. SPS is based on the conjoint application of fast heating rates, high axial pressure and field (electric current - based) assisted sintering. Potentially, SPS has many significant advantages over the conventional powder processing methods, including the lower process temperature, the shorter holding time, dramatically improved properties of sintered products, low manufacturing costs, and environmental friendliness. Practical implementations of the SPS' bright potential, however, were limited by the lack of theoretical concepts enabling the process predictiveness and optimization.

This project's fundamental research activities have been aimed at the determination of the SPS dominant driving forces, contributing to the formulation of the general theory of spark-plasma sintering. Thereby the project specifically addressed the following issues: (i) modeling of the heat transfer during SPS of powder materials; influence of the heating rate on the consolidation and grain structure evolution; analysis of the impact of the thermal runaway effect on the "flash" sintering phenomenon; (ii) experimental de-convolution of the thermal and non-thermal phenomena occurring during SPS; (iii) coupled densification – grain growth – electromagnetic field – temperature distribution modeling at micro- and macroscopic levels; (iv) optimized (based on the developed model and experimental concepts) low-pressure SPS and free pressureless SPS processing and characterization of novel functionally structured porous nuclear fuel materials enabling the damage-free fission product escape.



Fundamental comparative experiments on current-assisted vs. current-insolated modes of SPS.

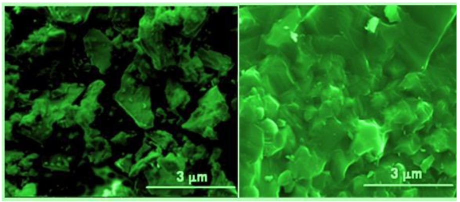
The collaborative component of the proposed program involved interactions between SDSU and General Atomics - one of the world's leading resources for the high-technology systems development. The developed concepts have been implemented in a novel modeling framework describing spark-plasma sintering for the optimization of the fabrication of functional porous structures of nuclear fuel for modular multiplier reactors. The porous structure is an essential element of the design of novel nuclear fuel pellets enabling fission product evolution. Thereby, the main applied aspects of the project are concerned with exploring the previously non-investigated applications of spark-plasma sintering to the fabrication of structurally strong porous materials, which are of great interest for nuclear fuel and other energy-related applications.



New SPS tooling design.

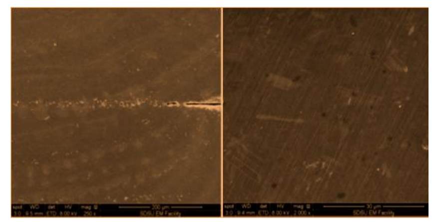
The conducted research indicates that the understanding of the material constitutive behavior during SPS is impossible without the analyses of mechanical consolidation, heat transfer and electric field-induced phenomena at multiple scale levels. The project introduced important mechanisms of both thermal and non-thermal nature in a novel generic micro-macro modeling framework for the description of spark-plasma sintering. The modeling activities were supported by unique experiments on the de-convolution of the heating rate - driven and electromagnetic field - imposed effects at various scale levels. The developed new constitutive models of SPS and the interconnected codes at different analysis scales ultimately led to the creation of the generic multi-scale framework for modeling of spark-plasma sintering.

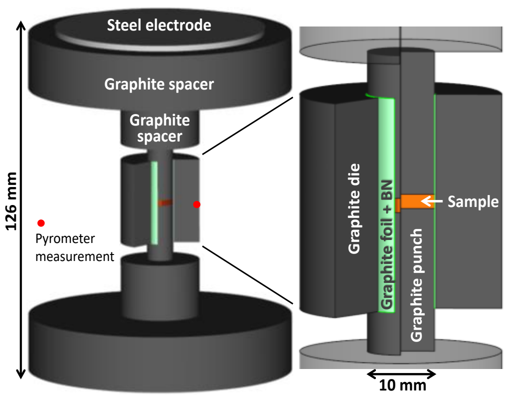
Based on the developed modeling framework, a novel tooling design, consisting in the tailored drilling of axial cylindrical or ring-shaped holes within the punch, has been individuated and optimized through a campaign of fully coupled thermal, electrical and mechanical finite element simulations. The analysis of the numerical results, experimentally assessed, allowed for a comprehensive understanding of the phenomena underlying radial temperature distributions in SPS and led to the individuation of a technological solution for the uniformization of temperature distribution.



SEM micrograph of SiC powder (left), and SiC specimen processed by flash SPS (right)

In addition, during the progress of the conducted project, new, exciting capabilities of SPS have been revealed, including the new potentially transformative Flash Hot Pressing (Flash SPS) approach, as well as the possibility of the SPS usage for seamless joining of ceramic and metallic materials. Investigations conducted at SDSU showed that the consolidation efficiency can be dramatically further improved by enabling an ultra-rapid “flash” regime of processing, when super-hard powder materials can be consolidated in a matter of few seconds. The idea of the “flash SPS” is based upon the idea of recently explored “flash sintering, however, it does not require the usage of higher voltage ranges, employed by “flash sintering” setups (and, therefore, not achievable in the industrially produced SPS devices.) Hence, flash SPS can be conducted in regular SPS devices. Flash SPS utilizes the theoretical idea of the thermal-runaway-based origin of the flash sintering phenomenon. As opposed to flash sintering, which should generally render uncontrollable clustered area heating of the processed specimen and therefore lead to highly spatially non-uniform distribution of temperature, density and of microstructure parameters, Flash SPS explores the possibility of the pressure-controlled thermal runaway, under which the mass transport driven by externally applied pressure should equalize the distribution of temperature and stabilize the process of consolidation. In contrast to flash sintering, which should have drastic scalability problems, Flash SPS has a potential of being employed for large scale specimens, where the uniformity of relative density and grain size is of great importance.

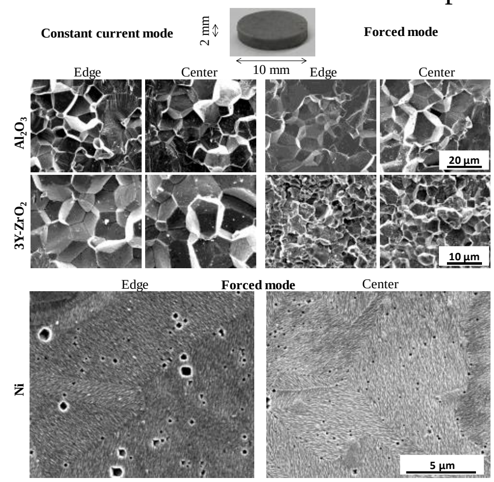

Joint with a visible seam (left) vs. seamless joint (right) between two SiC disks



The lateral graphite foil is coated with a boron nitride spray to electrically insulate the die and concentrate the electric current on the sample)

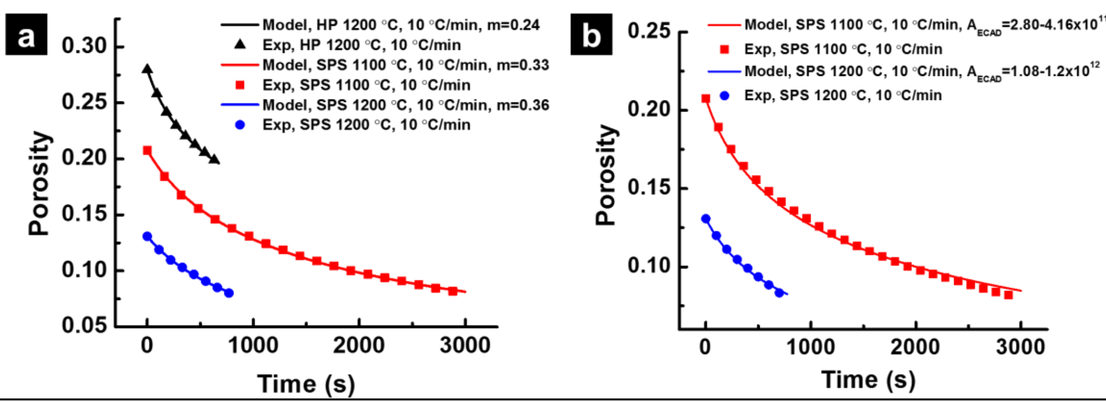
At SDSU, we have demonstrated the potential of SPS to produce practically seamless joints between SiC components without using any filler material. Both the localized and rapid heating contributed to the inherent energy saving of electric current assisted joining technique. Our research results showed that especially by rightly adjusting electric current, applied pressure and heating time, almost perfect joint within seconds can be obtained so that the heat-affected zone can be markedly reduced.

Thus, a new flash (ultra-rapid) spark plasma sintering method applicable to various materials systems, regardless of their electrical resistivity, was developed. A number of powders ranging from metals to electrically insulative ceramics have been successfully densified resulting in homogeneous microstructures within sintering times of 8-35 s. A finite element simulation revealed that the developed method, providing an extraordinary fast and homogeneous heating concentrated in the sample's volume and punches, is applicable to all the different samples tested. The utilized uniquely controllable flash phenomenon was enabled by the combination of the electric current concentration around the sample and the confinement of the heat generated in this area by the lateral thermal contact resistance. The presented new method allowed: extending flash sintering to nearly all materials, controlling sample shape by an added graphite die, and an energy efficient mass production of small and intermediate size objects. This approach represents also a potential venue for future investigations of flash sintering of complex shapes.



SEM images in the centers and edges of nickel, zirconia and alumina samples for constant and forced current modes.

The densification mechanism of conductive powders was revealed by comparing the electric current-assisted spark plasma sintering (SPS) of ZrN powder with conventional hot pressing (HP) carried out with the same powder and under the same pressure and temperature. For the first time, by taking into account the explicit influence of the electric current effect on the SPS densification mechanism, the constitutive equations describing the electric current-assisted hot pressing of powders have been developed. The densification mechanism of ZrN was determined by the inverse regression of the new SPS constitutive equations and by utilizing the experimental results on ZrN powder consolidation with and without the participation of the electric current effect. To determine the actual temperature inside ZrN powder, a sacrificial thermocouple was directly inserted into the powder during the SPS process. The spatial distribution of the electric current passing through the powder was calculated using the finite element modeling. The porosity-interparticle neck area geometrical relationship was applied to estimate the electric current density inside the powder volume subjected to SPS. For the first time, by taking into account the explicit influence of the electric current effect on the SPS densification mechanism, the constitutive equations describing the electric current-assisted hot pressing of powders have been developed.



(a) Experimental porosity evolution curves of ZrN specimens processed by HP or SPS fitted by constitutive equation developed, (b) experimental porosity evolution curves of ZrN specimens processed by SPS fitted by constitutive equation developed (Black triangle: HP with 1200 °C and 10 °C/min, red square: SPS with 1200 °C and 10 °C/min, and blue circle: SPS with 1200 °C and 10 °C/min). Applied compaction pressure was a 60 MPa.

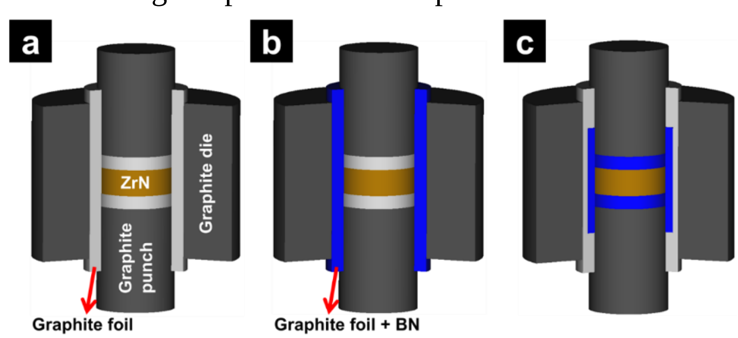
A new and straightforward method of the identification of porosity-dependent sintering constitutive parameters adaptable to a regular spark-plasma sintering device was proposed. Compared to classical creep mechanism studies, this comprehensive experimental approach can reveal the in situ porous structure morphology influence on the sintering process.

This project addressed the two great challenges of the spark plasma sintering (SPS) process: The sintering of complex shapes and the simultaneous production of multiple parts. A new controllable interface method was employed to concurrently consolidate multiple shapes by SPS. An energy efficient SPS configuration is developed to allow the sintering of a large-scale powder assembly. The stability of the developed process was studied by electro-thermal-mechanical (ETM) simulation. The ETM simulation reveals that homogeneous densification conditions can be attained by inserting an insulative powder at the sample/punches interfaces, enabling the energy efficient heating and the thermal confinement of the processed powder. Finally, the feasibility of the fabrication of the near net shape complex shape components with a very homogeneous microstructure is demonstrated.

The net-shaping capability in spark plasma sintering of ultrahigh-temperature ceramics has been explored. The annular or ring-like shape has been considered as the first step to a more complex geometry compared to a solid cylinder or disk. ZrC powders have been SPS processed in specially designed graphite tooling to achieve the annular shape geometry. Experimental runs have been carried out to determine the optimal processing parameters for producing highly dense ZrC specimens in this geometry. Finite-element modeling framework has been constructed to determine the internal stress evolution, as well as densification, during the SPS of the annular-shaped ZrC. The formulated processing schemes for ZrC have been adapted to process SiC/ZrB_2 composite powder with the purpose of making tooling components for SPS applications. The applicability of the obtained composite SPS tooling has been evaluated at high temperature and high pressure associated with SPS regimes.

Theoretical studies on the densification kinetics of the new spark plasma sinter-forging (SPS-forging) consolidation technique and of the regular SPS have been carried out based on the continuum theory of sintering. Both modeling and verifying experimental results indicate that the loading modes play important roles in the densification efficiency of SPS of porous ZrC specimens. Compared to regular SPS, SPS-forging was shown to be able to enhance the densification more significantly during later sintering stages. The derived analytical constitutive equations were utilised to evaluate the high-temperature creep parameters of ZrC under SPS conditions. SPS-forging and regular SPS setups were combined to form a new SPS hybrid loading mode with the purpose of reducing shape irregularity in the SPS-forged specimens. Loading control was imposed to secure the geometry as well as the densification of ZrC specimens during hybrid SPS process.

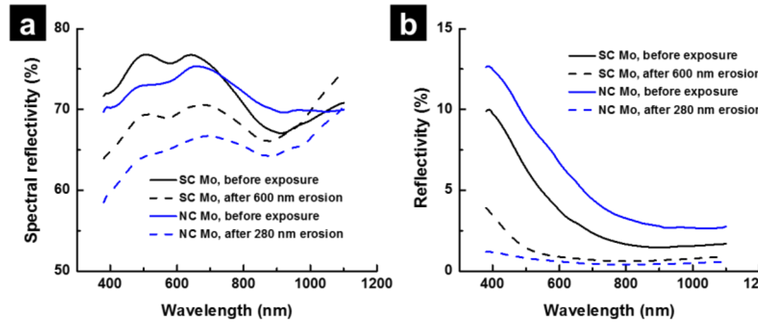
The stability of the proportional–integral–derivative (PID) control of temperature in the spark plasma sintering (SPS) process was investigated. The PID regulations of this process are tested for different SPS tooling dimensions, physical parameters conditions, and areas of temperature control. It is shown that the PID regulation quality strongly depends on the heating time lag between the area of heat generation and the area of the temperature control. Tooling temperature rate maps are studied to reveal potential areas for highly efficient PID control. The convergence of the model and experiment indicates that even with non-optimal initial PID coefficients, it is possible to reduce the temperature regulation inaccuracy by positioning the temperature control location in highly responsive areas revealed by the finite-element calculations of the temperature spatial distribution.



Schematics of spark plasma sintering setup enabling the different current density flow into ZrN powders. Black, gray, gold and blue color indicate the graphite component, graphite paper, ZrN, and boron nitride.

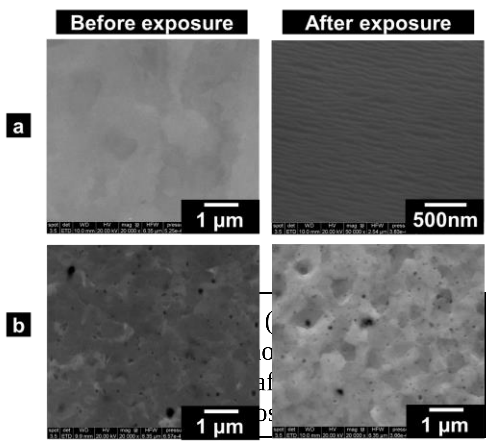
The impact of the electric current on sintering is revealed by introducing the three heating modes during spark plasma sintering enabling the different electric current density flowing into the electrically conductive powders under the same temperature. The experimental evidence of the electric current effect on sintering is demonstrated by the determination of the electric current related constitutive parameters obtained from the three heating modes.

The enhancement of the dislocation motion and the reduction of the flow stress under the electric current passage are experimentally proven by the ex-situ mechanical strength tests and using the X-ray diffraction results analyzed by the modified Williamson-Hall equation.



(a) Specular reflectivity of single crystal (SC) and nanocrystal (NC) Mo before and after plasma exposure (45° illuminations and 45° collection), (b) Diffuse reflectivity of SC and NC Mo and (45° illuminations and 35° collection).

Mo nanopowders were synthesized by ball milling and the following hydrogen reduction of MoO_3 powders. The densification mechanism of Mo nanopowders during spark plasma sintering was analyzed by the combination of the regression of the experimental data on regular SPS and on the SPS multistep pressure dilatometry based on the continuum theory of the sintering. The Mo mirror with 400 nm average grain size and 93% relative density was fabricated by the SPS. The performance of the mirrors made from a single crystal Mo and from the hydrogen-reduced sintered Mo nanopowder was analyzed. The microstructure and optical properties of the mirrors were characterized before and after plasma exposure, and no substantial degradation of the reflectivity was observed. The densification mechanism of Mo nano-powders during spark plasma sintering was analyzed by the combination of the regression of the experimental data on regular SPS and on the SPS multistep pressure dilatometry based on the continuum theory of the sintering.



Surface-oxidized molybdenum nano-powders have been compacted by spark plasma sintering. The oxide impurity behavior was analyzed under various sintering temperatures. The densification mechanism of the nano-powders with a melted oxide phase was identified in situ by regression analysis of the experimental data on the temperature-dependent porosity change and on the SPS multistep pressure dilatometry. To increase the density of the compacted pellets, the nanopowders with the oxide phase were consolidated by SPS using the two in situ oxide removal methods: carbothermic reduction and particle surface cleaning by the electric current flow through the powders.

Spark plasma sintering has been successfully used to produce all-solid-state lithium-ion batteries (ASSLibs). Both regular and functionally graded electrodes are implemented into novel three-layer and five-layer battery designs together with solid-state composite electrolyte. Scanning electron microscopy revealed that the functionally graded structure can eliminate the delamination effect at the electrode–electrolyte interface and, therefore, retains better performance.

Spark plasma sintering was adopted to fabricate transparent AlON ceramics, using a bimodal c-AlON powder synthesized by the carbothermal reduction and nitridation method. High heating rates ranging have been selected to rapidly sinter transparent aluminum oxynitride (AlON) ceramics by spark plasma sintering. The high heating rates and short holding duration of the SPS utilized resulted in the fine grain size of the obtained ceramics compared to that of the AlON ceramics fabricated by the conventional sintering method. This effect of high heating rates was confirmed by the coupled densification-grain growth modeling.

Porous Ti5Al2.5Fe alloy was successfully fabricated using the spark plasma sintering technique. The compressive strength of the porous samples was found to be mainly dependent on sintering temperature,

and the porous compacts exhibiting good biocompatibility properties.
An energy efficient spark plasma sintering method enabling the densification of large size samples assisted by very low electric current levels has been developed. In this method, the electric current is concentrated in the graphite foils around the sample. High-energy dissipation is then achieved in this area enabling the heating and full densification of large parts at relatively low currents. The experiments confirmed the possibility of full densification of large alumina samples. This approach allows using small (and low cost) SPS devices for large-size samples. The developed technique enables also an optimized energy consumption by large-scale SPS systems.

3. What opportunities for training and professional development has the project provided?
Two visiting scholars, three post-doctoral, four PhD, and three MS students have been involved in carrying out the project activities. The project has resulted in four Ph.D. and two M.S. dissertations successfully defended.

4. How have the results been disseminated to communities of interest?
Please see "Products". The results have been disseminated via publications in refereed journals, presentations at the international scientific conferences and via SDSU Powder Technology Laboratory website: www.ptl.sdsu.edu.

PRODUCTS
The results of the research conducted in 2012-2021 have been published in 1 book (monograph), 1 edited book, 59 refereed journal papers, 31 proceedings papers at international scientific conferences, and 4 patent applications.

Book
E. A. Olevsky and D. V. Dudina, Field-Assisted Sintering: Science and Applications, Springer Nature IP, ISBN 978-3-319-76031-5, 400p. (2018)

Edited Book
E. Olevsky, Spark-Plasma Sintering and Related Field-Assisted Powder Consolidation Technologies, MDPI, ISBN 978-3-03842-383-6, 187 p. (2017)

Refereed Journal Papers
1. M. Radhakrishnan, E. Torresani, E. Olevsky, R. McCabe, S. A. Maloy, O. Anderoglu, Joining of Nanostructured ferritic 14YWT alloys by spark plasma technique, J. Mater. Eng. Perform., 30, 5736-5741 (2021)
2. A. Maximenko, O. Izhvanov, E.A. Olevsky, Modeling of fuel-cladding stresses in porous UC/SIC fuel pins, Nucl. Eng. Design, 359, 110455 (2020)
3. G. Lee, C. Manière, J. McKittrick, E.A. Olevsky, Electric current effects in spark plasma sintering: From the evidence of physical phenomenon to constitutive equation formulation, Scripta Mater., 170, 90-94 (2019)
4. G. Lee, C. Manière, J. McKittrick, A. Gattuso, C. Back, E.A. Olevsky, Oxidation effects on spark plasma sintering of molybdenum nanopowders, J. Amer. Ceram. Soc., 102, 801-812 (2019)
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13. G. Lee, E.A. Olevsky, C. Manière, A. Maximenko, O. Izhvanov, C. Back, J. McKittrick, Effect of electric current on densification behavior of conductive ceramic powders consolidated by spark plasma sintering, Acta Mater., 144, 524-533 (2018)
14. Y. Shan, X. Sun, B. Ren, H. Wu, X. Wei, E.A. Olevsky, J. Xu, J. Li, Pressureless sintering of highly transparent AlON ceramics with CaCO3 doping, Scripta Mater., 157, 148-151 (2018)
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INTELLECTUAL PROPERTIES DETAIL

1. Patent: Sacrificial Mold for Complex Shape Component Production Using Spark Plasma Sintering

Authors: Eugene Olevsky, Charles Maniere, Elisa Torresani

The invention relates to manufacturing processes using spark plasma sintering, and in particular to a process for producing a sintered powder manufactured item. In a single production, the process comprises the steps STEP 1 - fabricating a sacrificial porous mold, wherein the sacrificial porous mold is made from a first material such as clay or ceramic having a sintering temperature higher than a second powder material (component powder) such as metal, metal-alloy, different from the first material, the second powder material used to create a manufactured item, wherein the sacrificial porous mold is fabricated using a 3D printing method, STEP 2 - loading the second powder material into the sacrificial porous mold and placing the sacrificial porous mold into a sintering die chamber to form a powder assembly, STEP 3 - sintering of the powder assembly, and STEP 4 - releasing a sinter-powder cast manufactured item from the sacrificial porous mold to obtain the sinter-powder cast manufactured item. In a batch production process, multiple stacked disks of sacrificial molds are placed in the sintering die chamber.

Country: United States (USA)
Patent App. Number: 63/014,463

2. Patent: Selective Sinter-Based Fabrication of Fully Dense Complex Shaped Parts
Authors: Geuntak Lee, Eugene Olevsky, Charles Maniere

A novel method to make fully dense metal and ceramic complex shape components is developed. Known additive manufacturing technologies producing complex shape components using binders, include the complex and time-consuming debinding process and render low green density products. Using the proposed combination of selective sintering and 3D printing technology, fully dense complex parts can be easily produced. The total process is composed of the following steps: 1. Fabrication of sacrificial powder mold, 2. Injection of powders or slurry to the mold, 3. Isostatic pressing of the sacrificial mold and powder assembly, 4. Sintering. Here, the sacrificial powder mold, made from powders with high sintering temperature and binder can be made using a regular AM method such as the binder jetting method. This sacrificial mold performs 3 consecutive functions in the complex shape fabrication process: 1. Shaping of the complex part by pouring the powders or slurry into the mold, 2. Pressure transmission during isostatic pressing to increase the green density of the article prior to sintering, 3. Self-destruction during sintering by using the binder which swells during heating (Figure 2).

Country: United States (USA)
Patent App. Number: 17/050,835

3. Patent: In Situ Partially Degradable Separation Interface for Fabrication of Complex Near Net Shape Objects by Pressure Assisted Sintering
Authors: Charles Manière, Eugene Olevsky

A novel powder consolidation technique that efficiently facilitates the fabrication of fully dense complex shapes has been developed. The advanced pressure assisted sintering techniques such as spark plasma sintering, which involves high pressures (up to 100 MPa) and very high temperatures (up to 2500 °C), enable the consolidation of nearly all the powders from polymers to high temperature materials (such as silicon carbide) with the possibility to control the microstructure. These techniques are very useful for the fabrication of high-performance materials, but their main drawback are the difficulties to generate complex shapes. In most of these processes a certain level of post-processing porosity remains, when complex shapes' fabrication is attempted, due to the high complexity of the tooling involved in the production of these shapes. To address this problem a general approach involving a simple tooling geometry and an internal separation interface with a complex geometry has been developed. This method named "deformed interface approach" has proven its ability to generate highly complex shape components but the generation of the internal separation interface by traditional approaches such as the imprint in powder bed or the use of a graphite foil container is still difficult and represents a new challenge. The present approach enables the integration of the advanced complex shapes methods of 3D printing and the high quality of the material microstructures obtained by the pressure assisted sintering techniques. In this approach, a polymer skeleton with potentially a very high complex shape is generated by 3D printing (or other polymer manufacturing techniques). This polymer skeleton enables a very easy generation of a complex interface in a powder bed. After a simple heat treatment, the polymer decomposition in situ generates a graphite interface that preserves the initial complex geometry of the polymers. The powder assembly can then be sintered by any pressure assisted technique to full densification and the graphite interface (inert) allows the release of the internal fully densified complex shape part. In summary, the advantages of this approach are: 1) the possibility to generate fully dense very high complex shapes thank to the use of the process like 3D printing, 2) the possibility to fabricate high performance materials, using consolidation techniques like SPS, HP or HIP and 3) the possibility to generate multiple parts by sintering them simultaneously thereby considerably increasing the productivity of the method. To conclude, the present approach is all-materials, all-shape inclusive, enabling high performance properties thanks to the potential combination of 3D printing and SPS, and highly productive due to its intrinsic concept.

Country: United States (USA)
US Patent App. Number: 17/042,176

4. Patent: Process Stabilizing Tooling for Spark Plasma Sintering
Authors: Diletta Giuntini, Eugene Olevsky, Jan Raethel, Michael Herrmann

A novel punch design for Spark Plasma Sintering (SPS)/Field-Assisted Sintering Techniques (FAST) procedures has been developed. Temperature spatial non-uniformity is a major challenge preventing the practical implementation of the emerging technology of Spark-Plasma Sintering. This problem becomes especially important in the large size components produced in a real-world industrial environment by SPS. In order to mitigate the significant temperature gradients occurring in the powder specimen along the radial direction, the graphite punch geometry was altered according to two different strategies. The first new design consists in the drilling of a variable number of concentric ring-shaped holes. Such holes direct the electric current flow along a pre-defined path, redistributing thermal gradients accordingly. The pattern, number and dimensional details of the holes to be drilled can be adapted to the size of the tooling setup and powder material employed. As a general indication, in case of electrically insulating specimens, the holes are tailored in a fashion such that the punch's mass is concentrated in its center, so that the overheating of the sample's edge, due to the current flowing through the die only, is annihilated. An opposite strategy is applied to conductive specimens. The second new design is constituted by the deposition of a thin layer of hexagonal boron nitride on the surface of the punch. Boron nitride has a significantly higher electrical resistivity with respect to graphite, and therefore acts as an insulator with respect to the current flow. The coating covers only a partial ring-shaped area of the punch surface, adjacent to the edge for insulating specimens and to the center for conductive ones, according to the same principle described in the previous paragraph. The extension of the boron nitride layer in the radial direction is again regulated based on the size of the tooling setup and on the materials employed. If high loads need to be applied during the SPS/FAST process, a thick solid layer of boron nitride is deposited, after the removal of the appropriate amount of graphite by means of mechanical machining.

Country: United States (USA)
US Patent App. Number: 62/086,694

TECHNOLOGIES AND TECHNIQUES DETAIL

1. Description:
Fully Coupled 3D Thermo-Electro-Mechanical Analysis of SPS:

PI and co-workers have overcome the challenge of fully coupled 3D thermo-electro-mechanical analysis of the material processing under electric-current-assisted hot pressing conditions. The developed modeling framework, however, incorporates the conventional models of hot pressing and does not take into account the SPS-specific field-assisted constitutive mechanisms of material transport at multiple scale levels.

2. Description:
Preliminary Results on Seamless SPS-Joining Technique:
The preliminary investigations showed the potential of SPS to produce practically seamless joints between SiC components without using any filler material.

3. Description:
An energy efficient spark plasma sintering method enabling the densification of large size sample at very low current is developed. In this method, the electric current is concentrated at the specially designed interfaces. A high heating dissipation is then created in this area enabling the heating and full densification of large parts at low current.

4. Description:
Flash Hot Pressing (Ultra-Rapid Spark-Plasma Sintering) Technique:
The investigations showed that the consolidation efficiency of spark plasma sintering can be dramatically further improved by enabling an ultra-rapid "flash" regime of processing, when super-hard powder materials can be consolidated in a matter of few seconds.

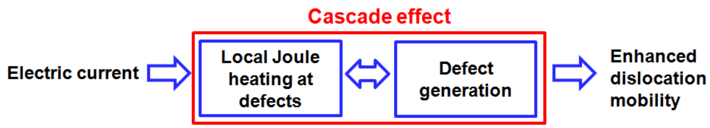
IMPACT

1. What is the impact on the development of the principal discipline(s) of the project?
The conducted research indicates that the understanding of the material constitutive behavior during SPS is impossible without the coupled analyses of mechanical consolidation, heat transfer and electric field-induced phenomena at multiple scale levels. The achievement of the ultimate goal of the formulation of the general theory of spark plasma sintering becomes possible due to the conducted research performed in a systematic way identifying the contributions of all the thermal and non-thermal factors in the enhancement of mass transport under SPS processing conditions. The SPS-specific non-thermal factors are related to the direct impact of electromagnetic field on the diffusion mass transport through electromigration, electroplasticity mechanisms, and dielectric breakdown of oxide films at grain boundaries. In addition, new, exciting capabilities of SPS have been revealed by PI's research group, including the new potentially transformative energy efficient net-shape spark plasma sintering method enabling the densification of large size sample at very low current, as well as the possibility of the SPS usage for seamless joining of ceramic and metallic materials. These new developments and the need for a physically consistent modeling framework are the major incentives of the research on the fundamentals of spark-plasma sintering.

2. What is the impact on the development of human resources?
Two visiting scholars, three post-doctoral, four PhD, and three MS students have been involved in carrying out the project activities. The project has resulted in four Ph.D. and two M.S. dissertations successfully defended.

3. What is the impact on technology transfer?
Four patent applications have been submitted.

Effect of Electric Current on Spark Plasma Sintering



New Constitutive equation for SPS

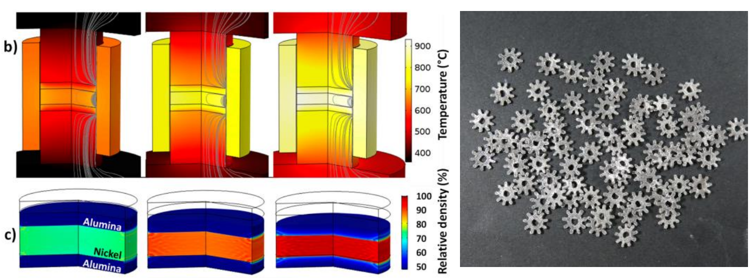
$$\dot{\theta} = -[A_{TD} + A_{ECAD}](\frac{3\theta}{2})^{\frac{m+1}{2m}}(1-\theta)^{\frac{m-3}{2m}}(\frac{\sigma_z}{G})^{\frac{1}{m}}$$

$$A_{TD} = \frac{G}{A_0 T}\left(\frac{b}{d}\right)^p \exp(\frac{-Q}{RT})$$

$$A_{ECAD} = \beta^{\omega}\left[\int_{t_0}^{t_f} \frac{J_{OL}{}^2 \lambda}{G} dt\right]^{\omega}$$

A_{TD}: Thermal deformability of the powders during the sintering (1/s)

A_{ECAD}: Electric current assisted deformability of the powders (1/s)



Left: Modeling of controlled electric current pathways during spark plasma sintering. Right: One hundred micro-gears processed during one spark plasma sintering cycle.

M. Radhakrishnan, E. Torresani, E. Olevsky, R. McCabe, S. A. Maloy, O. Anderoglu, J. Mater. Eng. Perform., 30, 5736-5741 (2021)

G. Lee, C. Manière, J. McKittrick, E.A. Olevsky, Scripta Mater., 170, 90-94 (2019)

Scientific Achievement

A new constitutive model of spark plasma sintering taking into account the effect of electric current is developed.

Significance and Impact

Based on the enhanced understanding of the role of electrical current in spark-plasma sintering, a new processing approach integrating complex shapes-rendering methods of 3D printing and the high quality of the material microstructures obtained by the pressure assisted sintering techniques is developed.

Research Details

– The densification mechanism of conductive powders is revealed by comparing the electric current-assisted spark plasma sintering with conventional hot pressing carried out with the same powder and under the same pressure and temperature.

– Spark plasma sintering of complex shape parts has been successfully carried out for conductive, semi-conductive, and electrically-isolative materials.

U.S. DEPARTMENT OF ENERGY | Office of Science

Work was performed at San Diego State University

SAN DIEGO STATE UNIVERSITY

All-Materials-Inclusive Flash Spark-Plasma Sintering

Top: Consolidation of silicon carbide at the moment of flash
Bottom: The SEM micrograph of SiC powder (left), and SiC specimen processed by flash SPS (right)

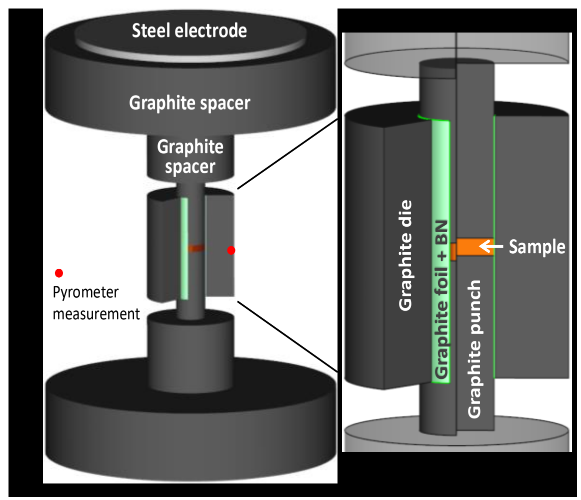
E.A. Olevsky, S.M. Rolfing, A.L. Maximenko, *Nature Sci. Rep.*, 6, 33408 (2016). DOI: 10.1038/srep33408

Scientific Achievements

Developed a new ultra-rapid process of flash spark plasma sintering that stabilizes the thermal runaway by applying an external pressure.

This process is further advanced to make it scalable and all-materials-inclusive due to the efficient energy re-distribution.

This process is combined with 3D-printing of controlling interfaces to enable net-shape capabilities.



Localized supply of energy along interfaces

Net shaping via 3D printing of interfaces

E.A. Olevsky, C. Maniere, G. Lee. , *Nature Sci. Rep*, (2017). DOI: 10.1038/s41598-017-15365-x

U.S. DEPARTMENT OF ENERGY | Office of Science

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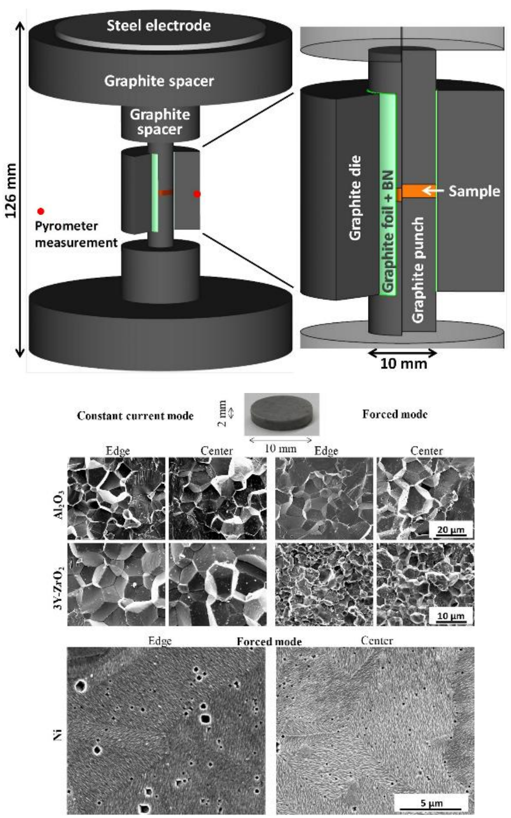
All-Materials-Inclusive Flash Spark Plasma Sintering



Top: Net shape flash spark plasma sintering configuration, the lateral graphite foil is coated with a boron nitride spray to electrically insulate the die and concentrate the electric current on the sample.
Bottom: SEM images in the centers and edges of nickel, zirconia and alumina samples for constant and forced current modes.

Charles Manière, Geuntak Lee & Eugene A. Olevsky, *Nature Sci. Rep.*, 7, 15071 (2017). DOI: 10.1038/s41598-017-15365-x

Scientific Achievement

A new flash (ultra-rapid) spark plasma sintering method applicable to various materials systems, regardless of their electrical resistivity, is developed.

Significance and Impact

The presented new method allows: extending flash sintering to nearly all materials, controlling sample shape by an added graphite die, and an energy efficient mass production of small and intermediate size objects. This approach represents also a potential venue for future investigations of flash sintering of complex shapes.

Research Details

- A number of powders ranging from metals to electrically isolative ceramics have been successfully densified resulting in homogeneous microstructures within sintering times of 8–35 s.
- The utilized uniquely controllable flash phenomenon is enabled by the combination of the electric current concentration around the sample and the confinement of the heat ("forced mode") generated in this area by the lateral thermal contact resistance.