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Constitutive Modeling and Simulation of Spark Plasma Sintering with Applications to Fabrication of Functionally Structured Mono-Carbides

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# Publication Date

2013

Peer reviewed|Thesis/dissertation

#### UNIVERSITY OF CALIFORNIA, SAN DIEGO

#### SAN DIEGO STATE UNIVERSITY

Constitutive Modeling and Simulation of Spark Plasma Sintering with Applications to Fabrication of Functionally Structured Mono-Carbides

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Engineering Science (Mechanical and Aerospace Engineering)

by

Wei Li

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The Dissertation of Wei Li is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

Co-Chair

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Chair

University of California, San Diego

San Diego State University

2013

### DEDICATION

This dissertation is dedicated to my parents, without whom I could never have finished this ordeal. Their support kept me going through the darkest times, and I will be eternally grateful.

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# LIST OF SYMBOLS

$A_{C}$	cross sectional surface area of specimen, cm <sup>2</sup>
α	specific surface energy, $J/m^2$ ; or surface tension, N/m
$\alpha_{CTE}$	thermal expansion coefficient, $1 \times 10^{-6}/K$
$\alpha_{DC}$	material parameter of Du & Cocks model for normalized bulk modulus
$\alpha_{Hs}$	material parameter of Hsueh model for normalized bulk modulus
$\alpha_{TD}$	thermal diffusivity, m <sup>2</sup> /s
a <sub>SR</sub>	material parameter of Svoboda & Riedel model for normalized sintering
	stress
В	function of microstructure, m
b	Burger's vector
b <sub>DC</sub>	material parameter of Du & Cocks model for normalized bulk modulus
b <sub>He</sub>	material parameter of Helle model for normalized bulk modulus
b <sub>Hs</sub>	material parameter of Hsueh model for normalized bulk modulus
b <sub>SR</sub>	material parameter of Svoboda & Riedel model for normalized sintering
	stress

$b_{VR}$	material parameter of Venkatachari & Raj model for normalized bulk
	modulus
С	elastic stiffness, GPa
$C_p$	specific heat capacity at constant pressure, J/kg/K
$C_{pV}$	volume specific heat capacity at constant pressure, $J/m^3/K$
D	diffusion coefficient, m <sup>2</sup> /s
d	diameter of the cylindrical SPS graphite punch, mm
$\delta_{ij}$	Kronecker delta (1 as $i = j$ , 0 as $i \neq j$ )
ė	volume strain rate, 1/s
e <sub>total</sub>	total normalized volume strain
e <sub>thermal</sub>	volume strain due to thermal expansion or shrinkage
e <sub>creep</sub>	volume strain due to creep
e <sub>elastic</sub>	volume strain due to elastic deformation
ė <sub>creep</sub>	normalized volume strain rate due to creep, 1/s
Ė <sub>ij</sub>	true strain rate tensor, 1/s
Ė <sub>kk</sub>	summation of normal strain rate tensor, 1/s
$\dot{\varepsilon}_{ij}'$	true shear strain rate tensor, 1/s

Ė	true strain rate, 1/s
€ <sub>creep</sub>	true creep strain
ε	true strain
ε <sub>ij</sub>	true elastic strain tensor
$\mathcal{E}_{CTE}$	true strain due to thermal expansion or shrinkage
$\epsilon_r$	relative permittivity
E <sub>epot</sub>	electric potential, V/m
η	effective shear viscosity, Pa.s
$\eta_0$	power law creep frequency factor of fully dense material, Pa.s <sup>m</sup>
$\eta_g$	viscosity of gas, Pa.s
F	transverse rupture strength testing load, N
arphi	normalized shear modulus
G	grain size (or particle size for single crystal powder), $\mu m$
G <sub>0</sub>	initial grain size (or particle size for single crystal powder), $\mu m$
Ġ	grain growth rate, µm/s
G <sub>e</sub>	elastic shear modulus, GPa
g	gravitational acceleration, m/s <sup>2</sup> (N/kg)

Ϋ́	measured true shear strain rate, 1/s
$h_f$	fully dense specimen height, cm
h	specimen height for the transverse rupture strength test, mm
$I_S$	electric current passing through SPS specimen, A
I <sub>max</sub>	maximum allowed SPS system electric current, A
J <sub>h</sub>	Joule heating power, W
k	thermal conductivity, W/m/K
k <sub>0</sub>	thermal conductivity for fully dense material, W/m/K
k <sub>B</sub>	Boltzmann's constant, J/K
Κ	elastic bulk modulus, GPa
L	specimen thickness, cm
т	strain rate sensitivity exponent
М	mass of filling powder or processed specimen, g
μ	Coulomb friction coefficient
$\mu_p$	permeability, Darcy or cm <sup>2</sup>
ν	Poisson's ratio
$ u_P$	Poisson's ratio for porous material

$v_{pi}$	Poisson's ratio for perfect isotropic material
$\nu_0$	Poisson's ratio for fully dense bulk material
n	stress sensitivity exponent
$n_g$	grain growth power exponent
$n_N$	normal vector
$\Delta P$	differential pressure, Pa
Р	total electric power within SPS specimen and tooling, W
P <sub>max</sub>	maximum achievable electrical power based on maximum current, W
$P_T$	electric power within SPS tooling, W
$P_S$	electric power within SPS specimen, W
$P_L$	sintering stress (Laplace stress), MPa
$P_{L0}$	initial sintering stress, MPa
$P_{LR}$	relative sintering stress
$Q_{pc}$	activation energy for power law creep, J/mol
$Q_{gb}$	activation energy for grain boundary diffusion, J/mol
$Q_j$	heating power density generated by Joule heating, $W/m^3$
$Q_{gf}$	gas flux, cm <sup>3</sup> /s

R	universal gas constant, J/mol/K
$R_S$	electrical resistance of SPS specimen, ohm
$R_T$	electrical resistance of SPS tooling, ohm
$R_N$	normalized Poisson's ratio
r <sub>e</sub>	effective specimen radius for transverse rupture strength test, mm
ρ	relative density change rate, 1/s
ρ	relative density
$ ho_m$	material density, g/cm <sup>3</sup>
$ ho_{th}$	material theoretical density, g/cm <sup>3</sup>
σ	true stress, MPa
$\vec{\sigma}$	stress vector, MPa
$\sigma_0$	material power law creep frequency factor constant, MPa.s <sup>m</sup> .K
$\sigma_b$	body stress gradient tensor, MPa/m
$\sigma_e$	material electric conductivity, S/m
$\sigma_{f}$	friction stress tensor, MPa
$\sigma_n$	normal stress, MPa
$\sigma_z$	z axis true stress tensor, MPa

$\sigma_{e0}$	electrical conductivity for fully dense material, S/m
$\sigma_{kk}$	summation of all the hydrostatic parts of the true stress tensor, MPa
$\sigma_{ij}$	true stress tenosr, MPa
$\sigma_{ij,j}$	true stress gradient tenosr, MPa/m
$\sigma_{SBC}$	Stephan-Boltzmann constant, $W/m^2/K^4$
$\sigma_{TRS}$	transverse rupture strength, MPa
$\sigma(W)$	equivalent stress driving power law creep, MPa
$\psi$	normalized bulk modulus
Т	absolute temperature, K
T <sub>amb</sub>	radiation ambient temperature, K
T <sub>ref</sub>	reference temperature for thermal expansion
$\Delta T$	the maximum value of temperature rise, K
$ au_s$	specific time of sintering
θ	porosity
θ	porosity change rate, 1/s
$\theta_c$	critical value to represent the transition from open to closed porosity
$\theta_0$	initial porosity

U	applied voltage, V
U <sub>max</sub>	maximum applicable voltage based on maximum allowed current, V
u	displacement, m
<i>Ϋ</i>	volume change rate, cm <sup>3</sup> /s
V	instantaneous specimen volume, cm <sup>3</sup> /s
V <sub>volt</sub>	electric voltage, V
W	equivalent strain rate, 1/s
ζ	effective bulk viscosity, Pa.s

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### ACKNOWLEDGEMENTS

I would like to acknowledge Professor Randall M. German for his support as the chair of my committee. He is a great mentor who lights up the path for my research.

I would like to acknowledge my co-advisor, Professor Eugene A. Olevsky for his countless advices, supports, and inspirations. His theory laid down the basis of this work.

I would also like to acknowledge my co-advisor, Professor Joanna McKittrick for her encouragement and support for broad collaboration really built the confidence for me.

I have special thanks for Dr. Jose Alvarado-Contreras, Dr. Andrey Maximenko, and Dr. Steve Barlow for helping me improve my research results.

I would also like to thank my committee members, Professor Vitali F. Nesterenko and Professor David J. Benson for their time and consideration of my work.

I appreciate the sponsorship from General Atomics for my project, as well as the advice, support, inspiration from Dr. Christina Back and Dr. Oleg Izhvanov.

I am extremely grateful for all of PTL members, who I loved working with, and consider my friends Timothy H. Young, Yen-Shan Lin, Xialu Wei, Evan A. Khaleghi, Diletta Giuntini, William Bradbury, Cristina Garcia Cardona, Geuntak Lee. Chapter 4, in part, is a reprint of the content as it appears in Journal of Materials Science.

W. Li, E. A. Olevsky, J. McKittrick, A. L. Maximenko and R. M. German, "Densification Mechanisms of Spark Plasma Sintering: Multi-Step Pressure Dilatometry," *Journal of Materials Science*, vol. 47, no. 20, pp. 7036-7046, 2012.

The author of the dissertation is the primary investigator and author of the paper.

Thanks to my parents and girlfriend, Ke Ma's for their consistent support always.

### VITA

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### FIELDS OF STUDY

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### **ABSTRACT OF THE DISSERTATION**

Constitutive Modeling and Simulation of Spark Plasma Sintering with Applications to Fabrication of Functionally Structured Mono-Carbides

by

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Doctor of Philosophy in Engineering Science (Mechanical and Aerospace Engineering) University of California, San Diego, 2013 San Diego State University, 2013

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The so called spark plasma sintering (SPS) is a relatively new hot consolidation technology that is getting rapidly growing attention for the academic research and industrial development. Although there is no evidence of plasma existence yet, substantial experiment trials have been done and often delivered superior material properties with high processing efficiency. However, the majority of fundamental modeling and simulation work done to now is still limited to the study on interactions of electrical-thermal fields; while few of the studies included analyses of stress distribution,

densification, or grain growth. This study is the first modeling and simulation work to fully couple electrical-thermal-mechanical fields together with porous body consolidation and grain growth. This study uses a power law creep based model with a novel grain size - density correlation model to describe the material densification and microstructure coarsening under mechanical pressure at high temperature. Realistic boundary conditions at the contact interfaces between punch-die-specimen are also included in calculations. A novel multi step pressure dilatometry approach is introduced to determine the material parameters for modeling, including strain rate sensitivity (responsible for hardening effect), activation energy, and the vibrational frequency. With the experimentally determined material parameters and handbook properties, the model predictions are close to experimental density data on SPS of copper ( $R^2$  90.4%) and vanadium carbide ( $R^2$ 99.7%) powders. Copper was used for the fundamental study with the aim to characterize electric current impact on SPS consolidation. Another system of vanadium carbide was used as a surrogate material with the aim to investigate the feasibility of fabricating functionally structured uranium carbide nuclear fuel pellets by SPS.

#### **Chapter 1** Introduction

### 1.1 Evolution of Spark Plasma Sintering Technology

It has long been recognized that one of the methods to activate the sintering process involves the use of electric current. The recent widespread application of this approach has been enabled by the availability of commercially built devices [1]. Commercial and research units, which have been developed over the past decades, include "plasma-assisted sintering" (PAS) [2], "pulsed electric current sintering" (PECS) [3], "electro-consolidation" (also known as electric pulse assisted consolidation (EPAC) [4], "field assisted sintering technology" (FAST) [5], and the so called "spark plasma sintering" (SPS) [6]. In many regards these approaches share the key common features which are uniaxial mechanical pressure assisted sintering heated by electric power applied through graphite tooling.

Although the existence of plasma during the process is still highly debatable [7], the so called spark plasma sintering (SPS) is currently (1922 to 2007) the most widely published technique name among the current activated consolidation processes, which consists of 66.2% within the 1,005 related publications.



Figure 1. Technical Terminology Distribution adapted from Orru [8]

Academic and industrial attentions have been focused on SPS within the recent two decades (2003 to 2013), while the technology concept had been demonstrated more than hundred years ago. The milestones of the development of SPS technology are listed as the following:

W. L. Velker, Manufacture of Incandescing Electric Lamps, US Patent No.660,475

- J. Lux, Improved Manufacture of Electric Incandescent Lamp Filaments from
   Tungsten or Molybdenum or an Alloy Thereof, GB Patent No. 9020 & No.
   27,002
- 1913 W. D. Coolidge, Production of Refractory Conductors, US Patent No. 1,077,674
- 1922 F. Sauerwald, Apparatus for Direct Resistance Heating to High Temperatures under High Pressure, Zeitschrift fur Elektrochemie, 28, 181-183
- 1933 G. F. Taylor, Apparatus for Making Hard Metal Compositions, US Patent N,896,854
- 1955 F. V. Lenel, Resistance Sintering under Pressure, Trans. AIME, 293, (1), 158-167, 1955
- 1962 K. Inoue, Electric-Discharge Sintering, US Patent N3,241,956
  - K. Inoue, Apparatus for Electrically Sintering Discrete Bodies, US Patent N3,250,892
- 1970s Research on Spark Sintering and Electric-Spark Sintering in USA and USSR, respectively
- 1980s Research on the so called "Plasma Activated Sintering" in Japan

- 1990s SPS Machines are developed by Sodick Co. and Sumitomo Coal Mining Co. Ltd., Japan
- 2000s Extensive experimentation throughout the world on SPS of various material systems.

Statistic surveys were summarized and conducted by the author of this dissertation on SPS related techniques. The patent statistics data was from Grasso [9], who collected the relevant patents (642 patents in total, published between 1906 to 2008) from the Japanese Patent Office (342 patents), the United State Patent and Trademark Office (175 patents), the Chinese State Intellectual Property Office of P. R. C. (69 patents), and the World Intellectual Property Organization (12 patents). It was found that, there were 87 relevant patents issued between 1900 and 1989, and the number of patents was almost doubled to 156 between 1990 and 1999. Within most recent decade, up to 399 patents was issued between 2000 and 2008.

According to the data collected by the author of this dissertation from Web of Science® database, the journal publication rate on the SPS related technologies was about 50 papers per month in 2012; while in the 1990s, the rate was only up to about 50 papers per year (shown in Figure 2).



Figure 2. Number of Spark Plasma Sintering Related Publications per Year

The citation of the SPS relevant publications grows even faster than the publication rate (data collected from Web of Science®). It had reached to approximately 7,000 per year in 2012 as shown in Figure 3.



Figure 3. Number of Spark Plasma Sintering Related Publication Citations per Year

Another survey was conducted by the author of this dissertation to find the territory sources of SPS relevant publications based on the data collected from Web of Science® database. The result shows that China and Japan have the largest number of publications on this topic (as shown in

#### Table 1).

Field: Countries/Territories	Record Count	% of 4008	Bar Chart
PEOPLES R CHINA	1364	34.032 %	
JAPAN	1168	29.142 %	
USA	440	10.978 %	
SOUTH KOREA	362	9.032 %	
FRANCE	247	6.163 %	
GERMANY	173	4.316 %	1
SWEDEN	158	3.942 %	1.00
ITALY	135	3.368 %	1
SPAIN	115	2.869 %	1
INDIA	101	2.520 %	1

#### Table 1. Global Distribution of Spark Plasma Sintering Related Publications
The research activity on SPS is growing rapidly (as summarized above) due to its potential in deliver superior material properties, and new material structures for novel applications. Examples are shown below.

Publications reported various benefits obtained by using SPS for material processing are listed as the following:

Earlier densification onset: Shen *et al.* [10] found SPS densification onset for Al<sub>2</sub>O<sub>3</sub> powder with 0.4  $\mu$ m mean particle size at 1223 K and 50 MPa pressure in 2002, and they obtained 99.3% relative density (1.6  $\mu$ m final grain size) at 1423 K and 50 MPa pressure with 3 min holding time for the same alumina powder. McClelland *et al.* [11] hot pressed 0.3  $\mu$ m mean particle size alumina powder at 1773 K and 41 MPa pressure, and they obtained 99.6% ± 1.0% with 4 hours holding time. Yoshida *et al.* [12] found SPS densification onset for un-doped Y<sub>2</sub>O<sub>3</sub> powder with 20 nm mean particle size at 873 K and 83 MPa pressure in 2008, and they obtained relative density > 97% (500 nm final grain size) at 1123K and 83 MPa pressure with 60 min holding time; while in conventional hot pressing, Dutta *et al.* [13] reported their sintered relative density of 99.6% (final grain size 1  $\mu$ m) by using commercial Y<sub>2</sub>O<sub>3</sub> powder (99.99% purity,

American Potash & Chemical Corp, Lot #1115) at 1773K temperature and 48 MPa pressure with 120 min holding time.

Higher densities: in 2008, Kanamori *et al.* [14] reported that, for SPS of  $ZrW_2O_8$ , 98.6% relative density was obtained at 873 K with 10 min dwelling and 50 MPa uniaxial pressure; while in hot pressing, only 63.1% relative density was obtained at the same temperature and uniaxial pressure for 1 hour dwelling. In 2003, Scarlat *et al.* [15] reported that SnO<sub>2</sub> obtained 92.4% relative density at 1163 K with 10 min dwelling and 40 MPa uniaxial pressure, while for conventional sintering, only 61.3% relative density was obtained at 1273 K and 3 hours dwelling.

Lower sintering temperatures: in 2009, Gubicza *et al.* [16] reported that, ultrafine Ni powder was consolidated by SPS at 773 K for 1 minute dwelling under 150 MPa uniaxial pressure; while for hot isostatic pressing it needed 973 K and dwelling for 150 minutes under 140 MPa isostatic pressure.

Publications reported various special applications of SPS for material processing are also listed the following:

Additive free composites: in 2009, Guo [17] reported fabrication of fully dense ZrB<sub>2</sub>-15 vol.% MoSi<sub>2</sub> by SPS at 2023 K, dwelling for 7 min under 30 MPa uniaxial

pressure; while for hot pressing, temperature higher than 2373 K was required for the same level of densification.

Transparent ceramics: in 2007, Kim *et al.* [18] reported that transparent  $Al_2O_3$  was fabricated by SPS at 1427 K with heating rate of 8 K/min, and dwelling for 20 min under 80 MPa uniaxial pressure; while for hot pressing, 4 to 8 hours were required to achieve the similar structures.

Densification of metastable phases: in 2005, El-Eskandarany *et al.* [19] reported the densification of Co65Ti20W15 alloy by SPS (heating rate 300 K/min) to 99.6% relative density with retained amorphous microstructure.

Controlled porosity: in 2000, Oh *et al.* [20] reported fabrication of high strength alumina foam with controlled porosity by SPS at 1223 K, dwelling for 15 minutes under 6 MPa uniaxial pressure; while for hot pressing under the same conditions, 1573 K was required to fabricate the similar structure.

Good bonding: in 1996, Yoo *et al.* [21] bonded cubic BN onto Cu in SPS at 1273 K, dwelling for 3 minutes under 57 MPa uniaxial pressure. Super-plasticity consolidation: in 2005, Zhan *et al.* [22] reported super-plastic densification of  $Al_2O_3$  (vol. 50%) –  $Al_2MgO_4$  (vol. 50%) in SPS. The strain rate of  $10^{-2}$ /s was achieved at 1273 K and 75% relative density.

Although SPS is capable of delivering superior material properties, its processing capacity (quantity) is incomparable to conventional die compaction – pressureless sintering approach. In addition, SPS requires rigid tooling and minimum load (3.0 kN) for conducting electrical current, therefore, its net shaping capability is generally limited to symmetrical geometries. However, for applications where material properties are the most important or the material processing difficulties are extreme (e. g. extremely high melting temperature), SPS can be used as a highly effective material processing tool. With SPS high processing efficiency in terms of energy and time, it has absolute potential to substitute the conventional hot pressing for industrial applications. For example, Tokita [23] has already reported SPS industrial applications in producing 3D complex shaped blasting nozzles, M78 pore-free binderless WC materials, and glass-lens molding-die components, and WC/Co/Ni functional gradient material with three-layered structure and sharp corner rectangular geometry.

Between the years of 2000 to 2013, more than hundreds of laboratories around the world have demonstrated the advantages of SPS in thousands of material systems with variety of compositions and structures [24]. The majority of the works were based on experimentation trials to show evidence that SPS indeed is an effective way of producing bulk materials with pre-determined shapes, nanostructure retention, and in many cases surprisingly positive effects on various of properties. However, the underling science of "why" SPS works superior to conventional hot pressing technology still remains speculative. Limited but notable efforts to build the scientific framework of SPS have been made [7] [25]-[31] [36], but more in-depth fundamental investigations for enabling more effective predictions and efficient designs are waiting.

## 1.2 Modeling and Simulation of Spark Plasma Sintering

Modeling and simulation studies on SPS process have been carried generally for two purposes [37]: (1) to verify the role of the assumed critical parameters of the process and to make predictions on their effects, and (2) to explain observations obtained in the processing of various materials by this technology. However, this is not enough, eventually modeling and simulation will help the designers and users of this technology to optimize the process for the achievement of better material properties and higher fabrication efficiency.

The classic Fourier's law, Ohm's law, Joule's first law, Hook's law have been embedded in commonly available commercial numerical software packages to simulate the heat transfer, conduction of electric current, resistive heating, and elastic behaviors of dense solid materials. Given the comprehensive material property database, predictions of the basic electrical, thermal, and mechanical phenomena in the solid SPS tooling (typically graphite) can be obtained. However, when the porous powder compact in the spark plasma sintering tooling is considered, additional models (taking into considerations the pore effects) are needed to describe those phenomena in the porous body.

Modeling of spark plasma sintering, in this document, is about the derivation of constitutive models based on the fundamental physics involved in the SPS process. SPS is actually a hot consolidation process assisted by mechanical pressure, and electric current. Modeling relevant to this general process has been studied by many authors [33]-[36] [38]- [41] in the recent decade.

Heian *et al.* [38] modeled the synthesis of MoSi<sub>2</sub>–SiC composites by field activation inside a die (representing the SPS method) using the electrostatic equation and the Fourier heat transfer equation with terms added to represent chemical and electrical heat sources. The composite reaction was modeled as two separate simultaneous second order reactions, using Arrhenius kinetics with different activation energies and reaction rates. The porous nature of the starting powder compacts was accounted for by some scaling factors in thermal and electrical conductivities. The model did not account for evolving densification, which could lead to an overestimation of electrical resistance within the samples. For example, when Al (NaCl) porous foam was densified from 30% to 35% in relative density, its relative electrical conductivity increased from 17% to 23% [42] [43].

In 2006 to 2007, Olevsky *et al.* [33] [39] derived constitutive models of sparkplasma sintering for conductive material taking into consideration the direct contribution of electric current to grain-boundary diffusion, as well as the contributions of sintering stress (surface tension) and external load on densification. Their calculations indicate that the electro-migration related material flux can be a significant component of the electriccurrent-accelerated diffusion, and the calculated results from their model agree satisfactorily with the experimental data on Al powder's SPS in terms of shrinkage kinetics.

In 2007, Olevsky et al. [34] studied the impact of high heating rates on the consolidation enhancement during spark-plasma sintering. They considered the interplay of three mechanisms of material transport during SPS which include surface diffusion, grain-boundary diffusion, and power-law creep (which combines volume diffusion and dislocation climb). Their results showed that high heating rates reduce the duration of surface diffusion (a process helpless to densification). This favors the sinterability of the powder systems, and accelerated grain-boundary diffusion intensifies the densification. Their results also indicate that, the high heating rates not only accelerate the densification but also diminish the grain growth, and they claimed that the impacts of high heating rates are dependent on the particle size. Experiments of an aluminum alloy powder consolidated by SPS confirmed the predictions by the proposed model. However, they also empathized that their particular work only considered the heating rate impact on densification, while other thermal nature factors (different from conventional powder processing techniques) which were not included may also be responsible for the enhancement of consolidation during SPS.

In 2009, Olevsky et al. [35] investigated the influence of thermal diffusion as another thermal nature SPS consolidation factor. They believe that the Ludwig-Soret effect of thermal diffusion causes concentration gradients in two-component systems subjected to a temperature gradient. The thermal diffusion-based constitutive sintering mechanism was investigated through the analysis of spatial temperature gradients, which is the driving force of vacancy diffusion. This mechanism is a commonly omitted in addition to the free surface curvature-driven diffusion considered in conventional sintering theories. They considered the interplay of three material transport mechanisms during SPS in their paper, including surface tension- and external stress-driven grain boundary diffusion, surface tension and external stress-driven power-law creep, and temperature gradient-driven thermal diffusion. Their calculations and case study results of alumina powder sintered by SPS have shown that the effects of thermal diffusion can be significant for ceramic powder systems. However, their study considered only one of many possible mechanisms of the consolidation enhancement during SPS.

In 2013, Olevsky *et al.* [36] commented about some available ambiguity experimental data on the presumably faster SPS densification kinetics compared with conventional hot pressing of powders. They discussed the possibility of controlling SPS densification efficiency by interparticle contact area growth. They argued that the properly controlled interplay between surface diffusion and external pressure-imposed creep can further improve the densification efficiency of SPS process. The preliminary recommendations given by them are: a gradual increase in the applied external pressure towards the final stage of the process is beneficiary for ceramic powders; and the application of high pressure from the beginning of the process appears to be the optimal SPS strategy for metal powders.

All of the above modeling works conducted by Olevsky and his colleagues were incorporated in the framework of continuum theory of sintering [44]. The contributions from various mechanisms to densification were expressed in an equivalent stress form, which determines the strain rate of deformation during consolidation. This approach enables the constitutive modeling and simulation for predictions of internal stress, and dimension evolutions of the net shaped porous components. This is very important, because the industrial users of the powder consolidation techniques cannot optimize their process without the knowledge of those stress and dimension evolution kinetics.

So far, although very difficult, several theorists in this area have laid down the some significant foundations for the modeling of SPS process. Those works are inspiring

for further exploration in the future. However, for the next steps, substantial difficulties exist in the isolation of multi-consolidation mechanisms taking places simultaneously (e.g. mechanical, thermal, and electrical), as well as in the experimental determination of the relevant material parameters. This dissertation introduces one novel method to isolate the thermal and mechanical effects during dynamic consolidation, and the details are discussed in the following chapters.

Simulation of spark plasma sintering process is about the calculations and predictions of SPS tooling and compact system statuses (temperature, displacement, stress, density, and grain size etc.) based on the constitutive models and material properties under the known initial and boundary conditions. Typically, limited calculations are done based on available analytical solutions; the calculations need numerical tools such as finite element codes which are either developed in-house or within commercial software packages.

From 1989, when the first simulation of spark plasma sintering publication came out, to 2012, there are 45 papers (based on the SPS relevant key words searches in Web of Science® and Science Direct® databases) [5] [28] [45]- [87].

Statistics analysis shows a development trend. As shown in Figure 4, the accumulated number of publications on this topic is gradually growing. However, the total publication amount on SPS simulation is much less comparing to those published SPS experimentation work.



Figure 4. Number of Journal Papers on Simulation of Spark Plasma Sintering over the Years

The source countries of the SPS simulation papers have been plotted in Figure 5 (based on the first author affiliated institute and country for the 45 SPS simulation papers), which shows that China, Belgium, and Japan are the countries with top three contributions, while USA, Ukraine, and Italy contributed equally as rank four.



Figure 5. Distribution of the Source Countries for the Journal Papers on Spark Plasma Sintering Simulation

The earliest research on SPS simulation started from coupling electrical-thermal fields only for temperature prediction. This accounts for thirty publications out of forty five (67% of the total SPS simulation work) [5] [28] [51]- [78]. Four of these works were about steady state analysis [54] [62] [64] [71] [78], while the other twenty six included time dependent analysis. The investigated material systems in this group were broad, from ceramics (electrical insulator) such as alumina [87], metals (electrical conductor) such as copper [47], and composites such as tungsten carbide – cobalt [67] (intermediate electrical conductor).

A successful implementation example of the electrical-thermal models coupled analysis was shown by the work of Vanmeensel *et al.* [63] in 2007. They used the commercial finite element modeling (FEM) package ANSYS<sup>®</sup> to conduct the electricalthermal models coupled analysis for the prediction of temperature distribution within the tooling during spark plasma sintering. Their study investigated the zirconia – titanium nitride system, for which the ratio of electrical non-conductive phase (ZrO<sub>2</sub>) and conductive phase (TiN) varies in the range of 35 to 90 vol.%. Experiments were conducted to extrapolate the electrical properties dependence on composition, and the obtained electrical conductivity model was used as material property inputs in the FEM simulation. Figure 6 shows the calculated temperature gradient results for thermally insulated and non-insulated tooling boundary cases. Their experimental and simulation results demonstrated the effectiveness of tooling boundary thermal insulation as an option for minimizing the temperature gradient during spark plasma sintering.



Figure 6. Influence of Carbon Felt Insulation, Surrounding The Graphite Die, On The Calculated Thermal Gradients In A Sintering ZrO<sub>2</sub>--Tin (60/40) Composite Powder Compact Throughout The Whole Sintering Cycle (b). The Temperature Distributions During The Final Dwell at 1500°C (Central Pyrometer Temperature) In a Fully Dense ZrO<sub>2</sub>--Tin (60/40) Composite Sample are Shown in Case No Thermal Insulation Was Used (a) and In Case Porous Carbon Felt Was Used To Minimize The Radiation Heat Losses (c); adopted from reference [63]

One work published in 2002 by Keum *et al.* was dedicated to electrical-thermalgrain growth coupled analysis for spark plasma sintering [74]. The temperature prediction was based on the classic Ohm's law and Fourier's law governed electrical-thermal models coupled analysis, and the calculation was conducted by FEM. The temperature distribution in the sintered body was then used as input information in a Monte Carlo Method (MCM) based model for grain growth prediction. The grain growth of alumina samples in the center and at the exterior interface next to the die was simulated for sintering temperatures of 1450°C and 1650°C. The comparison between the simulation results and the SEM observed micrographs shows good agreement (Figure 7).



Figure 7. Comparison of Grain Growth of Al<sub>2</sub>O<sub>3</sub> between Simulation and SEM Micrograph at the Sintering Temperature of 1650°C, adopted from reference [74]

They claimed that the classical models derived for conventional mechanicalthermal driven powder consolidation is applicable for the prediction of spark plasma sintering densification [74].

Simulation of spark plasma sintering with the focus only on densification was done by Chaim and Margulis in 2005 [75]. They constructed densification maps by using processing conditions of the spark plasma sintering to evaluate the validity of the hot isostatic pressing model for the SPS process, as shown in Figure 8. Their resultant density values versus SPS pressure, temperature, and the initial grain size exhibit high similarities to those from the experiments, and therefore support the applicability of the hot isostatic pressing model for the spark plasma sintering process. In addition, their calculated densification maps revealed that the attainable density, at the nanoscale particle size, is very sensitive to the chosen SPS temperature. The agreements found between their experimental spark plasma sintering data and their calculated densification maps reveal that the densification by spark plasma sintering may be described via the known plastic deformation and diffusion processes. However, their study had not taken the grain growth kinetics into account. This is especially important at the final stage of densification. Also, temperature non-uniformity was not considered in their study, which could be a very

important aspect for complex geometry net shaping by spark plasma sintering. This issue can be handled by coupling the electrical-thermal-densification during analysis.



Figure 8. Densification Maps Showing the Dominating SPS Densification Mechanisms at 800°C for:
(a) 20 nm, (b) 40 nm, and (c) 50 nm Particle Size Nanocrystalline MgO in the Density–Pressure
Coordinates; the Isochronal Contours are Shown by the Dotted Lines; adopted from reference [75].

Analyses with the coupling of electrical-thermal-densification models were reported by Chaim [28] in 2007 and Maizza *et al.* [76] in 2009 respectively. Chaim's study focused on MgO ceramic material properties' microscopic responses in the electrical and mechanical stress fields, but he simplified the compact and tooling geometry effects in a steady state analysis [28]. Maizza et al. [76] attacked the problem from a macroscopic point of view with the help from commercial finite element modeling software package COMSOL®. They investigated the consolidation of pure ultrafine WC powder in SPS. A moving mesh finite element scheme was employed to handle the large displacement of graphite punch during densification. Their model considered contact resistance between interfaces, and they linked the material electrical and thermal properties to relative density of the compacts. However, their simulation of densification is not truly based on a densification model which is capable to make predictions. Instead, they used experimentally recorded punch displacement data, and translated it into density information. The translated density information was used as inputs for electrical and thermal coupled calculations. Their example calculation results for temperature contour in spark plasma sintering are shown in Figure 9.



Figure 9. Isothermal Maps in °C for 2100A after (a) 40 s and (b) 153 s; adopted from reference [76].

Analyses with coupling of electrical-thermal-mechanical models added the capability to predict the stresses in the spark plasma sintering tooling structure [77] [79]-[80][81][82] [85]. For this category of SPS simulation work, the mechanical field calculation is limited to the elastic strain-stress relationship within the tooling governed by Hook's law, and the porous compact is not included.

Wang *et al.* used in house developed finite element code to conduct time dependent calculations for copper and alumina systems [81]. They used material property data directly from literature without their own validation experiments.

Antou *et al.* [78] developed model for zirconium carbide system in COMSOL<sup>®</sup> finite element modeling software package, and their calculations were time dependent. They also used material property data directly from literature without their own validation experiments.

Grasso *et al.* [79] developed an experimental-numerical combined methodology to aid the optimization of pure ultrafine tungsten carbide powder densification by spark plasma sintering operating in electric current control mode. The emphasis of their work was on the pressure effects on densification. The utilized numerical tool was also COMSOL<sup>®</sup>, but the analysis was on steady state.

Munoz and Anselmi-Tamburini [80] published their work on the analysis of SPS with the coupling of electrical-thermal-mechanical models developed in ANSYS<sup>®</sup>, and their work was the first to demonstrate the multi-physics capability of ANSYS® for spark plasma sintering simulation application. Their analysis was time dependent, and they conducted their own experiments to validate the tooling and powder sample material properties. Their stress distribution results for alumina and copper samples processed in spark plasma sintering are shown in Figure 10. They found that a stress spike was experienced by the alumina sample at the beginning of the cooling stage, and that was

caused by the differences in contractions between the sample and the die. They had also proved that, using a controlled cooling stage, those stress spikes can be easily eliminated.



Figure 10. Hydrostatic Stress Distribution inside (a) Alumina and (b) Copper Samples; Hydrostatic Stress Distribution along the Lines AB and CD of the Samples' Cross Section Surfaces for the (c) Alumina and (d) Copper Samples; All at Time t = 350 s; adopted from reference [80].

Wang *et al.* [81] also implemented a thermal–electrical–mechanical coupled dynamic finite element model to analyze of the temperature and stress distribution during spark plasma sintering process. The real time densification behavior was integrated by the moving mesh technique in COMSOL<sup>®</sup>, and a broad range of die sizes, heating rates and uniaxial stresses were considered. They had conducted further experiments to validate the simulation results. Their detailed microstructure investigations generally demonstrated

that the temperature and stress profiles obtained in their model are correct. But further development of densification model with the consideration of grain growth is still needed for more precise predictions of sintering progress and microstructure evolution in SPS.

A very practical and interesting work on the analysis with the coupling of thermal–electrical–mechanical models for spark plasma sintering simulation was published by Allen and Walter [82] from U.S. Army Engineer Research and Development Center in 2012. This is also a time dependent analysis developed in COMSOL<sup>®</sup>. In addition, they added a proportional-integral-derivative (PID) module to their model, which enabled the realistic and real time optimization. This is a highly desired feature that should be included in the future efforts.

Analysis with the coupling of electrical-thermal-mechanical-densification models is a further advancement contributed by Mondalek, Song, Matsugi, and Wolff *et al.* in the recent years [83]- [86]. The densification model can be considered as a complementary part of mechanical module, but this is based on a different governing law dedicated to compressible porous structure. The porous material densification theory is more complicated than the elasticity theory governing the incompressible bulk solid structure behavior. Incorporation of densification model into the coupled analysis of SPS is a significant progress for SPS simulation. However, two more important parts that are still left behind are sintering stress and microstructure evolution. Moreover, these works used models based on the simplification assumption of uniaxial hot pressing in rigid die, which makes stress prediction unrealistic for both the specimen and the die [83]- [86]. Other than those modeling concerns described above. Song *et al.* [84] used densification model based on hot working of metals under creep, and Wolff et al. used an empirical densification constitutive law for porous material without considering mass conservation for the specimen [86]. An example of calculated inhomogeneous relative density distribution for lead powder consolidated by spark plasma sintering is shown in Figure 11. The inhomogeneity in relative density distribution was caused by the inhomogeneous temperature and stress distribution within the spark plasma sintering tooling and the powder compact.



Figure 11. Properties Distributions within the Sample of (a) Relative Density and (b) Temperature at the End of the SPS Cycle for Time t = 60 s; the Temperature is Clearly Higher in the Center of the Specimen Than in the Edge of the Specimen, Inducing a More Intense Densification. A Clear Link between Temperature and Relative Porosity is Observed; adopted from reference [86].

Analysis with the coupling of electrical – thermal – mechanical – densification - microstructure models is the most comprehensive simulation for spark plasma sintering process so far. In a recent publication by Olevsky *et. al* [88], microstructure evolution was described by a grain growth model, and this model was linked with densification and thermal modules in COMSOL<sup>®</sup>. However, the stress analysis of this work was limited within the domain of porous specimen only due to the lack linkage between the elastic tooling and viscous porous specimen deformations. The temperature, relative density and

grain size evolutions with time for two different sample sizes under three different heating rates were calculated in their work, and are shown in Figure 12.



Figure 12. Modeling Results for 56 mm (left) Versus 15 mm (Right) Specimens: (a) and (b) Temperature Evolution in the Center of the Specimen; (c) and (d) Relative Density; (e) and (f) Grain Size. The Calculation Results are Given for Different heating Rates of 100°C/min, 225°C/min (200°C/min for the 15 mm Specimen), and 300°C/min; adopted from reference [88].

As can be seen from the above, the modeling and simulation of spark plasma sintering has made significant progresses in the past decades, but there is still a lot of work to be done to make accurate and applicable predictions of specimen density and microstructures evolutions.

## **1.3 Processing and Densification of Mono-Carbides**

In addition to being materials of great interest to the scientific community, carbides are useful materials with numerous industrial applications and a promising future for further developments. Although most of their applications are relatively recent, the refractory carbides and nitrides have been known for over one hundred years. Titanium and tungsten carbides were extracted from steel and properly identified around the middle of the nineteenth century. In 1890, E. G. Acheson produced the first silicon carbide, trademarked Carborundum, and by 1900 the French chemist Moissan [89] had synthesized most other refractory carbides in his electric arc-furnace.

Typically, carbide materials have high melting temperature greater than 1800°C; in addition, they have a high degree of chemical stability and high mechanical hardness.

Most elements form carbides, and they can be divided into several types with different physico-chemical structures and characteristics. However, only the interstitial and covalent materials meet the refractory qualification. This includes the carbides of the nine transition elements of Groups IV, V, VI, and the 4th, 5th, and 6th Periods, as well as the carbides of boron and silicon. The carbides and nitrides of the lanthanides (the rare-earth elements) and actinides are well-defined. They belong to unique families of materials with promising applications, such as fabrication of fuel pellets for nuclear industry.

The industrial importance of the refractory carbides is growing rapidly, not only in the traditional and well-established applications based on the strength and refractory nature of these materials, such as cutting tools and abrasives, but also in new and promising fields such as electronics and optoelectronics. Some typical applications are as follows:

- Boron carbide: abrasive blast nozzles;
- Silicon carbide: fibers, whiskers, burner tubes for gas furnaces, high-temperature semiconductor devices, and blue light - emitting diode (LED);
- Tungsten carbide: cutting tools;
- Tantalum carbide: rocket nozzle, and scramjet components [90] [91].

Such a wide range of applications reflects the variety of these materials and the diversity of the industry, from small research laboratories (developing new ideas) to large plants (manufacturing cutting tools, textile machinery, electronics and semiconductor components, as well as many other products). Together, these organizations form an essential part of the ceramic industry throughout the world [89].

This research will focus on the consolidation of bulk mono carbide materials by using spark plasma sintering. With the advancement of the power control, temperature monitoring, hydraulic pressurization, as well as vacuum technologies in the past decades, spark plasma sintering has emerged as a promising powder hot consolidation option capable of producing highly dense bulk materials with very high efficiency. A number of researchers have reported consolidations of mono carbide powders by using spark plasma sintering or equivalent technologies [76] [78] [79] [92]- [119]. Many of the representative works have been summarized and discussed comprehensively in a review article published by Orru *et al.* [8] in 2009 on electric current activated and assisted sintering.

Silicon carbide has melting point of 2730°C (3003 K). According to the 0.7 homologous temperature sintering rule, the required conventional solid state sintering temperature should be around 1829°C (2102 K). The reported representative works on spark plasma sintering or equivalent technologies of this material system are listed in the following paragraphs [92]- [101]:

SiC powders ( $\alpha$  and  $\beta$  type) doped with a low content of Al<sub>2</sub>O<sub>3</sub> (2.64 wt.%) and Y<sub>2</sub>O<sub>3</sub> (1.76 wt.%) oxide or Al<sub>4</sub>C<sub>3</sub> (2.04 wt.%), B<sub>4</sub>C (0.39 wt.%) and C (1.77 wt.%) nonoxide additives were rapidly consolidated by SPS [93]. Powders mixtures were processed under Ar atmosphere in a SPS-1050 machine at 1700°C for 10 min, with 100°C/min heating rate and 47 MPa applied pressure. The relative density of the obtained products was in the range of 95.2–99.7%. Different products microstructures were obtained when using the oxide or non-oxide additives. Moreover, compared with the Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub>-doped SiC ceramics, the Al<sub>4</sub>C<sub>3</sub>–B<sub>4</sub>C–C-doped SiC ceramics obtained higher densities, lower fracture toughness, and higher hardness.

The consolidation by SPS of the Al<sub>4</sub>C<sub>3</sub>(2.04 wt.%)-B<sub>4</sub>C(0.4 wt.%)-doped nano  $\beta$ -SiC powders (30 nm) was investigated [94]. In all SPS experiments (SPS-1050), the sintering temperature and applied pressure were maintained at 1600°C and 47 MPa, respectively, while heating rates were varied in the range of 100–400°C/min, and the holding time was set to 2 or 5 min. A near to full densification (relative density higher than 99.5%) was achieved. A significant grain growth was observed to occur during the sintering process and grain size increased with the increase of heating rate (cf. Figure 13).



Figure 13. SEM Micrographs of the Plasma Etched Surfaces of the SPSed SiC Ceramics When Varying the Heating Rate (1600°C Sintering Temperature, 5 min Holding Time): (a) 100°C/min; (b) 200°C/min and (c) 400°C/min. adapted from Zhou *et al.* [94].

An intense research activity on SPS densification of nanostructured  $\beta$ -SiC powders (5–20 nm grain size) prepared by reactive ball milling was conducted by a joint collaboration between Japan and US group [95]- [100]. Consolidations were carried out under vacuum using a SPS-1050 apparatus under 40 MPa pressure, sintering temperatures in the range of 1000–1900°C, with heating rate of 180°C/min, and holding time ranging from 0 to 30 min. High-density (>98%) nanostructured SiC products (30–50 nm grain size) were obtained by sintering at 1700°C for 10 min holding without the use of additives (cf. Figure 14). It was evidenced that the densification process was enhanced by a disorder–order transformation.



Figure 14. TEM Micrograph of the SiC Dense Product Fabricated Using Ball Milled Powders by SPS at 1700°C and 10 min Holding Time, adapted from Yamamoto *et al.* [95].

The effects of grain size and relative density on the mechanical properties of the obtained products were also studied and the corresponding values were compared with those ones of the reference samples fabricated by using commercial  $\beta$ -SiC powder with B–C sintering additive [98]. It was found that Vickers hardness, bending strength, and Young's modulus of SPS products (which are ball milled powders without additives) increased with the increase of relative density. However, those properties were lower than those corresponding ones of reference samples with sintering additives but of the similar relative densities. This behavior was reported to be likely caused by the difference of grain bonding strength due to the presence of sintering additives.

Further studies of the sintering temperature effects on the characteristics (grain size, density, thermal and electric properties) of the obtained nanostructured SiC dense materials have been conducted [99]. By maintaining the constant applied pressure (100 MPa), heating rate (180 K/min), and holding time (10 min), it was found that the grain size increased from 26 nm to 61 nm when increasing the temperature in the range of 2073–2173 K while relative density remained about the same (99.4%). Correspondingly, both thermal and electrical conductivities of SiC were observed to increase as a consequence of grain growth.

More recently, the influences of sintering temperature, holding time and applied pressure on the consolidation and grain growth kinetics during SPS of a pure commercially available fine SiC powder (mean grain size 0.5 mm) was investigated [101]. Two SPS machines, i.e. the SPS-2050 and SPS-2080 models, were used. The temperature was raised automatically to 600°C, and then first increased to 1600°C at 100°C/min and, subsequently, from 1600°C to the final temperature (1750°C to 1850°C) with a rate of 50°C/min. Initial pressure was set to 50 MPa. Afterwards, two pressure conditions were used: 75 MPa were applied when the final temperature was achieved, while in the other case the same pressure level was maintained since 1000°C were

reached. Moreover, holding time was examined in the range of 1 min to 10 min. Sample density was found to increase with the increase of temperature and holding time. This SiC powder was consolidated up to 92% at 1850°C for 5 min under 75 MPa. It was also observed that the diffusion and migration mechanisms that promote grain growth were strongly dependent on temperature, which is strictly related to pulsed current intensity. In addition, to make grain morphology and size remaining unchanged, it was evidenced that the temperature at the application of ultimate pressure must be close to the maximum temperature of that specific process.

Tantalum carbide has melting point of 3880°C (4153 K). According to the 0.7 homologous temperature sintering rule, the required conventional solid state sintering temperature should be around 2634°C (2907 K). The reported representative works on spark plasma sintering or equivalent technologies of this material system [102]- [105] are selectively listed in the following paragraphs.

Khaleghi *et al.* [102] conducted experiments in the Dr. Sinter Lab 515S SPS machine using a set temperatures ranging from 1900°C to 2400°C, holding times from 5 to 20 min, pressures from 30 to 75 MPa, with -325 mesh TaC starting powder, and carbon nanotube additive from 0 to 0.77 wt.%. They obtained relative densities ranging from 68

to 97%, rupture strength 315 to 550 MPa, harndess 11 GPa, and average sintered grain size from 0.3 to 9.0  $\mu$ m. The carbon nanotube added to the matrix was found to be effective in improving the rupture strength by increasing the relative density for 4% and lowering the average grain size by about 10%.

Titanium carbide has melting point of 3160°C (3433 K). According to the 0.7 homologous temperature sintering rule, the required conventional solid state sintering temperature should be around 2130°C (2403 K). The reported representative works on spark plasma sintering or equivalent technologies of this material system are listed in the following paragraphs [106] [107].

A plasma activated sintering method was employed for the densification of  $Ti_{44}C_{56}$  nanostructured powders (3 nm grain size and average particle diameter less than 0.4 mm) synthesized by ball milling of elemental Ti and graphite powders [106]. Sintering was performed in vacuum at 1963 K under applied pressure in the range of 20 MPa to 38 MPa for 300 s. A fully dense product (99.98% of the theoretical density) with TiC average grain size of approximately 70 nm was obtained. Moreover, the obtained compacts were characterized by 32 GPa hardness, 273 GPa bulk modulus, 181 GPa shear modulus and Poisson's ratio of 0.261.

TiC samples to be used as substrate for hot filament diamond deposition were recently fabricated by pulsed discharge sintering using TiC and TiH<sub>2</sub> (less than 18 wt.%) as raw materials [107]. Porous products were needed to create more nucleation sites thus improving the adhesion of diamond films onto the substrate. Pulsed discharge sintering was performed in vacuum at 50–60°C/min heating rate, 1000–1200°C holding temperature, 5 min holding time and 50 MPa. It was found that the porous substrate obtained at 1050°C was accompanied by a gain in nucleation density as compared to the nonporous samples. The optimal temperature of the resulting substrate in terms of highest growth rate was found to be in the range of 900–1000°C.

Tungsten carbide has melting point of 2870°C (3143 K). According to the 0.7 homologous temperature sintering rule, the required conventional solid state sintering temperature should be around 1927°C (2200 K). The reported representative works on spark plasma sintering or equivalent technologies of this material system [76] [79] [106] [108]- [113] are selectively listed in the following paragraphs.

The fabrication of dense binderless tungsten carbide was widely investigated using several electric current activated sintering techniques. For example, WC nanopowders (grain size of about 7 nm), prepared by a solid-state reaction process of
WO<sub>3</sub>, Mg and C followed by MgO leaching, were consolidated in vacuum using a plasma activated sintering method [106]. Densification was carried out at 1963 K for 300 s under applied pressures in the range 19.6–38.2 MPa. A near to fully dense WC material was obtained. The consolidation process led to a slight grain growth with an average size of approximately 40 nm.

The plasma pressure compaction was also utilized for the obtainment of bulk WC starting from three different powder particle sizes (0.2, 0.8 and 12 mm) [108]. Consolidation experiments were performed in vacuum at 1500°C for 1 min with an applied pressure of 45 MPa and under conditions of pulse and no pulse current. It was found that the application of a DC pulse current resulted in samples with higher density and micro-hardness as compared to those obtained without pulsing the powders before consolidation (cf. Figure 15). The maximum relative density value achieved was 96%.



Figure 15. Bar graphs Depicting the Comparison of Pulse with No-Pulse Conditions at Different Powder Particle Size on (a) Micro-hardness and (b) Density of Bulk Tungsten Carbide Samples Obtained by Plasma Pressure Compaction, adapted from Srivatsan *et al.* [108].

Dense bulk WC was obtained by the SPS process using different WC powders sizes, i.e. 0.57, 1.33 and 4.06 mm [109]. Powders were sintered in vacuum at temperature range of 1550–1800°C, 100°C/min heating rate, without holding time and under 50 MPa mechanical pressure. The full density was reached when the sintering temperature was equal to or higher than 1700°C. The density of the sintered compact was observed to

decrease as particle sized decreasing. This fact was due to the decarburization occurring during the sintering process which is enhanced by the higher amount of surface oxide in the finer WC particles. In addition, an abnormal grain growth was observed when the sintering time was over 1 min at sintering temperatures higher than 1700°C. The latter phenomenon corresponded to an increase in the fracture toughness.

Tungsten carbides materials were also produced by the field activated pressure assisted combustion synthesis process using tungsten and carbon powders with different W:C mole ratio, i.e., 1:1, 1:1.1, 1:1.2, 1:1.3, and 1:1.4 [110]. Sintering was performed in vacuum under 60 MPa mechanical pressure, 3000 A electric current, 3 min processing time. The corresponding maximum temperature and heating rate were 1250°C and 1200°C/min, respectively. When considering the mixtures beside that with molar ratio 1:1, a combustion synthesis reaction was observed to occur at about 850°C. Conversely, when the stoichiometric W plus C mixture was processed, the starting powders reacted at higher temperature (about 1200°C). In all cases, XRD analysis revealed the presence of WC and W<sub>2</sub>C in the final samples. Their relative densities were in the range of 81.1 to 89.9%, and Vickers micro-hardness at 1 kg force was in the range of 423 to 731 kg mm<sup>-2</sup>.

Ultra-fine WC powders (200 nm) were sintered without the addition of any binder phase in a SPS-2040 apparatus under vacuum using a maximum uniaxial pressure of 60 MPa, 3 K/s average heating rate, 1573–1873 K sintering temperature, and 0–8 min holding time at the sintering temperature [111]. The density of the final samples increased when increasing either the temperature or the holding time (cf. Figure 16).



Figure 16. Relative Density of WC SPSed Samples Plotted vs. the Sintering Temperature at Different Holding Time, adapted from Huang *et al.* [111].

In particular, samples with density over 98% were obtained at 1673 K, and almost fully dense samples (99.6%) were obtained when sintering at 1773 K for 4 min. Only a slight grain growth was observed during the SPS process. Regarding mechanical properties, Vickers hardness were over 2600 HV, and the fracture toughness is in the range of 9–15 MPa•m<sup>1/2</sup>, respectively.

The consolidation of binderless WC samples by using the plasma pressure compaction method was investigated using three different WC powder size particles (0.2, 0.8, and 1.2 mm) and in the sintering temperature range of 1600–1700°C [112]. During the process a uniaxial pressure of 10 MPa was first applied for 3 min (first stage) and, subsequently, it was increased to 35 MPa for 1 min (second stage). A pulsed electric current of 1000 A, 60 Hz was used with 50 cycles. The obtained products were characterized in terms of grain size, and mechanical properties, i.e. hardness, fracture toughness, and wear resistance. It was seen that samples obtained from finer powders ended up with a larger final grain size thus indicating that the experimental conditions adopted are accompanied by a significant grain growth. The highest Vickers hardness value (HV100 = 19.2 GPa) was obtained by using 1.2 mm mean particle diameter powder sintered at 1600°C. For fracture toughness, K<sub>IC</sub>, values between  $6.6 \pm 0.7$  and  $8.7 \pm 0.8$ MPa•m<sup>1/2</sup> were obtained for the investigated specimens at the 30 kg maximum testing load. Regarding wear resistance characteristics, very low wear constant values (approximately  $10^{-8}$  mm<sup>3</sup>/N•m) were obtained in all cases, indicating an excellent tribological performance.

WC and WC–xVC materials (x = 1–16wt.%) were consolidated by using a Type HP D 25/1 (FCT Systeme) apparatus, and WC plus VC commercial powders without metallic binder additives [113]. Densification experiment was conducted under vacuum in the temperature range of 1600–1900°C for 1.5–4 min holding time, and 200–300°C/min heating rate. The applied pressure varied during the process, from 16 to 30 MPa at 1050°C, and from 30 to 60 MPa during the heating stage from 1050°C to the sintering temperature. Fully dense WC and WC–1wt.%VC products were obtained at 1900°C for 1.5 min (cf. Figure 17).



Figure 17. SEM Micrographs of the Polished and Fractured WC (a and c) and WC1VC (b and d) Grades, Pulse Electric Current Sintering for 1.5 min at 1900°C, and the Polished WC4VC (e) and WC12VC (f) Grades, Pulse Electric Current Sintering for 1.5 min at 1800°C, adapted from Huang *et al.* [113].

The increasing of VC content was found to favor the compact densification [113]. Specifically, when x = 16 wt.%, full consolidation was obtained at  $1600^{\circ}$ C. This fact was related to the formation of a (V,W)C solid solution during the process. It was also observed that, as the VC content was increased, the grains size grew rapidly.

Regarding the mechanical properties of the sintered samples, a maximum Vickers hardness (HV10) of  $27.39 \pm 0.13$  GPa and fracture toughness of  $4.38 \pm 0.18$  MPa•m<sup>1/2</sup> were obtained for pure WC and WC–1wt.% VC materials, respectively [113]. By increasing the VC content, hardness was found to decrease linearly down to  $21.41 \pm 0.20$  GPa when x = 16 wt.%, and the fracture toughness also decreases slightly. This feature was attributed to the presence of the VC phase as well as the grain growth.

Zirconium carbide has melting point of 3532°C (3805 K). According to the 0.7 homologous temperature sintering rule, the required conventional solid state sintering temperature should be around 2390°C (2664 K). Several representative works on spark plasma sintering of this material system [78] [114]- [119] are found, and one of them is discussed in the following paragraph [116].

Gendre *et al.* [116] reported their work in 2010. Zirconium oxycarbide powders with controlled composition  $ZrC_{0.94}O_{0.05}$  were synthesized by carboreduction of zirconia.

The obtained powders were further subjected to spark plasma sintering (SPS) under several applied loads (25, 50, 100 MPa). They studied the densification mechanism of zirconium oxycarbide powders during the SPS by using an analytical model derived from creep deformation studies of ceramics. These mechanisms were elucidated by evaluating the stress exponent and the apparent activation energy from the densification rate law. It was concluded that at low macroscopic applied stress (25 MPa), an intergranular glide mechanism governs the densification process, while a dislocation motion mechanism operates at higher applied load (100 MPa). Their transmission electron microscopy observations confirmed those calculation results. The samples treated at low applied stress appear almost free of dislocations, whereas samples sintered at high applied stress present a high dislocation density, forming sub-grain boundaries. High values of apparent activation energy (e.g. 687-774 kJ/mol) are reached irrespective of the applied load, indicating that both mechanisms mentioned above are assisted by the zirconium lattice diffusion which thus appears to be the rate-limiting step for densification.

#### **1.4 Literature Survey Conclusions**

The historical evolution of SPS has been reviewed and the various names of the SPS equivalent technologies are summarized. Through identifying the milestone discoveries, the SPS technology development is briefly introduced and discussed. The statistics survey of SPS related publications shows that the number of new publications coming out every year has been more than ten times of what was in 10 years ago. The citation record of those publications is also growing exponentially. China and Japan are found to be the countries published the most papers in the SPS area. The development trend of SPS shows a rapid growth with huge potential.

Benefits and applications of SPS technology have been reviewed. The most widely reported benefits, superior to conventional sintering or hot consolidation techniques, include earlier densification onset, enhanced densification rate, higher densities, lower sintering temperatures, and enhanced reaction rate. The most attractive applications discovered include the fabrication of additive free composites and transparent high strength ceramics, the densification of metastable phases, controlled porosity functional structure, high strength bonding, as well as superplastic consolidation. All of those reported benefits and applications indicate that SPS is a very promising technology that worth further investigations.

The conducted literature survey on the modeling and simulation of SPS indicates that the prediction and optimization possibilities for SPS process depend on the availability of reliable process models, which are currently of high demand. Only few attempts have been undertaken to develop SPS-specific comprehensive constitutive models for powder material consolidation; most of the modeling and simulation works on SPS were dedicated to the numerical (predominantly, finite element) analyses of temperature and electric current distributions evolutions in the SPS tooling and fully dense specimens during SPS processing. The relative density evolution of the porous SPS compact with time was ignored and the nonrealistic deformational behavior of the porous SPS compact was assumed (e.g. elastic only). Although some publications have taken into account the displacement of electrode-punches, they neglected the non-uniformity of the relative density distribution within the SPS porous compact due to non-uniform temperature spatial distribution and friction at the interfaces between SPS porous compact and SPS tooling (e.g. punches and die). Therefore a comprehensive fully coupled modeling framework taking into account all of the mechanical (elastic, densification, grain growth), electrical and thermal interactions is waiting to be developed.

# **Chapter 2** Research Incentives and Objectives

## **2.1 Research Incentives**

In many high performance material processing areas, SPS is a useful technology. However, the prediction and optimization possibilities for spark plasma sintering depend on the availability of reliable process models. The development of such a comprehensive modeling framework will help enable and accelerate a broader scale industrial utilization of SPS.

This research focused on determining if the constitutive relationships derived for general hot consolidations (e. g. hot pressing) can still be applied to the modeling of spark plasma sintering densification. The coupling of the porous material densification model with the electrical-thermal-mechanical models has been done in FEM software package COMSOL Multiphysics® 4.3a with customized and specifically implemented initial and boundary conditions for SPS.

Similar to work on hot pressing and hot isostatic pressing, the modeling work within this study assumes creep-based mass transfer is the dominant mechanism for densification. The electrical field is only considered for the contribution of Joule heating through tooling and porous compact. Only the temperature and stress gradients caused by different heating mechanism in SPS were considered as the major differences comparing to hot pressing. Those temperature and stress gradients have been analyzed and counted in densification of porous SPS compact by coupling the electrical-thermal-mechanical models in FEM simulation. The material properties evolution model on porosity, temperature, and pressure are incorporated in the developed modeling frame work for realistic simulation of SPS process.

## 2.2 Research Objectives

The research objectives of this research include the following five aspects:

- (1) Identification of the power law creep-based mass transfer mechanisms for spark plasma sintering process, specifically on SPS of copper and SPS vanadium carbide.
- (2) Formulation of the fundamental densification and grain growth constitutive models for spark plasma sintering process.

- (3) Establishment of a fully coupled finite element modeling simulation framework for the analysis of spark plasma sintering process.
- (4) Fabrication of a functionally structured vanadium carbide pellet to validate the applicability of spark plasma sintering technology in processing high melting temperature mono carbide fuel for nuclear industry.
- (5) Providing an optimization guide for the vanadium carbide pellet fabrication process by spark plasma sintering.

# 2.3 Research Tasks

- a. Formulate and utilize the proper constitutive equations for describing the SPS process, and couple the mechanical, electrical, and thermal interactions.
- b. Identify the key constitutive parameters and derive the analytical expressions of these parameters, including the strain rate sensitivity, power law creep activation energy, and material power law creep frequency factor at reference temperature.
- c. Derive the analytical solution for the uniaxial densification of porous materials in rigid die, and map the hot consolidation conditions for uniaxial pressing in rigid die at high temperature.

- d. Design a novel multi-steps pressure dilatometry fundamental experiment to isolate the temperature and mechanical stress effects for the determination of individual material constitutive parameters.
- e. Find out if a set of constitutive parameters could fit the SPS experimental data by using hot pressing model as a basis.
- f. Characterize the powder materials used for the fundamental experiments.
- g. Identify and establish the realistic and practical initial and boundary conditions for FEM simulation of SPS process.
- h. Enable the fully coupled analysis for the spatial distribution of porous SPS compact density, grain size, internal stress, temperature and electric current density by FEM simulations.
- i. Calibrate the equipment (temperature and mechanical pressure measurement), and validate the modeling-simulation predictions of the relative density and grain size within porous SPS specimen by comparing to experimental results (density and microstructure).
- j. Analyze the experimental and simulation results to suggest the SPS densification mechanisms.

- k. Analyze the SPS specimen material property (particularly the electrical conductivity)
   effects on SPS heating and densification behaviors
- 1. Apply the results obtained from fundamental analysis of SPS to the optimize the fabrication functionally structured mono carbide by SPS.
- m. Characterize and test the fabricated functionally structured carbide in terms of density, microstructure, porosity, transverse rupture strength, hardness, thermal conductivity, heat capacity, and permeability.

# 2.4 Roadmap of Research

The following flow chart demonstrates the research road map of this present study.



Figure 18. Flow Chart of the Proposed Research Plan

The following diagram shows the logical organization of the developed FEM simulation framework with all the coupled modules and real time updated material property database.



Figure 19. Schematic Showing the Coupling of Multiple Modules for Modeling and Simulation of

**SPS Process** 

# Chapter 3 Analysis of Constitutive Relationships in Spark Plasma Sintering

The constitutive model of Spark Plasma Sintering is based on the following assumptions:

- a. The electrical field only affects the heating pattern and therefore temperature distribution throughout the SPS tooling and porous compact by generating in-situ Joule heat.
- b. The consolidation of powder porous compact in SPS is a stress (mechanical and sintering stresses) assisted densification process governed by power law creep and continuum theory of sintering under high temperature.
- c. The deformation of SPS tooling is governed by elasticity theory

#### **3.1 Modeling of General Hot Consolidation**

Spark plasma sintering belongs to the hot consolidation technology category for powder material processing. Hot pressing is a hot consolidation technology that is the most similar to SPS. The following schematics compare the conventional hot pressing and SPS setups:



Figure 20. Hot Pressing and SPS Comparison, adapted from Grasso *et al.* [9]

Hot pressing utilizes radiation heat transfer in vacuum, and radiation plus convection heat transfer in inert atmosphere. It has relatively larger thermal mass (including heating element, chamber space, graphite tooling and specimen) than SPS (graphite tooling and specimen only). Therefore, its heating is slow and with low energy efficiency.

Typically, SPS utilizes electric current to generate Joule heat directly within the graphite tooling. When electrical conductive materials are processed by SPS, the heat is generated directly within the specimen the graphite tooling at the same time as electric current passing through. Conduction is the dominant heat transfer mechanism in both vacuum and inert atmosphere. Heating mechanism for SPS can achieve more

homogeneous heating inside the specimen. SPS setup usually has relatively small thermal mass (including the graphite tooling and specimen only), therefore, its heating is rapid and with high energy efficiency.

The following schematic shows the electric current path inside the specimen when SPS is processing electrical conductive powder specimen. This schematic indicates how the heat is generated at inter-particle local neck spots. The inter-particle necks are the spots where both heat and stress are highly concentrated at. Therefore, the existence of such special type of spots may be the reason for earlier onset of densification at lower measured tooling surface temperatures.



Figure 21. Schematic of SPS Heating within the Powder Compact Specimen, adapted from Hennicke and Kessel [120]

Although it is found that SPS has different heating mechanism compared to hot pressing, however, these two technologies also share significant amount of similarity in terms of mechanical aspects. They both use graphite tooling and utilize uniaxial pressure to densify powder specimen in the graphite die during heating (Figure 20). Therefore, it is reasonable to consider SPS as a device similar to hot press but with much more flexible heating rate.

There are also researchers who believe that electric current could enhance the diffusion process during consolidation, however, there are no direct evidence obtained yet due to the difficulties in isolating electrical field effects from thermal effects. Therefore, in the present study, the driving forces for densification are limited to the externally applied mechanical stress, and sintering stress. The electrical and thermal effects are accounted for by incorporating an apparent activation energy into an exponential function responsible for describing the temperature dependent material resistance to stress driven deformation. The electric current enhancement for diffusion is reflected by a decrease of the apparent activation energy (corresponding to material's ability to deform at lower temperature). The densification mechanisms are hypothesized as power law creep based.

The sub categories of creep mechanisms are identified based on the results and observations of this present study.

Based on the continuum theory of sintering derived by Olevsky [44], the hot consolidation of a powder material can be described by the following equation:

$$\sigma_{ij} - P_L \delta_{ij} = \frac{\sigma(W)}{W} \varphi \dot{\varepsilon}'_{ij} + \frac{\sigma(W)}{W} \psi \dot{\varepsilon} \delta_{ij}$$
 Equation 1

where  $\sigma_{ij}$  is the externally applied true stress tensor,  $P_L$  is the sintering stress derived from Laplace effective pressure of surface tension,  $\delta_{ij}$  is the Kronecker delta,  $\sigma(W)$  is the equivalent stress, W is the equivalent strain rate,  $\varphi$  is the normalized shear modulus,  $\dot{\varepsilon}'_{ij}$  is the true shear strain rate tenor,  $\psi$  is the normalized bulk modulus, and  $\dot{e}$  is the volume strain rate.

Sintering stress is also called Laplace stress which comes from the natural tendency of reducing free surface energy of the solid particles (or porous compact) subjected to sintering. Sintering stress depends on the specific surface energy which is the ratio between total free surface energy and the total free surface area of a porous specimen body. Specific surface energy is the internal physical property of a specific material type, while specific free surface area is determined by the porosity and the particle radius (curvature dependent). Sintering stress can be normalized with respect to the ratio of the specific surface energy and 1/6 of the particle size for different powders to obtain the normalized sintering stress (which is the porosity dependent part).

The expressions of normalized sintering stress have been derived by different authors from different approaches, and those representative examples are listed in the following table.

SourcesNormalized Sintering Stress,  $P_{LR}$ Ashby 1st Stage [121] $(1-\theta)^2 \frac{2(1-\theta)-(1-\theta_0)}{\theta_0}$ Ashby 2nd Stage [121] $\sqrt[3]{\frac{6(1-\theta)}{\theta_0}}$ Bouvard & McMeeking [122] $(1-\theta)^{\frac{5}{3}}$ Svoboda & Riedel [123] $\sqrt[3]{1-\theta} \left(\frac{a_{SR}}{\sqrt[3]{\theta}} + b_{SR}\right)$ Skorohod [124] $(1-\theta)^2$ 

Table 2. Expressions of Normalized Sintering Stress, reorganized and adapted from Olevsky [44]

Note:  $\theta$  is the porosity,  $\theta_0$  is the initial porosity,  $a_{SR}$  and  $b_{SR}$  are two Bouvard - McMeeking material parameters.

The normalized sintering stress generally increases as the porosity decreases. In the present study, the expression derived by Skorohod is used due to the best reported experimental data fitting [33] [34].

Porous material densification rate depends on the driving force as well as the material resistance against densification. In the creep based densification, the material resistance to densification is called effective bulk viscosity. The porosity dependence of

the effective bulk viscosity is called normalized bulk modulus. This normalized bulk modulus determines the resistance of a porous material to densification at different porosity levels.

The expressions of normalized bulk modulus have been derived by different authors from different approaches, and those representative examples are listed in the following table.

Sources	Normalized Bulk Modulus, $oldsymbol{\psi}$
Cocks [125]	$\frac{(m+1)(1+\theta)(1-\theta)^{\frac{2}{m+1}}}{3\theta}$
Du & Cocks, 1 <sup>st</sup> Stage [126]	$(1- heta)^{5.26}$
Du & Cocks, 2 <sup>nd</sup> Stage [126]	$\frac{(1-\theta)^{5.26}}{b_{DC}\theta^{\alpha_{DC}}}$
Duya & Crow [127], Sofronis & McMeeking [128], Wilkinson & Ashby [129], Mackenzie $(m = 1)$ [130],	$\frac{2}{3} \left( \frac{1 - \theta^m}{m \theta^m} \right)^{\frac{2}{m+1}}$
Helle et al., 1 <sup>st</sup> Stage [121]	$\frac{2(1-\theta)(\theta_0-\theta)^2}{b_{He}{\theta_0}^2}$
Helle et al., 2 <sup>nd</sup> Stage [121]	$\frac{1-\theta}{b_{He}\sqrt{\theta}}$
Hsueh et al. [131]	$\frac{1-\theta}{2b_{Hs}\theta^{\alpha_{Hs}}}$
McMeeking & Kuhn, 1 <sup>st</sup> Stage [132]	$\frac{3(1-\theta)^3(\theta_0-\theta)}{\theta_0} \left(\frac{16\sqrt{3\theta_0}}{27\pi\sqrt{\theta_0-\theta}}\right)^m$
Ponte Castaneda [133]	$\frac{27(1-\theta)^{\frac{2}{m+1}}}{8\theta}$
Rhaman et al. [134]	$(1-\theta)exp(-2\theta)$
Skorohod [124]	$\frac{2(1-\theta)^3}{3\theta}$
Venkatachari & Raj [135]	$\frac{ln\theta + 0.5(1-\theta)(3-\theta)}{b_{VR}(\theta-1)}$

Table 3. Expressions of Normalized Bulk Modulus, reorganized and adapted from Olevsky [44]

Note: *m* is the strain rate sensitivity exponent,  $b_{He}$  is the Helle model material parameter,  $b_{Hs}$  and  $\alpha_{Hs}$  are the two Hsuch model material parameters,  $b_V$  is the Venkatachari – Raj model material parameter. The normalized bulk modulus generally increases as the porosity decreases, and it approaches infinity as the porosity approaches zero. In the present study, the expression derived by Skorohod is used due to the relevant reported experimental data fit [34] [130].

A classical sintering experiment for spherical glass powder (amorphous) under uniaxial stress was used to fit the continuum theory of sintering developed by Skorohod and Olevsky [44] expressed as the following for densification of linear viscous materials:

$$\frac{\dot{\theta}}{1-\theta} = \frac{P_L}{2\eta_0\psi}$$
$$\tau_s = \int \frac{P_{L0}}{\eta_0} dt$$

where  $\dot{\theta}$  is the porosity changing rate,  $P_L$  is the sintering stress,  $P_{L0}$  is the initial sintering stress,  $\eta_0$  is the viscosity for fully dense material,  $\psi$  is the normalized bulk modulus,  $\tau_s$  is the specific time of sintering. The data fitting is presented in the following figure.



Figure 22. Comparison with the Experiment (Rahaman & De Jonghe) [130], calculation adapted from Olevsky [44]

As can be seen above, the combination of Skorohod's sintering stress and normalized bulk modulus models has the best fit of Rahaman and De Joughe's experimental data.

Normalized bulk modulus determines the resistance of a porous material body to densification depending on porosity, while normalized shear modulus determines the resistance of porous material body to deformation depending on porosity. To fully describe the porous material body behavior under stress, one needs both moduli. The following table summarizes the three most popular model combinations for the normalized bulk and shear moduli sets:

 Table 4. Expressions of the Selected Comparing Normalized Shear and Bulk Moduli for the Three

 Models, relisted and adapted from Alvarado-Contreras [136]

	Shorohod [124]	Sofronis and McMeeking [128]	Cocks [137]
Shear modulus, $\varphi$	$(1-\theta)^2$	$\left(\frac{1-\theta}{1+\theta}\right)^{\frac{2}{m+1}}$	$\frac{3(1-\theta)^{\frac{2}{m+1}}}{3+2\theta}$
Bulk modulus, $\psi$	$\frac{2(1-\theta)^3}{3\theta}$	$\frac{2}{3} \left( \frac{1 - \theta^m}{m \theta^m} \right)^{\frac{2}{m+1}}$	$\frac{(m+1)(1+\theta)(1-\theta)^{\frac{2}{m+1}}}{3\theta}$

The above moduli are plotted against porosity in the following figure to check the

trend of the moduli evolution with porosity.



Figure 23. A Comparison of Skorohod [124], Sorinis and McMeeking [128] and Cocks' [137] Models for the Evolution of the (a) Normalized Shear and Bulk Moduli Respect to Porosity, re-plotted and adapted from Alvarado-Contreras [136]

As can be observed from the above plots, the Skorohod model falls into the intermediate value range among all three types of models. Therefore, it is relatively

neutral, neither too aggressive nor too conservative. This is the reason that this present study chooses Skorohod moduli models.

Since SPS has similar mechanical initial and boundary conditions with hot pressing, and this study assumes that the electrical field contribution in SPS is limited to heating only, constitutive relationships developed for porous materials subjected to general hot consolidation are used for the modeling of SPS densification of porous compact. The possible electric current contribution to densification (or mass transfer) is accounted for by calculating the apparent activation energy in the term of material deformation resistance (or viscosities) which is responsible for describing the temperature dependence.

#### 3.2 General Discussion of Spark Plasma Sintering Modeling

Although the SPS process is very similar to the hot pressing from mechanical perspectives, their heating patterns are quite different. Therefore, the modeling of spark plasma sintering needs the coupling of electrical-thermal models to get the SPS specific spatial temperature distribution, and this is the key to the successful and proper modeling of temperature dependent densification process during SPS.

Most of the modeling work in SPS has been dedicated to the numerical analysis of temperature and electric current distributions during SPS [5] [28] [51]- [78]. However, it is also obviously necessary to couple the electrical-thermal equations with mechanical equations, to form a complete model capable of describing densification and grain growth. Most FEM simulation software is not capable of coupling three types of boundary conditions simultaneously, with COMSOL Multiphysics® being the only available. Some researchers have included mechanical module in their modeling. But their treatment of porous specimen density evolutions is typically by using the integral shrinkage (through z-axis displacement changes). This type of density calculation ignores the density gradient caused by temperature and stress gradient existed in the SPS tooling and specimen, therefore provides no fundamental understanding of the density and microstructure variations and evolutions during SPS processing [5] [76] [81].

To successfully model SPS process, one needs to develop or identify the proper constitutive models to describe the electrical-thermal-mechanical phenomena during SPS for both the fully dense solid SPS tooling material and the porous SPS specimen material. Mechanical field modeling should include three sub model categories. The first mechanical sub model category is the elasticity model to calculate the stress due to thermal expansion or shrinkage, as well as the mechanical load applied directly by the hydraulic system through the punch. The second mechanical sub model is the creep model to describe the densification process during SPS under stress. The last mechanical sub model is the grain growth model to describe the material microstructure coarsening during SPS process, because the mechanical response of the material is dependent on the microstructure factor such as grain size [138] [139].

Electrical field modeling should include the Joule heating constitutive equation based on Ohm's law, which links the conversion of electrical energy to thermal energy.

Thermal field modeling should include the heat transfer models based on Fourier's law. Heat transfer models should include the conduction heat transfer within and between the solids, and the radiation heat transfer on the tooling surface. These models help to analyze the spatial temperature distribution within the SPS setup, so that the mechanical models can have an accurate reference temperature to predict the thermal stress, dimension change, densification and grain growth.

There are three recently published modeling and simulation papers on SPS process which are relatively the most comprehensive so far. They were published by Olevsky et al. [87], Song et al. [84], and Matsugi [85] respectively. All of the three papers successfully coupled electrical field and thermal field with densification constitutive equation very well. However, the first paper did not include the proper mechanical model boundary conditions necessary to describe the specimen and graphite tooling interactions, therefore the failure analysis of graphite tooling under pressurization during SPS is not feasible. The latter two papers did not include the grain growth model; therefore they are incapable of describing the change of material mechanical behaviors under stress with evolving microstructure. Besides, the other incomplete aspect of the third paper is that it did not include the mechanical modeling capability, so it is incapable of stress and strain calculations for the SPS tooling and specimen.

#### 3.3 Fundamental Experiments for Spark Plasma Sintering Modeling

Recently, extensive efforts have been made towards the development of instruments for rapid densification of materials at a relatively low temperature [28]. Although SPS has been employed for fabrication of various materials [102] [140]- [143],

there exists a significant gap in the understanding of the SPS fundamental densification mechanisms [54].

To properly model and simulate SPS process, fundamental experiments need to be conducted to understand the mechanisms of SPS densification process so that suitable model can be developed or selected for the modeling purpose.

Currently, investigations of the densification mechanisms of SPS have been limited. Evaporation-condensation, plastic deformation, surface diffusion, grain boundary diffusion, electromigration, volume diffusion, and thermal diffusion are considered as the possible dominant mass transport mechanisms [33]- [35] [144]- [147]. All of those solid mass transfer mechanisms can be related to four types creep behaviors: diffusional creep, grain boundary sliding based creep, dislocation motion controlled creep, and a special case called dispersion strengthened alloys creep (a very slow lattice deformation process).

In 2007, Chaim attempted to explain the densification mechanisms of nanocrystalline ceramics, focusing on the electric current and field [54] interactions with microstructure. He found that nano particle compacts enable accumulation of high electric charge and discharge under conventional voltages used for the SPS.

In 2007, Frei, Anselmi-Tamburini and Munir [148] reported current effect on the inter-particle neck growth in the sintering of copper spheres attached to copper plates. The inter-particle neck growth kinetics was investigated under the applied pulsed electric current conditions. It was shown that the current had a marked effect on neck growth between the spheres and the plates. The enhancement of sintering under the effect of the current was attributed to electromigration. Microstructural observations on fracture surfaces of necks formed under high currents showed considerable void formation. It was also observed that the current resulted in increased evaporation and the formation of bunched evaporation steps. Formation of these steps and their location relative to the neck were consistent with current density distributions. The results of this investigation provide direct evidence for the role of the current in the sintering in the pulse electric current sintering method.

The fundamental experiments focused on identifying creep mechanisms for SPS are listed as the following: in 2007, Bernard-Granger and Guizard investigated SPS of zirconia powder using a nonlinear (power law) stress-strain constitutive relationship to identify the densification mechanism. The major conclusions were based on the assumption of constant grain size during the analyzed period of the SPS processing [149].
Recent publications by Langer, Hoffman and Guillon [150]- [152] compared studies on insulative alumina, ionic conductor yttria-doped zirconia, and semiconductor zinc oxide subjected to similar conditions in SPS and hot pressing. Due to the dependence of the consolidation kinetics on the evolution of the grain size, the grain growth kinetics was analyzed by microstructure characterization via interrupted processing.

Previously conducted studies had limited focus on the densification constitutive behavior of powder materials subjected to SPS. This constitutive behavior depends on the microstructure evolution. In previously conducted studies the required information on the microstructure evolution has been obtained through labor-intensive interruptive processing analysis or by using phenomenological equations describing grain growth and particle coarsening [153].

The present study chose to analyze the densification during SPS process by using the power law creep based model. Starting from earlier publications of Wilkinson [129] and Johnson [154], power-law creep has been considered to be the dominant mechanism contributing to densification of crystalline materials powders.

Previous studies focused primarily on the steady-state stage of creep behavior (which is generally considered as a result of a balance between work hardening and recovery softening) [155] led to the development of constitutive equations for describing various mechanisms of plastic flow. A generalized form of strain rate ( $\dot{\varepsilon}$ ) – stress ( $\sigma$ ) relationship function describing power law creep is expressed as follows [138]:

$$\dot{\varepsilon} = B \frac{DG_S b}{k_B T} \left(\frac{\sigma}{G_S}\right)^n$$
 Equation 2

where *D* is the diffusion coefficient;  $k_B$  is the Boltzmann's constant; *n* is the stress exponent (*n* is equal to 1/m, where *m* is the strain-rate-sensitivity exponent);  $G_S$  is the dynamic, un-relaxed, shear modulus; *b* is Burgers vector, and *B* is a function of microstructure (principally reflecting the influences of the grain size, sub-grain size, and dislocation density), and *T* is absolute temperature.

Various creep mechanisms can be described by these mechanisms are associated with specific values of parameter n by which the mechanism is defined uniquely. The four major types of creep mechanisms are summarized as follows:

• Diffusional creep is characterized by n = 1 (m = 1). Nabarro-Herring creep is a transport of matter by diffusion through the grain lattice [156]; Coble creep is a transport of matter by diffusion through grain-boundary diffusion, which is a specialized case of Nabarro-Herring creep [157].

- Grain-boundary sliding-based creep (also known as Coble creep) is characterized by n = 2 (m = 0.5). The activation energy of this mechanism is equal to the activation energy for grain-boundary diffusion,  $Q_{gb}$  [158].
- Dislocation creep includes two sub-category creep mechanisms which are [159] [160]:
  - Glide-controlled creep, n = 3 (m = 0.3)
  - Climb-controlled creep, n = 4-5, (m = 0.2 0.3)
- Dispersion-strengthened alloys creep is characterized by n > 8 (m < 0.1) [161]- [163].

Among all these creep mechanisms it is the grain-boundary sliding (GBS) mechanism that is believed to contribute the most to super-plastic behavior. Therefore, it is also the mechanism that is believed to often control the densification of particulate materials under high temperature consolidation. In the last three decades, quite a few models had been proposed for GBS [160]. The main three categories those models fall into can be summarized as rate controlling slip accommodation models, rate controlling diffusional accommodation models, and non-rate controlling diffusion accommodation models.

To identify which mechanism is dominant in the densification of particulate materials by SPS, strain rate – stress relationships have to be analyzed. If the stress

exponent n or strain rate sensitivity m is determined, the dominant densification mechanism can be identified accordingly. The accurately determined strain rate sensitivity constant is needed for calculating the SPS specimen porosity evolution by using the continuum theory of sintering and power law model.

# 3.4 Analysis of Consolidation Constitutive Relationships

Depending on different length scale basis, sintering or hot consolidation modeling methodologies are categorized as the following types: continuum, micromechanical, multi-particles, and molecular dynamics [164]. Different models have different emphasis, advantages, as well as limitations. Continuum models have benefits in terms of time and macroscopic level net shaping predication, which are the most desired features for industrial users and application orientated studies.

As a start for continuum approach, mass conservation is evoked through the following constitutive equation to link the densification and strain rate:

$$\dot{e} = rac{\dot{V}}{V} = rac{\dot{ heta}}{1- heta} = -rac{\dot{
ho}}{
ho}$$
 Equation 3

where  $\dot{e}$  is the volume strain rate (summation of first invariant of the measured true strain rate),  $\dot{V}$  is the volume shrinkage rate, V is the instantaneous volume of the porous body,  $\dot{\theta}$ 

is the porosity changing rate,  $\theta$  is the porosity,  $\dot{\rho}$  is the relative density changing rate, and  $\rho$  is the relative density.

The second governing equation for consolidation is about momentum conservation, which requires the force-stress equilibrium status:

$$\sigma_{ij,j} + \sigma_b = 0 \qquad \qquad \text{Equation 4}$$

where  $\sigma_{ij,j}$  is the externally applied true stress gradient within the, and  $\sigma_b$  is the body stress gradient defined as the following:

$$\begin{cases} \sigma_b = -\rho \rho_{th} g & in the vertical direction \\ \sigma_b = 0 & otherwise \end{cases}$$
 Equation 5

where  $\rho_{th}$  is the material theoretical density and *g* is the gravitational acceleration. The gravitational force can generate heterogeneous body stress status and therefore heterogeneous deformation. However, for the spark plasma sintering condition, the body gravitational force is about  $1.0 \times 10^{-6}$  to  $3.0 \times 10^{-5}$  of the applied mechanical uniaxial stress. Therefore, the body stress term can be neglected in the modeling of SPS process.

Lastly, the deformation strain rate (measured true strain rate) of porous compact can be linked to the stress by the viscous law according to the continuum theory of sintering developed by Olevsky [44] and also reported by McMeeking and Khun [132]. By combining the approaches used by Olevsky (stress – strain rate expression for nonlinear material creep behavior) and McMeeking (strain rate – stress expression for linear material behavior), this dissertation successfully translated the nonlinear material creep constitutive equations by matrix transpose from stress – strain rate expression into strain rate – stress relationship as the following:

$$\dot{\varepsilon}_{ij} = \frac{1}{9\zeta} \sigma_{kk} \delta_{ij} + \frac{1}{2\eta} \left( \sigma_{ij} - \frac{1}{3} \sigma_{kk} \delta_{ij} \right) - \frac{P_L}{3\zeta} \delta_{ij}$$
 Equation 6

where  $\dot{\varepsilon}_{ij}$  is the deformation strain rate tensor,  $\delta_{ij}$  is the Kronecker delta,  $\sigma_{kk}$  is the summation of all the hydrostatic parts of the true stress tensor  $\sigma_{ij}$ ,  $P_L$  is the sintering stress derived from Laplace effective pressure of surface tension,  $\zeta$  is the effective bulk viscosity, and  $\eta$  is the effective shear viscosity. The nonlinearity of the above relationship is embedded in the effective viscosities, which will be introduced in detail in the section 3.1.2 and 3.1.3. This format of expression is very helpful for the implementation of constitutive modeling into finite element simulation framework, because for SPS process, the applied stress is the input variable and the strain rate is the output variable. By expressing the stress as the independent variable will allow the specimen to interact with the loading stress applied through the elastic SPS tooling. In the finite element simulation, Equation 6 is solved simultaneously with Equation 4, and the solution is substituted into Equation 3 to update the porosity evolution of the porous body.

The reason to write the above equation in form of strain rate to stress is for easier understanding by using the similar analogy of linear viscous case (the simplified version). However, one important thing about the above equation is that, the analytical solution can only be obtained for isostatic pressing case, where  $\sigma_{kk}$  is known to be three times of applied stress; and for linear viscous case where  $\sigma_{kk}$  can be canceled by rearrangement eventually. For hot pressing of nonlinear material in rigid die (only one stress component is known – the processing parameter), this is much more complicated. There will be unknown part in  $\sigma_{kk}$ , therefore, the alternative form of this equation expressed by Equation 1 should be used to determine the other two principal stress components for the calculation of  $\sigma_{kk}$  and then the strain rate can be obtained accordingly.

Previously, Besson and Abouaf [165] had tried to formulate the strain rate – stress based nonlinear-viscous relationship for the consolidation of nonlinear porous materials. However, they had not obtained the explicit or continuous expression for the effective viscosity for the nonlinear cases. The effective viscosity values used in their calculations were obtained by interpolation and approximation of experimental data. In this present study, the explicit expressions for effective shear and bulk viscosity of nonlinear porous materials have been used, which are obtained by this study from a comprehensive transformation of continuum theory of sintering derived by Olevsky [44].

The formulation for sintering stress, the effective bulk and shear viscosity are detailed in following sections.

#### 3.4.1 Sintering Stress

The sintering stress  $P_L$  is the driving force for densification due to the reduction of interfacial energy of pores and grain boundaries. Following Skorohod and Olevsky [166] the sintering stress is derived and has the following expression:

$$P_L = \frac{6\alpha}{G} (1-\theta)^2 = \frac{6\alpha}{G} \rho^2$$
 Equation 7

where  $\alpha$  is the specific surface energy (a material constant which is the surface energy per unit surface area), and *G* is the grain size diameter (or particle size diameter when the single crystal powder is used). This expression assumes that the pores are attached to grain boundaries, which could lead to prediction deviation when the pores start to be detached from grain boundary close to the end of final stage of sintering.

Another assumption used in the derivation of the above expression for sintering stress is that the pores and particles are isometric quasi-spherical. Although this deviates

from the reality in most of the sintering practice in industry, however, it reflects the basic relationship between surface tension and porosity. It is also valid and continuous at extreme boundary conditions such as porosity equal to zero. The evolution trend is consistent with most of the reported popular models proposed by Ashby and Kwon *et al.* [121][167].

Even though the sintering stress is the only driving force for densification for conventional pressure-less sintering, its magnitude is only up to 3 MPa.

Under the SPS processing condition, where the applied uniaxial mechanical stress is in the range between 20 to 80 MPa, the densification contribution fraction from sintering stress is relatively low (up to 15%).

#### 3.4.2 Effective Bulk Viscosity

An expression for the effective bulk viscosity is obtained by assuming one single dominant densification mechanism. For this study, the power law creep mechanism is assumed to be the only dominant densification mechanism for crystalline powders. The effective bulk viscosity proposed by Skorohod and Olevsky [166] is reformulated as the following:

$$\zeta = \frac{\sigma(W)}{W}\psi$$
 Equation 8

where  $\sigma(W)$  is the effective material resistance depending on the temperature, strain rate, and porosity; *W* is the equivalent strain rate depending on the measured true strain rate and porosity; and  $\psi$  is the normalized bulk modulus depending on porosity.

The equivalent stress as a function of applied stress, sintering stresses, and porosity can be further expressed as the following:

$$\sigma(W) = \frac{1}{\sqrt{1-\theta}} \sqrt{\frac{\left(\frac{1}{3}\sigma_{kk} - P_L\right)^2}{\psi} + \frac{\tau^2}{\varphi}}$$
 Equation 9

where  $\tau$  is the shear component of applied stress, and  $\varphi$  is the normalized shear modulus.



Figure 24. Absolute Compressive Strain Rate versus Absolute Stress / Viscosity Ratio,  $m \in (0, \infty)$ .

For this study, the deformation is always obtained in compression mode, therefore, the strain is in the range of (-1, 0], while the strain rate is in the range of (-1, 0] per second. The strain rate sensitivity *m* is in the range of (0, 1).

The strain rate sensitivity exponent should not be negative. For a special case where m equals to zero, the normalized stress and strain rate relationship will be reduced to the case for perfect plastic material. Perfect plasticity means at a constant threshold normalized yield stress, the material will start deformation at an instantaneously infinite large strain rate. This is like what is typically observed for polycrystalline material yield deformation at room temperature. When m equals to 1, then the strain rate increases linearly with the increase of the applied stress. This is typically observed for amorphous material systems subjected to external stresses. When m is between 0 and 1, then the strain rate has nonlinear behavior with respect to the applied stress. This is typically observed for deformation of polycrystalline material systems subjected to external stresses at high temperatures.

Strain rate sensitivity determines how fast and intensively the achieved strain rate responds to change of applied stress. The larger the strain rate sensitivity, the easier the

deformation of a material at a specific stress level. For  $m \in (0, 1)$ , the strain rate increases slower than the increase of applied stress when the absolute ratio between the applied stress and material viscosity is smaller than  $(m)^{\frac{m}{1-m}}$  [s<sup>m</sup>], and beyond this point, the strain rate increases faster than the increase of the applied stress.

The equivalent strain rate as a function of applied stress and porosity can be further expressed as the following:

$$W = \left\{ \left(\frac{T}{\sigma_0}\right)^2 \exp\left(-\frac{2Q_{pc}}{RT}\right) \left(\frac{G_0}{G}\right)^4 \left(\frac{1}{1-\theta}\right) \left[\frac{\left(\frac{1}{3}\sigma_{kk} - P_L\right)^2}{\psi} + \frac{\tau^2}{\varphi}\right] \right\}^{\frac{1}{2m}}$$
 Equation 10

where  $\sigma_0$  is the material power law creep frequency factor at reference temperature,  $Q_{pc}$  is the activation energy for power law creep, *R* is the universal gas constant, *T* is the absolute temperature,  $G_0$  is the initial grain size, and *m* is the strain rate sensitivity exponent.

The equivalent strain rate represents the strain rate of the substance (solid part) in the porous body. As porosity is larger than zero, the equivalent strain rate is larger than the measured true shear strain rate intensity of the overall porous body, because the void volume (in the porous body) is canceled out for the strain rate calculation. As porosity reaches zero, the equivalent strain rate decreases and equals to the measured true shear strain rate intensity of the overall specimen body (with zero porosity) which has become fully dense by then.

The normalized bulk modulus dependence on porosity can be further expressed as the following:

$$\psi = \frac{2}{3} \frac{(1-\theta)^3}{\theta}$$
 Equation 11

This relationship is based on the assumption that the pores and particles are isometric quasi-spherical. The normalized bulk modulus is disproportional to the porosity. As the porosity is 1, the normalized bulk modulus is 0; and as the porosity is approaching 0, the normalized bulk modulus goes to positive infinity, which indicates incompressible and fully dense status.

The full expression of the normalized shear modulus has the following format:

$$\varphi = (1 - \theta)^2$$
 Equation 12

This relationship is based on the assumption that the pores and particles are isometric quasi-spherical. The normalized shear modulus is disproportional to the porosity. As the porosity is 1, the normalized bulk modulus is 0; and as the porosity is approaching 0, the normalized bulk modulus becomes 1, which is the value for fully dense materials. By substituting the above four equations into the expression for the effective bulk viscosity, one can obtain:

$$\zeta = \frac{2}{3} \frac{(1-\theta)^3}{\theta} \left\{ \left(\frac{\sigma_0}{T}\right) \exp\left(\frac{Q_{pc}}{RT}\right) \left(\frac{G}{G_0}\right)^2 \left[\frac{\theta(\sigma_{kk} - 3P_L)^2}{6(1-\theta)^4} + \frac{\tau^2}{(1-\theta)^3}\right]^{(m-1)} \right\}^{\frac{1}{m}}$$
 Equation 13

The effective bulk viscosity determines the difficulty for a porous body to have irreversible shrinkage or expansion in volume. It is proportional to the grain size, and disproportional to the temperature as well as porosity.

#### 3.4.3 Effective Shear Viscosity

An expression for the effective shear viscosity is obtained by assuming one single dominant densification mechanism. For this study, the power law creep mechanism is assumed to be the only dominant deformation mechanism for crystalline powders. The effective shear viscosity proposed by Skorohod and Olevsky [166] is rewritten as the following:

$$\eta = \frac{\sigma(W)}{2W}\varphi$$
 Equation 14

By substituting the three equations of equivalent stress, equivalent strain rate, and normalized shear modulus into the expression for the effective shear viscosity, one can obtain:

$$\eta = \frac{(1-\theta)^2}{2} \left\{ \left(\frac{\sigma_0}{T}\right) \exp\left(\frac{Q_{pc}}{RT}\right) \left(\frac{G}{G_0}\right)^2 \left[\frac{\theta(\sigma_{kk} - 3P_L)^2}{6(1-\theta)^4} + \frac{\tau^2}{(1-\theta)^3}\right]^{(m-1)} \right\}^{\frac{1}{m}}$$
 Equation 15

The effective shear viscosity determines the difficulty for a porous body to have irreversible shape deformation. It is proportional to the grain size, and disproportional to the temperature as well as porosity.

#### **3.4.4 Grain Growth Kinetics**

Grain size significantly influences sintering and densification behavior. To precisely model sintering and densification behavior, the effective bulk and shear viscosities used in this study are also given as a function of grain size as shown in the equations from previous sections.

By considering grain size and relative density correlation relationship reviewed and summarized by German in his critical sintering microstructure coarsening review article polished 2010 [168], the grain growth rate for solid state sintering is derived by the author in this study as the following:

$$\dot{G} = \frac{dG}{dt} = -\frac{n_g G_0}{\theta} \left(\frac{\theta_0}{\theta}\right)^{n_g} \frac{d\theta}{dt}$$
 Equation 16

where  $\dot{G}$  is the grain growth rate,  $G_0$  is the initial grain size, and  $\theta_0$  is the initial porosity,  $n_g$  is the grain growth power exponent (0.5 is used within this study).

This expression is valid and continuous through the porosity range of (0.60 to 1.00). The temperature dependence of grain growth rate is embedded in the porosity reduction rate. Because the grain growth activation energy for powders with wide particle size distribution is very small, after full activation, the grain growth process is controlled by the densification rate.

Experimental data compiled by Olevsky *et al.* [88] and simulation results from Tikare and Cawley [169] suggest that the above model is valid to finite small porosity range. However, when porosity decreases to zero, the grain size becomes infinitely large, which is unrealistic. In future research, one needs find another continuous mathematical function for addressing the grain growth rate for fully sintered microstructure.

# 3.4.5 Consolidation and Grain Growth Coupled Analysis

For the coupled modeling and simulation analysis of SPS consolidation of porous compact, the consolidation constitutive equation solution at first time step (based on initial conditions) feeds grain growth constitutive equation to solve for the grain size result after the first time step, and then the grain size result is substituted into the consolidation constitutive equation again to find the solution for the next time step. By setting up such iterations, the grain size dependent consolidation calculation is enabled.

# 3.4.6 Analytical Solution for Spark Plasma Sintering Consolidation

By substituting the continuum mass conservation equation and material parameter expressions into the strain rate stress relationship constitutive equation, then applying the boundary conditions for SPS (which is the hot pressing in a rigid cylindrical die for this study), one can obtain the following expression for densification rate (or porosity shrinkage rate):

$$\dot{\theta} = \frac{d\theta}{dt} = -\left[-\frac{(\sigma_z - P_L)}{\sigma_0} Texp\left(-\frac{Q_{pl}}{RT}\right) \left(\frac{G_0}{G}\right)^2 \left(\frac{3\theta}{2}\right)^{\frac{m+2}{2}} (1-\theta)^{\frac{3-m}{2}}\right]^{\frac{1}{m}}$$
 Equation 17

Solving the above differential equation by adaptive approach, one can obtain the  $\theta vs.t$  relationship.

#### 3.5 Analysis of Elastic Strain and Stress Spatial Distribution

The elastic constitutive relationship for the SPS tooling can be described by the classical Hook's law as the following:

$$\varepsilon_{ij} = \frac{1}{9K} \delta_{ij} \sigma_{kk} + \frac{1}{2G_e} \left( \sigma_{ij} - \frac{1}{3} \delta_{ij} \sigma_{kk} \right)$$
 Equation 18

where  $\varepsilon_{ij}$  is the true elastic strain, *K* is the elastic bulk modulus,  $G_e$  is the elastic shear modulus. The assumption made over here is that the tooling material is isotropic media (which have the same physical properties in any direction), therefore only two independent compliance constants the bulk modulus and the shear modulus are needed. These two moduli quantify the material's resistance to changes in volume and to shearing deformations, respectively.

Elasticity equation describes the stress-strain and strain-displacement relationships. It is also coupled with strain generated by thermal expansion:

$$\vec{\sigma} = \mathbf{C}: (\varepsilon - \varepsilon_{creep} - \varepsilon_{CTE})$$
 Equation 19

$$\varepsilon = \frac{1}{2} [(\nabla \mathbf{u})^T + \nabla \mathbf{u}]$$
 Equation 20

$$\varepsilon_{CTE} = \alpha_{CTE} (T - T_{ref})$$
 Equation 21

where  $\vec{\sigma}$  is the stress vector matrix, C is the elastic stiffness matrix,  $\varepsilon_e$  is the mechanical elastic strain vector,  $\varepsilon_{creep}$  is the creep accumulated strain vector solved from consolidation constitutive equations,  $\varepsilon_{CTE}$  is the thermal strain vector,  $\alpha_{CTE}$  is the

effective thermal expansion coefficient depending on porosity, and  $T_{ref}$  is the reference temperature where the measurement of thermal expansion coefficient starts at.

The spatial temperature distributions come from the solution of electrical-thermal constitutive equations. Taking into consideration of temperature spatial distributions enables the determinations of spatial distributions of porosity and grain size. However, those fully coupled analyses have to be done by finite element modeling simulation.

### 3.6 Analysis of Electric Current Density Spatial Distribution

Ohm's law is used for Joule heating analysis. Constitutive equations for joule heating are expressed as the followings:

$$\nabla \cdot J_h = Q_i$$
 Equation 22

$$J_h = \left(\sigma_e + \epsilon_r \frac{\partial}{\partial t}\right) E_{epotential}$$
 Equation 23

$$E_{epot} = -\nabla V_{volt}$$
 Equation 24

where  $J_h$  is the joule heat energy,  $Q_j$  is volume heating power density generated by Joule heating,  $\sigma_e$  is the material electrical conductivity,  $\epsilon_r$  is the relative permittivity,  $E_{epot}$  is the electrical potential, and  $V_{volt}$  is the electrical voltage applied between the top and bottom surfaces of the tooling setup.

Material properties are obtained from COMSOL Multiphysics® 4.3a database. In reality, these properties depend on microstructures (porosity and grain size), compositions, as well as the external environment (such as temperature and pressure). However, a comprehensive material property database taking into all of these dependences does not exist yet. This study uses what is available with the best access of information and applies approximations or interpolations when necessary.

#### 3.7 Analysis of Temperature Spatial Distribution

Based on Fourier's law and conservation of energy, constitutive equations for the heat transfer are as follows:

For conduction:

$$\rho_m C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + Q_j \qquad \text{Equation 25}$$

where  $\rho_m$  is the material density,  $C_p$  is the constant pressure specific heat capacity, T is the temperature in Kelvin, k is the thermal conductivity, and Q is the heat flow through the system. For radiation:

$$-\boldsymbol{n}_{N} \cdot (-k\nabla T) = \epsilon \sigma_{SBC} (T_{amb}^{4} - T^{4})$$
 Equation 26

where  $\mathbf{n}_N$  is the normal vector, k is the thermal conductivity,  $\epsilon$  is the emissivity,  $\sigma_{SBC}$  is the Stephan-Boltzmann constant  $\left[\frac{W}{m^2 K^4}\right]$ , and  $T_{amb}$  is the ambient temperature.

Material properties are also obtained from COMSOL Multiphysics® 4.3a database. Again, these properties are dependent on microstructures (porosity and grain size), compositions, as well as the external environment (such as temperature and pressure). However, a comprehensive material property database taking into all of these dependences does not exist yet. This study uses what is available with the best access of information and applies approximations or interpolations when necessary.

# Chapter 4 Fundamental Spark Plasma Sintering Experimentation

# 4.1 Material

Copper is used as in the present study as a baseline material, and the copper

powder characteristics is listed in Table 5.

Elemental Powder	Copper (Cu)	
Vendor	Alfa Aesar (MA)	
Designation	OFHC-43385	
Purity	99.9999%	
Fabrication Method	Water Atomized	
Particle Size		
D <sub>10</sub> (µm)	43	
D <sub>50</sub> (µm)	64	
D <sub>90</sub> (µm)	101	
Tap Density (g/cm <sup>3</sup> )	4.18 (46.7%)	
Theoretical Density (g/cm <sup>3</sup> )	8.96	
Melting Temperature [K]	1358	

 Table 5. Fundamental Study Material Copper Powder Characteristics

Copper does not undergo any phase transformation during sintering, and sinters through solid-state sintering. Copper has extremely high electrical conductivity, which makes it a very good representative material to study SPS process of conductive materials. - Powder Morphology SEM

Field emission scanning electron microscope (FESEM, Quanta 450, FEI, Oregon) was used to characterize the morphology of powders. It can be seen that the dominant large particles are spherical and polycrystalline with the mean grain size of about 48  $\mu$ m (Figure 25).



Figure 25. SEM Morphologies of Copper Powder, 300X (Left), 1600X (Right)

- Particle Size Distribution

A laser diffraction particle size and image analyzer (S3500SI, Microtrac, Japan) was used to characterize the particle size distribution for different powders. A 405 nm wavelength laser was used in the micro size detector, while a 480 nm wavelength laser

was used in the sub-micro size detector. Besides, 10% of nonionic hydrophilic surfactant Triton X100 was added to deionized water for dispersing the powders effectively. The powder samples were then tested in wet mode. Before the powder entering the laser chamber, further dispersion by ultrasonic vibration at 40 Watts for 60 seconds was applied to guarantee obtaining the accurate particle size distribution.



Figure 26. Copper Powder Particle Size Distribution

As shown in the above figure, the characterized copper powder has very narrow mono modal distribution, which is quite suitable for the modeling analysis.

#### 4.2 SPS Equipment and Tooling

The consolidation device used in this study was Dr. Sinter SPSS -515 (SPS Syntex Inc., Japan).

The tooling material used in this study is Isocarb Graphite I-85 (Electrodes, Inc., CA), with apparent density of 1.85 g/cm<sup>3</sup>, particle size smaller than 4  $\mu$ m, flexural strength of 97 MPa, electrical resistivity of 0.02047 Ohm/m, and with hardness (shore) 76. The manufacturer reported emissivity for this graphite is 0.85. All of these properties are values measured at room temperature and reported by the vendor.

The tooling consists of spacers, cylindrical die, and punches.

Graphite spacers: cylindrical, three different diameters of 100 mm (large), 40 mm (medium), 30 mm (small), all of the heights for different spacers are 20 mm.

Graphite punch: cylindrical, diameter of 15 mm, height of 20 mm.

Graphite die: cylindrical, internal diameter of 15.40 mm, external diameter of 30 mm, height of 30 mm.

The graphite foil used for tooling interface wrapping is of 0.20 mm thickness (ZCC, P. R. China). An additional layer of graphite paper with 0.4 mm thickness was

inserted between the large spacer and the electrode to ensure the best contact interface for smooth electric current and heat conduction.

The overall SPS tooling and specimen setup schematic is shown Figure 27.



Figure 27. SPS Tooling and Specimen Configurations, Interfaces between Specimen, Punches, and Die Wrapping with a Layer of Graphite Foil of 0.20 mm (Drawn in Scale)

# 4.3 Multi-Step Pressure Dilatometry Experimentation

A common approach for the determination of the creep mechanisms contributing to densification under high temperature consolidation processes, such as hot pressing or hot isostatic pressing, is to conduct series of experiments with the same heating rate and holding time at different stress levels. The grain size has to be interruptively characterized by microstructure analysis or XRD method (only for submicron sized grains), and then substituted into the strain rate – stress equation, for obtaining a specific value of parameter B. Then the recorded stress and strain values are to be plotted for different grain size ranges. Within each specific grain size range, the slope of the straight line section provides the value of parameter m for the analyzed material system.

This conventional methodology, however, requires a considerable amount of characterization studies for the determination of the grain size. Usually interruptive experiments with the same stress and temperature profiles, but different holding time periods are required, which makes the procedure further cumbersome. In addition, the accuracy of the involved grain size measurement techniques influences the reliability of the results (standard deviation for grain size measurement by SEM or XRD can be as high as 20 to 30% [149]). Therefore, the avoidance of the microstructure evolution influence in the determination of parameter m is the major advantage of the novel MSPD approach described in the next section.

Carefully designed experiment for the determinations of various material constitutive parameters or constants is the key for successful modeling of SPS

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densification process. The designed experiment must be able to isolate effects of different processing parameters (e.g. stress, and temperature), so that the material constant can be unambiguously determined.

The present study describes an alternative approach, based on the analysis of the instantaneous densification behavior, and thus does not need any explicit information on the microstructure evolution during SPS. This is a novel SPS Multi-Step Pressure Dilatometry (MSPD) technique, which enables the determination of the material strain rate sensitivity, bypassing the impact of the microstructure evolution.

For each experiment, the filling powder mass can be determined by the following equation:

$$M=\frac{\pi}{4}d^2h_f\rho_{th}$$

where *M* is the mass of filling powder in gram, *d* is the diameter of the cylindrical SPS graphite punch (1.5 cm for experiments in this study),  $h_f$  is the fully dense specimen height (0.3 cm for experiments in this study), and  $\rho_{th}$  is the theoretical density of the processing materials in gram per centimeter cubic (g/cm<sup>3</sup>). For the experiments within the present study, all the filling powder mass amounts (gram) can be calculated as 53%  $(\frac{\pi}{4}d^2h_f \approx 0.53cm^3)$  of their theoretical density values (gram/cm<sup>3</sup>).

All the experiments were conducted in vacuum (~ 50 Pa). A constant pulse to pause ratio of 12:2 (12 ms on, and 2 ms off) was applied for all the experiments. Temperature measurements for experiments below 1000°C were conducted by using a K-type thermocouple (K Class 2, KT09B-8278F, NCF600, CHINO, Japan) inserted into a 3 mm depth (1.6 mm diameter) hole in the middle point of the lateral graphite die surface, while for experiments above 1000°C a pyrometer (IR-AH, CHINO, Japan) was used by focusing on the thermocouple hole without inserting thermocouple. The temperature measurement error and compensation strategies are described in Appendix A.

For each experiment, there was an additional control blank experiment conducted under the same temperature and pressure conditions without putting the powder sample in the die. The obtained expansion / shrinkage curve was subtracted from the curve obtained with SPS specimen, so that a true densification curve without being affected by the tooling thermal expansion or shrinkage could be calculated.

#### **4.3.1 Design of Experiment**

Multi Step Pressure Dilatometry (MSPD) experimental design details are provided in following figure, including the temperature and loading stress profiles. The applied stress (axial stress) is of uniaxial type, starting from 20 MPa as the first stage, with 10 MPa for each increment up to 50 MPa. During the isothermal holding, each level of stress was kept for 2 min. The idealized regime would be an instantaneous stress change. However, in the real-world experiment, the stress level shift takes 10 seconds between each pair of the closest stress levels. As soon as the cooling stage started, the stress was decreased to the starting stress at 20 MPa. The selected two analysis points between two levels of stress were consistently separated by 20 seconds. One assumption used in this study is that the grain size is constant within this 20 seconds period of time during consolidation. This is a quite reasonable assumption since grain growth is a time consuming process based on relatively slow diffusion process.

The heating rate was 100°C/min. The isothermal holding period at peak temperature was 8 min for each individual experiment. With the help of continuum theory of sintering to adjust the relative density effect on densification rate, this MSPD design was successful in determining the net stress effect on densification at constant temperature and grain size.



Figure 28. Consolidation Temperature and Loading Stress Profiles for MSPD Experiment

Using 66% of the melting point in Kelvin (homologous temperature) as the temperature selection criteria for different material processing, 625°C or 898 K (heating ramp 6 min, dwelling 8 min) was used for copper experiments.

# **4.3.2 Experimental Results**

Determination of strain rate sensitivity procedure is described as the following:

Expressing densification rate (or porosity reduction rate) equation for two different experimental points and taking a ratio, one can obtain:

$$\frac{\dot{\theta}_1}{\dot{\theta}_2} = \left\{ \frac{\left[\sigma_{z_1} - \frac{6\alpha}{G_1}(1-\theta_1)^2\right]}{\left[\sigma_{z_2} - \frac{6\alpha}{G_2}(1-\theta_2)^2\right]} \frac{T_1}{T_2} exp\left(\frac{Q_{pc}}{RT_2} - \frac{Q_{pc}}{RT_1}\right) \left(\frac{G_2}{G_1}\right)^2 \left(\frac{\theta_1}{\theta_2}\right)^{\frac{m+1}{2}} \left(\frac{1-\theta_1}{1-\theta_2}\right)^{\frac{3-m}{2}} \right\}^{\frac{1}{m}}$$

By rearranging, the expression for strain rate sensitivity m is shown as:

$$m = \frac{2ln \frac{\left[\sigma_{z_1} - \frac{6\alpha}{G_1}(1 - \theta_1)^2\right]}{\left[\sigma_{z_2} - \frac{6\alpha}{G_2}(1 - \theta_2)^2\right]} + ln \left(\frac{T_1}{T_2}\right) + 2\left(\frac{Q_{pc}}{RT_2} - \frac{Q_{pc}}{RT_1}\right) + 4ln \left(\frac{G_2}{G_1}\right) + ln \left(\frac{\theta_1}{\theta_2}\right) + 3ln \left(\frac{1 - \theta_1}{1 - \theta_2}\right)}{2ln \left(\frac{\dot{\theta}_1}{\dot{\theta}_2}\right) - ln \left(\frac{\theta_1}{\theta_2}\right) + ln \left(\frac{1 - \theta_1}{1 - \theta_2}\right)}$$

According to the SPS processing condition (MSPD) employed in this study, the

expression of strain rate sensitivity m can be further reduced to the following:

$$m = \frac{2ln\left(\frac{\sigma_{z_1}}{\sigma_{z_2}}\right) + ln\left(\frac{\theta_1}{\theta_2}\right) + 3ln\left(\frac{1-\theta_1}{1-\theta_2}\right)}{2ln\left(\frac{\dot{\theta}_1}{\dot{\theta}_2}\right) - ln\left(\frac{\theta_1}{\theta_2}\right) + ln\left(\frac{1-\theta_1}{1-\theta_2}\right)}$$
Equation 27

By substituting the stress, densification rate and porosity values into the above equation, the strain rate sensitivity can be calculated accordingly.

A representative plot for copper powder with 45  $\mu$ m mean particle size processed by MSPD in SPS is shown in the following to demonstrate the co-evolution of relative density (or 1 - porosity) and densification rate (or - porosity reduction rate).



Figure 29. Relative Density and Densification Rate versus Time for Copper Powder with 45 μm Mean Particle Size Processed by MSPD in SPS, at 625°C (898 K) by 100°C/min Heating Rate, Dwelling for 8 min, under Uniaxial Mechanical Pressure from 20 to 50 MPa, 10 MPa Increment

The porosity and porosity reduction rate data were extrapolated from the above graph and used for strain rate sensitivity calculation for copper powder in SPS by employing Equation 27.

Table 6. Strain Rate Sensitivity Results for Materials

Parameter \ Material	Copper
<i>m</i> (Strain Rate Sensitivity)	$0.30\pm0.08$

m ranges from 0 to 1, the larger the m, the easier the densification (the material strain rate responds to applied stress more sensitively). When m equals to 0 the material

becomes rigid plastic yield behavior (no creep), while as *m* equals to 1 the material becomes linear viscous material behavior (linear relationship between applied stress and strain rate).

The determined strain rate sensitivity for copper powder processed by SPS corresponds to climb controlled creep [159] [160].

By rearranging, the densification rate (or porosity reduction rate) equation can be expressed as the following:

$$ln(\sigma_0) + \left(\frac{Q_{pc}}{R}\right)\frac{1}{T} = ln\left\{-\sigma_z T\left(\frac{G}{G_0}\right)\left(\frac{3\theta}{2}\right)^{\frac{m+1}{2}}(1-\theta)^{\frac{3-m}{2}}\left(\frac{1}{|\dot{\theta}|}\right)^m\right\}$$
 Equation 28

By substituting the stress, porosity, densification rate, and the strain rate sensitivity obtained from the step above, the right hand side (RHS) of the above equation can be calculated and plotted against the reciprocal of temperature (1/T), and the following graph can be obtained. After linear regression, the slope and intercept can be determined at R<sup>2</sup> of 97.79%. The linear fitting independent variable *x* corresponds to 1/T and the linear fitting dependent variable *y* corresponds to the right hand side (RHS) of the above equation.



Figure 30. RHS of Equation 28 Plotted Against the Reciprocal of Absolute Temperature for Copper Powder with 45 μm Mean Particle Size, Processed in SPS, under 20 MPa, Temperature Ranges from 20°C (298 K) to 625°C (898 K) by 100°C/min Heating Rate,

Material power law creep frequency factor:

The material power law creep frequency factor at reference temperature can be calculated by taking exponential power for the intercept of the linear fitting equation obtained from the above figure, and it is as expressed by the following equation,

$$\sigma_0 = exp(intercept)$$
 Equation 29

Activation energy:

The apparent power law creep activation energy can be calculated by multiplying

the slope value with universal gas constant R as shown in the following equation,

$$Q_{pc} = R \cdot slope$$
 Equation 30

The determined material power law creep frequency factor at reference temperature and the power law creep apparent activation energy are listed in the following table.

Parameter \ Material	Copper
Material Power Law Creep Frequency Factor [MPa.K.s <sup>m</sup> ]	45
Apparent Power Law Creep Activation Energy [J/mol]	7000

**Table 7. Power Law Creep Material Parameter Results** 

The larger the material power law creep frequency factor, the harder the densification, and the larger the apparent power law creep activation energy, the harder the densification (requires higher temperature or larger stress to consolidate).

Apparent power law creep activation energy determines the extent of the materials' behavior response on temperature change. From energy perspective, one can interpret its physical meaning by calculating how much temperature increase can be achieved by providing the material with the energy equal to the activation value:

$$\Delta T = \frac{Q_{pc}}{C_p}$$

For copper specifically, the determined activation energy is sufficient to increase temperature of 1 mole copper for 286 K in temperature.
#### 4.3.3 Microstructure Characterizations

The microstructure of SPS consolidated copper specimen was investigated to validate the temperature distribution to what will be predicted by the FEM simulation.

The copper specimen was cut, ground, and then impregnated with epoxy to avoid the pore smearing effects during polishing. The polished cross sectional surfaces were examined by SEM on selective spots as shown in the following schematic.



Figure 31. Schematic Showing the Selected Cross Section Surface Spots of the Cut Cylindrical SPS Specimen along Radius and Axis Directions

The locations shown in the above schematic are characterized and the microstructures are shown in the following figure. The top surface regions include center

(1), intermediate (2), and edge (3); while the middle plane regions include center (4), intermediate (5), and edge (6). The location IDs correspond to the marks in the above schematic.



Figure 32. Cross-Sectional Surface Microstructure of MSPD SPS Copper Powder with 45 μm Mean Particle Size Consolidated at Different Temperatures, by 100°C/min Heating Rate, Dwelling for 8 min, under Uniaxial Mechanical Pressure from 20 to 50 MPa, 10 MPa Increment

The above figure shows that the microstructures at different locations of the copper specimen are not different from each other. This indicates the temperature gradient through the specimen is very small due to the good thermal conductivity of copper. This conclusion will be further supported by the simulation studies in the next chapter.

#### 4.3.4 Discussion

Inhomogeneous electric current density distribution caused by geometric factor or material property difference existing between different components in the SPS setup can lead to inhomogeneous heating at different areas in the SPS setup. SPS is controlled by temperature reading monitored on the die surface, which can have overestimated temperature for nonconductive specimen or underestimated temperature for conductive specimen. The following equation calculates the power law creep activation energy deviation per centi degree (or Kelvin) temperature measurement deviation.

$$\frac{dQ_{pc}}{dT} = \frac{Q_{pc}}{T}$$
 Equation 31

The temperature dependence of power law activation energy estimation deviation per degree is plotted in the following figure.



Figure 33. Power Creep Activation Energy Deviation per Temperature Degree in Kelvin due to Temperature Estimation Deviation at Different Temperatures for  $Q_{pc}$  of 7000 [J/mol]

Considering the copper SPS experiment as an example, if the thermocouple measurement underestimates the temperature lower for about 20 to 30 K at the specimen, this will lead to an power law creep activation energy underestimation about 300 [J/mol/K]. This partially explains why SPS can consolidate conductive materials at temperatures lower than what are used in hot pressing.

Discussion of electric power and current distribution for SPS graphite tooling and specimen setup:

SPS is controlled by the input electric voltage parameter; however its system shutting down criteria is based on the output electric current value. Considering the case for constant electric voltage applied between the electrodes U, examining the specimen electric current share and electric power share. The graphite die (tooling) and powder compact specimen can be seen as the electrical resistors in parallel connection.

Electric current passing specimen:

$$I_S = \frac{U}{R_S}$$

Total power generated on both tooling and specimen:

$$P = P_T + P_S = \left(\frac{R_T + R_S}{R_T R_S}\right) U^2 = \left(\frac{1}{R_S} + \frac{1}{R_T}\right) U^2$$

$$U_{max} = \left(\frac{R_T R_S}{R_T + R_S}\right) I_{max}$$

where  $I_{max}$  is the maximum total electric current passing through the specimen and graphite tooling,  $I_S$  is the electric current passing the specimen,  $I_T$  is the current passing the graphite tooling,  $R_T$  is the graphite tooling electrical resistance,  $R_S$  is the specimen electrical resistance, P is the total electric power generated on the specimen and graphite tooling,  $P_T$  is the electric power generated on the graphite tooling,  $P_S$  is the electric power generated on the specimen,  $U_{max}$  is the maximum applicable electric voltage under maximum system electric current,  $P_{max}$  is the maximum achievable electric power from the system under maximum electric current.

Consider the situation where the maximum applicable voltage is always applied, the maximum power can be calculated accordingly as the following:

$$P_{max} = \left(\frac{R_T R_S}{R_T + R_S}\right) I_{max}^2$$



Figure 34. Calculated Maximum Total Power Generation throughout SPS Tooling and Specimen Depending on the Specimen to Tooling Electric Resistance Ratio under Maximum Allowed SPS System Electric Current (for Idealistic Contacts Conditions)

The total power throughout the SPS tooling and specimen should be as shown in the above Figure, and it increases rapidly in the beginning with the increased specimen to tooling electric resistance ratio, and it approaches the maximum total power under the maximum allowed system electric current eventually.

Specimen power share:

$$\frac{P_S}{P_T + P_S} = \left(\frac{R_T}{R_T + R_S}\right) = \frac{1}{1 + \frac{R_S}{R_T}}$$



Figure 35. Calculated Fraction of Specimen Energy Consumption versus the Tooling to Specimen Electrical Resistance Ratio (for Idealistic Contact Conditions)

The fraction of electric power distribution within the specimen keeps decreasing with the increase of the specimen to tooling electric resistance ratio, and it approaches zero at infinite large ratio value. This indicates that for specimen with high electric resistance, the heat generation will be concentrated in the surrounding graphite tooling, and the specimen could only be heated through conduction and radiation heating from the tooling. The extreme situation with electric current nonconductive material will become very similar to the heating mechanism in hot pressing.

Therefore, the above analysis gives the conclusion as the following: with the increasing specimen to tooling electric resistance ratio, the maximum total power generated through the SPS tooling and specimen will increase accordingly and it reaches a constant threshold as the specimen electrical resistance reaches infinite large value. The fraction of power generated in the specimen will decrease toward zero at infinite large specimen to tooling resistance ratio.

Macroscopic: temperature reading deviation leads to underestimation of power law creep activation energy for conductive materials processed by SPS. Microscopic: the high electric current density heats and softens the inter particle neck first. The stress is also highly concentrated at those inter particle necks. Once the inter particle necks are softened, the densification is accelerated for the conductive materials processed by SPS. This phenomenon will also lead to low apparent power law creep activation energy determined for the SPS densification process.

### 4.4 Electric Current Effects in Spark Plasma Sintering Consolidation

To determine the electric current effects on the consolidation of the copper powder by spark plasma sintering, two different MSPD experiments were carried under current-insulated (CI) and current-assisted (CA) conditions, respectively.

### 4.4.1 Design of Experiment

MSPD experiment design was used repeatedly to identify the densification mechanism difference for current-insulated and current-assisted SPS processes. The setup schematic is as shown in the figure below.



Figure 36. Tooling Setup for Multi-Step Current-Insulated (Upper) and Current-Assisted (Lower) Pressure Dilatometry

Although the consolidation conditions including temperature and pressure were kept the same for the current-insulated and current-assisted experiments, the sample size and setup were different for these two cases. The current-insulated experiment employed larger composite-graphite-alumina tooling to hold a smaller copper sample wrapped by an alumina insulation layer in the center, while the current-assisted experiment employed regular graphite tooling but larger copper sample within the tooling without the insulation layer.

#### **4.4.2 Experimental Results**

Figure 37 shows the current and voltage evolution for the current-insulated and current-assisted MSPD experiments at 625°C or 898 K(30-50 MPa). It should be noted that there is no straightforward relationship between current and voltage due to the dependence of the SPS setup resistance on the specimen's instantaneous microstructure and due to the dependence of the numerous contact resistances on the applied pressure. Along with this, the data on the voltage evolution, which is rarely included in the published experimental results on the SPS processing, can be rather useful for the identification of the densification mechanism.



Figure 37. Current and Voltage Curves for 625°C (898 K) MSPD Experiment (30 to 50 MPa, Current-Insulated vs. Current-Assisted)

During the heating stage, the resistance initially increased with time, and then as the densification progressed, the resistance decreased. This was due to the change of the electrical resistance of the overall graphite tooling setup and of the copper powder compact in the tooling center. Two factors are thought to be the reasons. Firstly, the increased overlapping area between the graphite punch and the graphite die lowered the electrical resistance of the overall tooling setup. Secondly, the copper compact with lower porosity should have lower electrical resistance. During the isothermal dwelling stage, the resistance gradually decreased. The densification was continued during isothermal dwelling stage, while the contact area between the graphite punch and graphite die increased (punches pressed against the powder compact and got deeper in the die cavity).

It was also noticed that the composite graphite-alumina tooling consumed more power (higher voltage and current) due to the larger heat capacity.

In the figure below, the temperature and pressure profiles are plotted for the current-insulated and current-assisted MSPD experiments at 625°C (30-50 MPa). The overheating during heating stage was  $\leq$  30 °C and lasted for about 30 seconds. Sharp pressure changes are consistent with the stepwise pressure design. The cooling stage temperature profiles indicate different cooling rates for these two different setups. The current-insulated setup had a cooling rate slower for 15°C/min than that of the current-assisted setup, probably due to the presence of alumina die as an additional thermal insulation layer and due to the larger volume of the tooling set and the specimen.



Figure 38. Temperature and Pressure Curves for 625°C (898 K) MSPD Experiments (30 to 50 MPa, Current-Insulated vs. Current-Assisted)

The relative density evolutions and pressure profiles were plotted for the currentinsulated and current-assisted MSPD experiments at 625°C or 898 K (30-50 MPa) in the following figure. Pressure profiles were exactly the same for both experiments. The two experiments started from the same initial relative density of 62.0%. The current-assisted process started earlier with slightly faster densification rate at around 200 seconds, which corresponded to the 200°C in-situ temperature. The final densities were 84.0% and 89.0% for the current-insulated MSPD and current-assisted MSPD, respectively. 5% relative density difference was observed between the two different setups with 8 minutes of isothermal holding at 625°C (or 898 K).



Figure 39. Relative Density and Pressure Curves for 625°C (898 K) MSPD (30 to 50MPa, Current-Insulated vs. Current-Assisted)

The relative density and densification rate evolution are plotted in the figure below for the 625°C (or 898 K) MSPD current-insulated and current-assisted experiments. Within each constant pressure section, the relative densities increased with decreasing densification rates. Every pressure shift lead to an instantaneous densification rate jump. The strain rate sensitivity component m was calculated based on those four densification rate inflection points for each type of MSPD. During the isothermal holding stage, the current-assisted MSPD experiment resulted in the higher relative density than the one achieved in the current-insulated MSPD experiment.



Figure 40. Isothermal Stage Relative Density and Densification Curves for 625°C (898 K) MSPD (30-50 MPa, Current-Insulated vs. Current-Assisted)

The densification rates versus densities for both the current-insulated and currentassisted 625°C (or 898 K) MSPD experiments indicate quasi-linear relationships. Generally, higher densification rates were observed to be correlated to higher temperatures and pressures at any specific density levels. The calculated strain rate sensitivity component m is plotted in the figure below. The *m* values were determined to be  $0.30 \pm 0.08$  and  $0.30 \pm 0.03$  for the current-insulated and current-assisted isotherms at 625°C (898 K), respectively, which correspond to the dislocation climb-controlled creep densification mechanism.



Figure 41. Strain Rate Sensitivity Component *m* of Current-Insulated (CI) and Current-Assisted (CA) MSPD (625°C or 898 K MSPD, 30-50 MPa)

#### 4.4.3 Discussion

The strain rate sensitivity m values were found to be approximately the same for the current-insulated as compared to the current-assisted SPS. The obtained assessment of the m value, while indicating the dominance of the dislocation climb mechanism, permits the assumption of the contribution of additional densification mechanisms during both the current-assisted SPS and the current-insulated SPS [155], such as grain-boundary sliding. In addition, higher density was observed for current-assisted SPS. There are several possibilities for the explanation of this phenomenon. First, Figure 40 shows that the densification rate for the current-assisted SPS is initially lower than in the case of the current-insulated SPS, and then in the course of the process the densification rate for the current-assisted SPS becomes higher than in the case of the current-insulated SPS. Second, there may be an additional term beyond the external stress term in the constitutive equation describing the densification process (such as a direct contribution of the electric current to the mass transport). One should also consider possible differences in the temperature distributions between the insulated and current-assisted cases, causing different extends of possible inaccuracy in the temperature measurement conducted at the die lateral surface points for the both analyzed cases.

The obtained results generally agree with the absence of a decisive impact of electric current on densification mechanisms during SPS of copper materials previously indicated in a number of publications [148] [170]. At the same time, the considerable difference of the densification rates for the current-assisted SPS and current-insulated

SPS in the beginning of the step-wise loading (see Figure 40) can be explained by the active formation of micro-contacts between powder particles during the current-assisted SPS, which prevents the inter-particle sliding and re-arrangement [171].

Chapter 4, in part, is a reprint of the content as it appears in Journal of Materials Science

W. Li, E. A. Olevsky, J. McKittrick, A. L. Maximenko and R. M. German, "Densification Mechanisms of Spark Plasma Sintering: Multi-Step Pressure Dilatometry," Journal of Materials Science, vol. 47, no. 20, pp. 7036-7046, 2012.

The author of the dissertation is the primary investigator and author of the paper.

# Chapter 5 Simulation of SPS Process

## 5.1 Initial and Boundary Conditions

From the SPS tooling geometry, FEM model was constructed. The die surface at central plane is the point for pyrometer or thermocouple temperature monitoring.

Since this structure is axial and central plane symmetric, only an axial 2D symmetric geometry model that covers <sup>1</sup>/<sub>4</sub> of the cross sectional plane is needed. This helped to save a lot of computation power.



Figure 42. Axial 2D Symmetry Model Configuration (1/4 of the cross sectional plane)

After setup the geometry model, next step will be defining the initial and boundary conditions, as well as the material properties, to solve the differential governing equation with the models described in the Chapter 3.

In mechanical field: initial and boundary conditions are needed for stress, strain, strain rate, friction at boundaries, porosity, and grain size.

In electrical field: initial and boundary conditions are needed for current, voltage, insulation, and contact resistance,

In thermal field: initial and boundary conditions are needed for temperature, radiation, and contact conduction.

#### **5.1.1 Mechanical Initial and Boundary Conditions**

Initial conditions include zero strain rates throughout all of the involved components, the assumed uniform distribution of initial porosity through the specimen, and the assumed uniform distribution of initial grain size throughout the specimen

The applied mechanical boundary conditions include the uniform load on the top of the large graphite spacer contacting the electrode and the friction force exists at the specimen - graphite die wall as well as the specimen – graphite punch end interfaces. This is shown in the following figure.



Figure 43. Mechanical Boundary Conditions Schematics (unmarked external boundary surfaces are free)

When the powder specimen is uniaxial pressed in the graphite die, it will expand radially and need substantial radial stress to restrain the specimen within the die without breaking. This radial stress provides the substantial normal contact stress which leads to the generation of vertical axial friction stress opposite to the moving direction of the punch. The friction stress along the die wall retards the densification of the specimen along the edges driven by the motion of graphite punch moving in the vertical direction.

Friction force also exists at the interface between the specimen and graphite punch end surface and the stress is along the radial inward direction.

To model the friction effect Coulomb friction is adopted as the following:

$$\sigma_f = \mu \sigma_n$$

where  $\sigma_f$  is the friction stress,  $\mu$  is the Coulomb frictional coefficient, and  $\sigma_n$  is the normal stress. In this study, a constant frictional coefficient of 0.1 is used for simplicity, because there is a layer of graphite foil wrapped on the specimen surfaces with contact enhancement and lubrication effects.

The initial relative density and initial grain size are considered as the input conditions for the consolidation models. The effective initial strain rate is set as an infinitesimal numerical value of  $10^{-12}$  [1/s] for the specimen to avoid infinity effective viscosities which will freeze the deformation of the SPS setup.

#### 5.1.2 Electrical Initial and Boundary Conditions

Initial conditions include zero electric current density and zero electric potential throughout all of the involved components.

Boundary conditions for electric current constitutive modeling are simple. An electric potential function is applied on the top surface of the large graphite spacer (where the electrode is located). This electric potential function can be defined as a linear stepwise function or can be an interpolation function from direct experiment measurement (or PID control signal). For all of those undefined external boundaries, electrical insulation is configured.

In the current study, the axial symmetric half model is used. Therefore the applied electric potential between the top spacer surface and the tooling (and specimen) cocentral plane is half of the experiment applied voltage.

Approximate observations have been obtained by Wei and Guitini's experiments in Powder Technology Lab, SDSU: the contact resistance will be average resistance of the die and the specimen multiplied by a coefficient between 0 and 1, and the coefficient is dependent on the contact pressure, which is around 1/60 [1/MPa] multiplied by the stress.



Figure 44. Electrical Boundary Conditions Schematics (unmarked external boundary surfaces are electrical insulated)

## 5.1.3 Thermal Initial and Boundary Conditions

Initial condition is that 300 K initial temperature is uniformly distributed throughout all of the involved components.

Boundary conditions are set as:

- Room temperature tap water cooled electrodes, 300 K constant temperature on the top surface of the large graphite spacer.
- Ambient chamber space temperature is measured and set up as 300 K for radiation simulation of the graphite tooling surface during SPS.



Figure 45. Thermal Boundary Conditions Schematics (unmarked external boundary surfaces are radiation surfaces to 300 K environment)

# **5.2 Material Properties Dependence**

Linear approximation of material property dependence on porosity is used as the following [39] [55] [87]:

$$\sigma_e = \sigma_{e0}(1-\theta)$$

where  $\sigma_{e0}$  is the electrical conductivity of fully dense material.

$$k = k_0(1 - \theta)$$

where  $k_0$  is the thermal conductivity of fully dense material.

Material properties dependence on temperature considered in this study was based

## 5.3 Electrical – Thermal – Mechanical Models Coupled Analysis

on the approximated polynomial functions built in COMSOL® 4.3a [172].

Summary: By coupling all of the following constitutive equations and solve them simultaneously in COMSOL® 4.3a, the FEM analysis for a fully coupled SPS modeling frame work can be performed.

Continuum mass conservation equation:

$$\dot{e}_{total} = rac{\dot{ heta}}{1- heta}$$

Deformation and densification constitutive equation:

$$\dot{\varepsilon}_{ij} = \frac{W}{9\sigma(W)\psi} \delta_{ij}(\sigma_{kk} - 3P_L) + \frac{W}{\sigma(W)\varphi} \left(\sigma_{ij} - \frac{1}{3}\sigma_{kk}\delta_{ij}\right)$$

Grain growth constitutive equation:

$$\dot{G} = \frac{dG}{dt} = \frac{G_0}{2\theta} \left(\frac{\theta_0}{\theta}\right)^{\frac{1}{2}} \left|\dot{\theta}\right|$$

Joule heating constitutive equation:

$$J_h = \left(\sigma_e + \epsilon_r \frac{\partial}{\partial t}\right) E_{epot}$$

Heat transfer constitutive equation

Conduction:  

$$\rho_m C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + \nabla \cdot J$$
Radiation:  

$$-\boldsymbol{n}_N \cdot (-k \nabla T) = \epsilon \sigma_{SBC} (T_{amb}^4 - T^4)$$

# 5.4 Consolidation Simulation of SPS

By substituting the material parameters determined in section 4.3 listed in Table 6

and

 Table 7, the simulation and experiment results comparison is obtained for SPS of

 copper powder in the figure below. This particular simulation considers only the

consolidation part of the constitutive models, therefore, homogeneous heating condition is assumed. But for copper powder, this is still valid to a very reasonable extent because the high thermal conductivity in a small specimen (15 mm diameter by 3 mm thickness) minimizes the thermal gradient.



Figure 46. Experiment and Simulation Temperature Profiles, and Relative Density Evolution for Copper Powder with Mean Particle Size of 45 μm, SPS at 625°C (898 K) by 100°C/min Heating Rate, under 20 MPa (R<sup>2</sup> = 90.4%)

The R-square for the fitting between experiment and simulation data is high and up to 90.4%. This is without further adjustment of the determined material parameters.

The calculations are conducted for the same heating condition but under different mechanical uniaxial stresses ranging from 20 to 80 MPa. The obtained results are plotted in the following figure to demonstrate the effect of mechanical pressure on copper powder densification by SPS.



Figure 47. Loading Stress Effects on Consolidation of Copper Powder with Mean Particle Size of 45 μm, at 625°C (898 K) by 100°C/min Heating Rate

As can be observed, the higher the mechanical pressure is, the higher the predicted relative density. However, the improvement extent of specimen relative density decays at higher mechanical pressures. This reflects the nonlinear relationship between the pressure and relative density for copper powder densification.

Another consolidation mapping calculation has been done to study the copper powder densification behavior under isothermal conditions with different temperature and mechanical uniaxial stress combinations. Two dwelling time cases, one for 100 seconds and the other for 1000 seconds, are shown in the following plot. This type of mapping can help to design the experiment to achieve the desired final porosity by using the optimal dwelling temperature (limited by the tooling material and device power) and mechanical pressure (limited by the tooling material) with given initial porosity.



Figure 48. Isothermal Porosity Mapping for Copper Powder with Mean Particle Size of 45 μm, at Loading Stress and Temperature Combinations, Green for 100 s and Gold for 1000 s Dwelling Time

### 5.5 Electrical-Thermal Models Coupled Simulation of SPS

The tooling material property and the three studied representative materials properties are listed in the following table. Simulations have been conducted to study the electrical-thermal behaviors of materials with three substantially different electrical conductivities. It is note that all of these properties are room temperature properties for fully dense materials reported in handbooks. The property dependences on microstructure, temperature and pressure are temporarily simplified and neglected at this phase. This study started from the simplified analysis to evaluate the basic electricalthermal responses of the SPS tooling and specimen setup.

 Table 8. Material Properties (Room Temperature Reported) used for Electric-Thermo Simulation

 [172]- [174]

Parameter \ Material	Graphite	Copper	Alumina	Silicon
Density [g/m <sup>3</sup> ]	1.95	8.96	3.96	2.33
Young's modulus [GPa]	25	125	300	188
Poisson's ratio [1]	0.3	0.35	0.222	0.275
Electrical conductivity [S/m]	$3.0 \times 10^{3}$	$5.998 \times 10^{7}$	$1.0 \times 10^{-5}$	$1.0 \times 10^{-2}$
Relative permittivity [1]	1	1	11.5	11.68
Specific heat capacity at constant pressure [J/kg/K]	710	385	900	707
Thermal conductivity [W/m/K]	150	400	27	149
Coefficient of thermal expansion [1/K]	4.3×10 <sup>-6</sup>	17.3×10 <sup>-6</sup>	8.0×10 <sup>-6</sup>	2.6×10 <sup>-6</sup>
Surface emissivity [1]	1	1	0.8	0.93
Melting Temperature [K] (°C)	4100 (2827)	1356 (1083)	2327 (2054)	1683 (1410)

The electrical conductivities of different materials are firstly normalized to copper which is the highest among the studied materials. The relative electrical conductivities are plotted in the following diagram in a logarithm scale to show the relative difference between different materials. Since vanadium carbide and zirconium carbide are the two materials relevant to the application section of this research, their values are compared in parallel together.



Figure 49. Normalized Electrical Conductivity Comparison for Different Materials

It is found that the electrical conductivity order from best to the poorest is as the following: copper, vanadium carbide, graphite, silicon, zirconium carbide, and alumina.

Other material properties listed in the Table 8 are also normalized to the material which has the highest value in corresponding category so that the relative difference can be seen more clearly. Again, the vanadium carbide and zirconium carbide material properties are compared and listed together. The normalized results are plotted in the following diagram.



Figure 50. Normalized Properties Comparison between Different Materials

Based on the above listed material properties, FEM simulations have been run to study the electrical-thermal behaviors of different systems. The boundary conditions are the same as what were described in section 5.1, except that the specimen is set to fully dense without densification and the applied voltage function on the top is increasing from 0 to 4 volts in 6 minutes and dwelling for 8 minutes.

The following schematic shows the interested spots for temperature analysis.



Figure 51. Schematic of Analyzed Internal and Symmetry Plane Boundaries of SPS Setup

The regions studied for temperature distribution include points' temperature comparison, continuous symmetric boundaries and internal boundary temperature distribution.

Points' comparison: specimen center, specimen edge and die surface which are on the radial central plane (as marked in Figure 51). The temperature and voltage results are plotted in the following diagram with the evolution of time.



Figure 52. Temperature Evolution with Time for Copper, Alumina, Silicon at Die Surface, Specimen Edge and Specimen Center; Applied Voltage Evolution is Shown Together

It is found that, alumina and silicon specimens achieve lower final temperature than copper heated under the same condition. The temperature evolutions with time are very close for alumina and silicon under the tested conditions.
The individual location temperature for different materials is plotted in the following column diagram to compare which location is warmer at the last moment of 840 seconds.



Figure 53. Temperature at Die Surface, Specimen Edge, and Specimen Center for Copper, Alumina and Silicon at 840 seconds under 4 volts Voltage

It is also found that for conductive copper, the specimen center is warmer than the die surface, which means the thermocouple measurement tends to underestimate the actual consolidation temperature inside the specimen. For nonconductive alumina and semi-conductive silicon, the specimen center temperature is lower than the die surface temperature, which indicates that the thermocouple measurement tends to overestimate the actual consolidation temperature inside the specimen. This conclusion is limited to the geometry and dimension studied in this research. The temperature is size and geometry dependent [51] [73].

Continuous temperature distribution along the radial central symmetry plane (as marked in Figure 51): the temperature distributions at 600 seconds along the radial location on the radial central symmetry plane are plotted for copper, alumina and silicon in the following diagram. 0 mm is the specimen center and the 15 mm is the die surface on the central plane. It is found that for copper, the center is always warmer than the edge. For the alumina and silicon, the surface is warmer than the specimen center, and the interface between the specimen edge and the die wall is the warmest spot.



Figure 54. Radial Temperature Distribution within the Radial Central Symmetry Plane for Different Material System SPS Setups at 4 volts Equilibrium Status (600 s); 0 mm is the location of specimen center, 7.5 mm is the location of specimen edge – internal die wall, 15 mm is the location of the external die surface.

Continuous temperature distribution along the axial symmetry plane (as marked in Figure 51): the temperature distributions at 600 seconds along the axial symmetry plane are plotted for copper, alumina and silicon in the following diagram. 0 mm is the location of the specimen center, 5 mm is the location of specimen top surface – punch interface, 25 mm is the location of punch – small spacer interface, 45 mm is the location of small – medium spacers interface, 65 mm is the location of medium – large spacers interface, 85 mm is the location of large spacer – electrode interface. It is found that for copper, the

center is as warm as the top surface due to high thermal conductivity. For the alumina and silicon, the top surface is cooler than the specimen center due to poor thermal conductivity.



Figure 55. Axial Temperature Distribution for Different Material System SPS Setups at 4 volts Equilibrium Status (600 s); 0 mm is the location of the specimen center, 5 mm is the location of specimen top surface – punch interface, 25 mm is the location of punch – small spacer interface, 45 mm is the location of small – medium spacers interface, 65 mm is the location of medium – large spacers interface, 85 mm is the location of large spacer – electrode interface.

Continuous temperature distribution along the axial parallel boundary on the internal die wall surface (as marked in Figure 51): the temperature distributions at 600

seconds along the axial parallel boundary on the internal die wall surface are plotted for copper, alumina and silicon in the following diagram. 0 mm is the location of the middle plane on the specimen edge, 2.5 mm is the location of top plane on the specimen edge, 15 mm is the location where die-top-surface meets die-internal-wall-surface. It is found that for copper, the middle point is as warm as the top surface along the specimen edge due to high thermal conductivity. For the alumina and silicon, the top surface is cooler than the specimen middle plane along the edge due to poor thermal conductivity. Those observations are similar to the situations along the central axis. It is also found that the top surface at the die is cooler than the middle plane due to the radiation heat loss at the top surface.



Figure 56. Axial Parallel Temperature Distribution along the Die Internal Wall for Different Material System SPS Setups at 4 volts Equilibrium Status (600 s); 0 mm is the location of the middle plane on the specimen edge, 5 mm is the location of top plane on the specimen edge, 15 mm is the location where die-top-surface meets die-internal-wall-surface.

Simulation animation shots at different time, middle of heating ramp (250 s), before (300 sec) and right after the end of heating ramp (360 s), middle of isothermal holding (400) are shown for the electric current density distribution (Figure 57) and temperature distribution (Figure 58).



Figure 57. 1000 K Electric Current Density Evolution Diagram: top copper, middle alumina, and bottom silicon; left 200 s, center-left 250 s, center-right 300 s, and right 400 s; current density color scale bar is 0 to  $8 \times 10^5$  A/m.

The electric current density color scale upper and lower boundary limits are  $8.0 \times 10^5 \frac{A}{m^2}$  and  $0 \frac{A}{m^2}$  respectively.



Figure 58. Temperature Evolution Diagram: top copper, middle alumina, and bottom silicon; left 200 s, center-left 250 s, center-right 300 s, and right 400 s; temperature color scale bar from 300 to 1000 K.

The temperature color scale upper and lower boundary limits are 1000 K (827°C)

and 300 K (26°C) respectively.

## 5.6 Fully Coupled Simulation of SPS

300 K

Distributions of electric current density, temperature, stress, porosity, and grain size through the cross section surface of SPS tooling-specimen setup are shown and discussed.

Copper SPS case study:



Figure 59. Schematic of Mesh Mapping for FEM Simulation

Extra fine size is used with maximum element size of 1.7 mm, and minimum element size of 6.38  $\mu$ m. Maximum element growth rate is 1.2, and the resolution of curvature is 0.25. Resolution of narrow regions is 1, and number of iterations is 8. Maximum element depth to process is 8. Complete mesh consists of 723 elements. Square mapped element is used.



Figure 60. Copper SPS Electric Current Density Distribution and Deformation at 500 s, under 3.53 kN Load, 2.1 volts Voltage, Color Scale Bar from 6.7 A/m<sup>2</sup> to 1.9×10<sup>7</sup> A/m<sup>2</sup>

The above figure shows high electric current density at the punch – die wall interface and punch spacer interface.



Figure 61. Copper SPS Temperature Distribution and Deformation at 500 s, under 3.53 kN Load, 2.1 volts Voltage, Color Scale Bar Ranging from 300 K (25°C) to 907 K (634°C).

The above figure shows the highest temperature is at the punch – spacer interface, which is consistent as the electric current density distribution result. This information gives a cautious signal for the prevention of tooling and system overheating.



Figure 62. Copper SPS Von Mises Stress Distribution and Deformation at 500 s; under 3.53 kN Load, 2 volts Voltage, Color Scale Bar Ranging from 0 MPa to 44 MPa.

The above figures shows the high von mises stress at the specimen – die wall interface and the corners of the punch. This information gives a clue for the mechanical failure analysis for graphite tooling used for SPS processing.



Figure 63. Copper SPS Zoomed in Specimen Relative Density Distribution and Deformation at 500 s, under 3.53 kN Load, 2.1 volts Voltage, Color Scale Bar Ranging from 84.5% to 84.6%.

The above figure shows that there are high density regions at the specimen top

surface due to the temperature difference between the center and the edge.



Figure 64. Copper SPS Zoomed in Specimen Grain Size Distribution and Deformation at 500 s, under 3.53 kN Load, 2.1 volts Voltage, Color Scale Bar Ranging from 68.0 μm to 68.1 μm.

The above figure shows that the grain size at the specimen edge is smaller than the grain size at the specimen center due to the temperature difference as well as the relative density difference.



Figure 65. Copper SPS Specimen Center Point Average Grain Size Evolution vs. Relative Density from Fully Coupled FEM Simulation for Copper Consolidated at 625°C (898 K) with 100°C/min heating rate, 60 MPa, for 8 minutes.

Grain size relationship with relative density is plotted in the above graph for the

same analysis. This is one individual point evolution at the specimen center.



Figure 66. Copper SPS 3D Temperature Distribution and Deformation at 750 s, under 3.53 kN Load, 2.1 volts Voltage, Color Scale Bar Ranging from 298 K (25°C) to 898 K (625°C).

The 3D temperature distribution and the deformation from the same analysis are shown in the above figure.

This study successfully coupled the consolidation, grain growth, mechanical, electrical, and thermal constitutive relationships for spark plasma sintering.

# Chapter 6 Application: Fabrication of Functionally Structured Mono-Carbide by Spark Plasma Sintering for the Nuclear Fusion Pellet Surrogate Study

## 6.1 Background

In most industrial applications a major task of powder processing, including Spark-Plasma Sintering (SPS) technology, is to create a product with maximum possible density. This task is consistent with the nuclear industry's demand for the consolidation of dense nuclear fuel, where the goal of achieving high content fission atoms in a unit with specific volume is very important. Presently, however, new tasks have emerged [175], where ensuring very high fuel burn-up of 20 to 30% supersedes other requirements. Naturally high burn-up is associated with high fuel swelling, which results in high hoop stresses in a fuel cladding.

The high temperature fuel, in particular uranium mono-carbide (UC), which is capable to sustain these conditions should:

- accommodate axial and radial forces in the fuel and cladding from UC swelling under burn-up up to 20% and temperatures up to 1500°C.
- accommodate the large quantity of fuel in a compact reactor to sustain 20 to 30 years operation.
- maintain mechanical integrity under high burn-up conditions, including high temperature, for long operating time in fast neutron spectrum.

The respective solution for the UC fuel material design should have the following features:

- Possess optimal microstructure that facilitates gaseous and volatile fission products' release to reduce swelling.
- (2) Provide internal voids to accommodate swelling within a fuel pellet.
- (3) Vent gaseous fission products released from fuel pellets to prevent high internal pressures in the fuel elements.
- (4) Enable controlled and limited swelling inside SiC composite cladding.

A fuel that incorporates these features should have large fraction of connected pores in the fuel material to allow fission product escaping from the fuel body to free space in the fuel rod where the gas can be removed so that the gas pressure in the fuel rod can be kept at low level even under high fuel burn-up. The microstructure arrangement enabling these capabilities is referred here as a bi-porous structure (see Figure 67). One method for providing this feature is to fabricate fuel spherical kernels with internal porosity and then sinter these spheres into fuel bodies with controlled, connected flow paths for the fission product gases to escape. The inter-sphere pores should provide volume for the accommodation of the fuel swelling. While the pores allow the gas release and the swelling accommodation, they reduce the amount of the available fuel, thereby reducing the energy generation. An optimum structure topology should be sought among structures which maintain low swelling rate, while providing needed power density.



Figure 67. Spherical Kernel based Annular Fuel Pellet

The emerging spark plasma sintering technology looks promising for the fabrication of stable porous ceramic structures. More effective densification is expected

due to a number of SPS-induced effects: high heating rates, which may enable higher sinterability; high local temperature gradients, which provide conditions for thermal diffusion; highly non-uniform local temperature distributions, which may cause melting within inter-particle contacts. Spark plasma sintering devices just started their way to nuclear material laboratories, and their current applications for fuel sintering purposes are still limited, but investigations are definitely worthwhile.

The present study employs vanadium mono carbide (VC) as a surrogate material for uranium carbide to investigate the potential of spark plasma sintering as a hot consolidation technique to densify the carbide fuel pellets for the next generation of nuclear power reactor applications. The reason for this choice is due to exactly the same cubic-cF8 crystal structure,  $Fm\bar{3}m$  No. 225 space group, and a number of similar physical properties between vanadium carbide and uranium carbide (see Table 9) [89] [176]-[180]. It should be also noted that, according to the reported property summary for vanadium carbide, this material has low thermal conductivity and thermal expansion coefficient, but high electrical conductivity and ultra-high melting temperature, which makes it very suitable as a high temperature conductor, especially for the applications in the thermo-electro conversion systems [181].

Property \ Material	Unit	Vanadium Carbide	Uranium Carbide
Chemical Formula		$V_8C_7$	UC
Crystal Structure		cubic, cF8	cubic, cF8
Space Group		Fm3m, No. 225	Fm3m, No. 225
Density	$[g/cm^3]$	5.77	13.63
Molar Mass	[g/mol]	62.95	250.04
Bulk Modulus	[GPa]	683	147
Shear Modulus	[GPa]	228	80
Heat Capacity - Mass	[J/g/K]	0.530	0.202
Heat Capacity - Volume	[J/cm <sup>3</sup> /K]	3.058	2.753
Heat Capacity - Mole	[J/mol/K]	33	51
Thermal Conductivity	[W/m/K]	39	19
CTE	[10 <sup>-6</sup> /K]	7.20	0.12
Melting Temperature	[K]	3083	2660
Electrical Conductivity	$[\mu\Omega/cm]$	37	60

Table 9. Vanadium Mono-Carbide and Uranium Mono-Carbide Physical Properties at 25°CComparison [89] [176]- [180]

One recently submitted paper by the authors of this paper reported free sintering result for the same vanadium mono-carbide powder used in this present study [182]. In that study , a green vanadium mono carbide pellet was cold pressed into 52% relative density, and then 10°C/min heating was used to ramp to 1550°C (maximum allowable dilatometer temperature) dwelling for 3 hours in vacuum (10 Pa). The final sintered density was not changed at all. The authors found it was impossible to densify binder-free vanadium mono carbide by conventional sintering. The above result further indicates that a much more powerful technique such as SPS is needed to achieve the densification goal.

This chapter is organized as follows. Section 6.2 describes the materials and processing in the framework of the conducted research to successfully consolidate additive-free (binder-free) vanadium mono-carbide. In Section 6.3, the results of the characterization of the density, microstructure, and composition phases of the vanadium carbide pellets processed by SPS are provided. The measured physical properties including transverse rupture strength, hardness, volume specific constant pressure heat capacity, thermal conductivity, porosity, and permeability are reported in Section 6.3 too. Section 6.4 includes the overall discussion of the obtained research results.

## 6.2 Material and Experimentation

#### 6.2.1 Materials Processed by Spark-Plasma Sintering

After dry milling in the WC-Co container by the WC ball, vanadium monocarbide ( $V_8C_7$ ) was received in the form of mixture including 5 to 10 µm powder and agglomerated particles of 200 to 300 µm (see Figure 68) with tap density of 1.97 g/cm<sup>3</sup> (34%). The material composition was identified by both combustion and X-Ray diffraction methods. Oxygen content was 0.017 wt.%. X-Ray fluorescent analysis revealed Ti, Fe, Ni, Ge, Ca, Al impurities at the level from 0.1 to 0.3%. Because the agglomerated powder has the potential to produce the desired bi-modal porous structure (favoring fission gas evolution while maintaining relatively high thermal conductivity), the as-received powders were used directly, with no special treatment before SPS processing. The powder characteristics are reported in Table 10.



Figure 68. Agglomerated Vanadium Mono Carbide Powder, (a) 100X-Scale Bar 500 μm; (b) 5000X-Scale Bar 10 μm; (c) 1000X-Scale Bar 50 μm

Carbide Powder	Vanadium Carbide
Vendor	Asian Light
Designation (lot)	VC120206
Purity	> 99%
Fabrication Method	Dry Ball Milled
Particle Size (µm)	
$D_{10}$	26
D <sub>50</sub>	232
D <sub>90</sub>	533
Tap Density (g/cm <sup>3</sup> )	(34.1% TD) 1.97
Theoretical Density (g/cm <sup>3</sup> )	5.77
Melting Temperature [K]	3083

**Table 10. Vanadium Mono Carbide Powder Characteristics** 

A laser diffraction particle size and image analyzer (S3500SI, Microtrac, Japan) was used to characterize the particle size distribution for different powders. The used laser in the micro size detector has a wavelength of 405 nm. 10% of nonionic hydrophilic surfactant Triton X100 was added to the deionized water to disperse the powders effectively and then test them in the wet mode. Before the powder entering into the laser chamber, further dispersion by ultrasonic vibration at 40 Watts for 60 seconds was applied to guarantee obtaining the accurate particle size distribution. The particle size distribution result is shown in Figure 69.



Figure 69. Vanadium Mono Carbide Powder Particle Size Distribution

The XRD analysis under the following configuration: copper target, K-Alpha band (1.54 Am), and generator setting of 40 mA at 45 kV, has been used to identify the exact phase of the vanadium mono carbide powder. According to the results plotted in Figure 70, the  $V_8C_7$  stoichiometry has been identified for this powder.



Figure 70. XRD Scanning of Vanadium Mono Carbide Powder (V<sub>8</sub>C<sub>7</sub> Ref. Code 00-023-1468)

#### 6.2.2 Consolidation of Vanadium Carbide Powder

A spark-plasma sintering apparatus (Dr. Sinter 515 SPS, Fuji Electronics Industrial Co, Ltd., Japan) with pulse duration of 3.3 ms was used. The machine default pulse sequence consisting of twelve pulses (39.6 ms) followed by two periods (6.6 ms) of zero current was chosen and termed 12:2, while the detailed effects of this configuration could be studied at the next investigation stage. Pellets of 15 mm in diameter and 4.00 gram in mass were prepared in vacuum, under uniaxial mechanical pressures of 20, 25, 60, or 75 MPa, applied from room temperature, and held constant until the end of the consolidation period. The temperature was measured by an optical pyrometer focused on

the surface of the graphite die and automatically regulated from 580°C to the final sintering temperatures of 1100, 1200, 1300 or 1400°C (the preliminary objective of the conducted consolidation was the fabrication of vanadium carbide pellets with relative density of about 75%. The heating rate was set to 100°C/min, which enabled high efficiency consolidation cycle while avoiding the undesired localized inhomogeneous overheating. The following hot consolidation regime has been used: (i) four minutes to heat from room temperature up to 580°C, and then one minute was given to increase the temperature from 580°C to 700°C to achieve a stabilized temperature condition; (ii) heating with the rate of 100°C/min from 700°C to the final hot consolidation temperature  $(T_F)$  and holding with the time periods of 5, 10, 15 or 30 min at this temperature; (iii) an on/off pulse sequence of 12:2 was utilized; (iv) vacuum condition of about 50 Pa was used for all the experiments from the processing beginning till the end. At the end of the holding time, the current was shut down, yielding a cooling rate of about 300°C/min from T<sub>F</sub> down to around 600°C. Another 30 min were reserved for cooling the pellet specimen to room temperature, and then the applied mechanical pressure was released afterward. The tooling and the pellet specimen configuration is shown in Figure 27.

## 6.2.3 Characterization of Processed Specimens

The characterization of the spark-plasma sintered vanadium carbide pellets consisted of the density measurements, microstructural analysis using Scanning Electron Microscopy (SEM), the determination of characteristic phases using XRD, mechanical properties measurements including transverse rupture strength and scale A Rockwell hardness, thermal properties measurements including constant pressure volume specific heat capacity and thermal conductivity, porosity measurement by pycnometry, and permeability measurement.

Since the porosity of the processed pellets was relatively high, the Archimedean immersion method was difficult to apply. The density of the vanadium carbide pellet specimens was measured by geometry method (accurate for the regular cylindrical pellet specimen shape). The pellet specimens were weighed three times on a high accuracy scale (resolution  $\pm$  0.0001 g); the diameter and height of the cylindrical pellet specimens were measured at three different locations; and the average density was calculated accordingly.

For the microstructural observations using SEM, the pellet surfaces were polished with successively smaller grinding medium down to  $0.04 \ \mu m$  of colloidal silica. Grain

boundary relief was produced by deep etching of VC pellet in the mixed HCl-HNO<sub>3</sub>-HF (10 : 20 : 10 ml) solution for 16 hours. Using the secondary electron mode in FE-SEM (FEI Quanta 450), micrographs of vanadium carbide pellets were taken and the average grain size was estimated from each micrograph by the line intercept method [183]. To determine the characteristic phase after sintering, X-ray diffraction (Panalytical, XPert Pro MRD) was performed on the pellets.

Measurement results for mechanical and thermal properties, porosity and permeability data are described in Section 6.3.

## 6.3 Processed Vanadium Carbide Pellets' Characterization Results

## **6.3.1 Structure Characterization Results**

## Relative density of the processed pellets:

The conducted tests indicate that, given a well-controlled SPS process, the desired pellet density (around 75%) can be achieved for the utilized VC agglomerated powder. The measured relative density data obtained for various SPS conditions are listed in Table 11.

Temperature [°C]	Stress [MPa]	Time [min]	Relative Density (±0.5%)
1100	20	5	57.5%
		10	60.3%
		30	61.7%
	25	10	62.4%
	60	5	64.4%
		15	67.8%
	75	5	68.5%
1200	20	10	65.5%
	25	10	65.1%
	60	5	70.2%
1300	20	5	67.1%
		15	68.0%
	25	5	68.4%
		10	75.0%
	60	15	77.2%
		30	79.5%
	75	10	79.2%
1400	20	5	69.7%
	60	10	80.1%
	75	30	84.3%

Table 11. SPS Consolidation Results for VC Powder Processed with 100°C/min Heating Rate

The data from Table 11 are selectively plotted in the form of a diagram (see Figure 71 to further explore the trend of the consolidated relative density dependence on temperature, pressure, and dwelling time. It is noticed that higher temperature, longer dwelling time and higher mechanical stress generally produce specimens with higher relative density, as expected.



Figure 71. Relative Density versus (a) Temperature, (b) Pressure, and (c) Time for SPS Processed VC Pellets

#### Processed pellets' microstructure:

Figure 72 reveals the grain size and pore size distribution in the processed vanadium carbide SPS pellets. The observed grain size falls within the range of 10 to 15  $\mu$ m without significant growth for low to high density specimens. However, the reduction of the pore size is obvious as seen in Figure 72. In the achieved relative density range, the grain growth is very slow due to the grain boundary pinning effects imposed by the relatively large amount of pores. The initial agglomeration in the green powder

disappears after SPS consolidation. The sintered grain size standard deviation is in a much smaller range ( $\pm 10 \ \mu m$ ) comparing to the starting powder ( $\pm 100 \ \mu m$ ) indicating no bimodal distribution characteristics.



Figure 72. Cross Sectional Surface (1000X Magnification) of VC Powder Consolidated under Different Conditions (a) 1100°C, 75 MPa, 5 min - with 69.7% Density; (b) 1300°C, 60 MPa, 30 min with 79.5% Density; (c) 1400°C, 75 MPa, 30 min - with 84.3% Density

Phase composition:

XRD analysis was used to determine the characteristic phases before and after SPS processing. Figure 73 shows the XRD pattern for the green powder and a pellet with 84.3% relative density sintered at temperature of 1400°C under 75 MPa pressure with 30 min holding time.



Figure 73. Vanadium Mono Carbide 84.3% Dense Pellet and Powder XRD Scanning Results Comparison

The crystal structure characteristic peaks for the two considered samples match very well indicating that the SPS process did not change the vanadium carbide powder characteristic phase present at room temperature. However, this does not mean that there was no phase change at high temperature during hot consolidation. Inspections of the constant pressure volume specific heat capacity data (see Figure 78) and of the phase diagram reported in the literature [180] indicate that there is a phase transformation from ordered to disordered structure around 1000°C. After cooling to the room temperature, the sintered pellet goes back to its original phase composition.

Porosity in the structure consists of two types, open porosity and closed porosity.

Total Porosity = 100% - Relative Density = Open Porosity + Closed Porosity

Pycnometer [184] was used to measure the closed porosity of the porous structure, and volumetric method was used to measure and calculate the total porosity. With the equation above, one can determine the fraction of open porosity within total porosity. The correlation between open porosity and relative density is plotted in Figure 74.



Figure 74. Open Porosity versus Relative Density for SPS-fabricated VC Pellets

The data are available only for relatively low density range (60 to 65%). In this range, open porosity contributes up to 90% of the total porosity.

Air was used as the pressurization gas to measure the permeability. The permeability test was conducted in the differential pressure range from 0 up to 100 kPa.

The average permeability versus different relative density is plotted in Figure 75. The permeability of porous structure drops as the relative density increases. Still, at density of 72%, the permeability is as high as 0.6 Darcy.



Figure 75. Permeability versus Relative Density for SPS VC Pellets
#### 6.3.2 Mechanical and Thermal Property Measurement Results

(1) Mechanical Properties of Processed Specimens

A customized Transverse Rupture Strength (TRS) procedure modified from ASTM C1499-09 Standard [185] was used. This procedure makes the approach more versatile for a range of pellet specimen sizes, particularly for difficult-to-machine materials like VC and processes like SPS where the processed specimen diameter is determined by the die size. The details of this testing method were firstly described in the listed reference [105]. The TRS loading rate configuration is: 0.001 in/sec (0.0254 mm/sec), on a conventional material testing frame (Model 5982, Instron, MA) with CMP 10V tool steel fixture set and 3 mm diameter WC indenter ball.

Transverse rupture strength of SPS-processed specimens is determined as:

$$\sigma_{TRS} = \frac{F}{h^2} \left[ (1+\nu) \left( 0.485 \log_{10} \frac{r_e}{h} + 0.52 \right) + 0.48 \right]$$
 Equation 32

where  $\sigma_{TRS}$  is the equivalent TRS value in MPa, *F* is the load in N,  $\nu$  is the Poisson's ratio (for VC is 0.35),  $r_e$  is the effective radius of a disk-shape sample (6.5 mm in the present tooling fixture), and *h* is the average thickness of the disk-shape sample in mm.

Olevsky had derived the Poisson's ratio for a porous material as follows [44]:

$$v_p = \frac{2 - 3\theta}{4 - 3\theta}$$
 Equation 33

where  $v_p$  is the Poisson's ratio for a porous material,  $\theta$  is porosity. The above expression was derived for perfect isotropic material with Poisson's ratio of 0.5 (when porous material skeleton is incompressible). In the present work the relative Poisson's ratio [186] (normalized to show the dependence only on porosity) is employed:

$$R_N = \frac{\nu_p}{\nu_{pi}} = 2\left(\frac{2-3\theta}{4-3\theta}\right)$$
 Equation 34

where  $R_N$  is the relative or normalized Poisson's ratio,  $v_{pi}$  is the Poisson's ratio for perfect isotropic materials (equal to 0.5). Then the actual Poisson's ratio for an imperfect porous material can be calculated as:

$$v = v_0 R_N = 2v_0 \left(\frac{2-3\theta}{4-3\theta}\right)$$
 Equation 35

where  $\nu_0$  is the Poisson's ratio for fully dense bulk materials, and  $\nu$  is the general material Poisson's ratio that is used for the transverse rupture strength calculation.

The mechanical properties for selected pellets are plotted in Figure 76. The data of four additional vanadium carbide pellets processed by traditional hot pressing are also included for checking the TRS dependence on a broader range of relative density. These hot pressing pellets data are from unpublished work from the author with the following processing parameters: peak temperature of 1400°C, heating rate of 14°C/min, uniaxial pressure of 20, 26 or 28 MPa, and dwelling time of 30 min.



Figure 76. Transverse Rupture Strength (TRS) versus Relative Density for SPS VC Pellet and Literature Reported TRS for TaC Specimen [102]

It is found that higher TRS strength and hardness are associated with higher relative density. It appears that vanadium carbide pellets' TRS has linear dependence on relative density.

The processed specimens were polished to 1000 grit SiC paper surface finish for conducting the hardness measurements.

To avoid the indentation on individual pores with off reading, the scale A Rockwell hardness (HRA) was evaluated at room temperature by a regular hardness tester (Rockwell 574, Wilson Instrument, Ontario, Canada) at minor load 10 kgf, major load 60 kgf, and dwell time for 2 seconds. There were three indents made in a row at the central area of each processed specimen to minimize the near edge effects.

The hardness value was observed to increase with the relative density (up to about 75%, see Figure 77).



Figure 77. Scale A Rockwell Hardness versus Relative Density for SPS-produced VC Pellet

Bulk vanadium carbide hardness is 2800 VHN [173] (about 136 HRA). The highest hardness achieved in the present study for a processed specimen with 75.7% relative density is about 64% (about 84 HRA) of the fully dense material.

(2) Thermal Properties of Processed Specimens

Vanadium Carbide constant pressure volume specific heat capacity and thermal conductivity were measured using a Netsch Differential Scanning Calorimeter (DSC) 404 F1 Pegasus and Laser Thermal Flash Analyzer (LTFA) 427, respectively. The measurements were performed on various VC specimens processed under different SPS conditions. The constant pressure volume specific heat capacity was determined by the differential ratio method using a sapphire standard. The constant pressure specific heat capacity data to determine thermal conductivity. All thermal analysis measurements have been conducted between room temperature and 1100°C in argon atmosphere.

Constant pressure volume specific heat capacity was found to increase with increasing relative density (see Figure 78). For a given volume, the higher relative density specimen has more substance (less voids) which requires more heat per degree of temperature increase. However, it should be noticed that samples sintered under different loads and for different times to similar densities show very similar constant pressure volume specific heat capacity. Therefore it is concluded that the different SPS processing could yield different bulk densities, but vastly different processing conditions used to achieve the same density do not produce an identifiable difference in constant pressure volume specific heat capacity.



Figure 78. Constant Pressure Volume Specific Heat Capacity versus Temperature for SPS-fabricated VC Pellets with Different Relative Density and the Bulk VC Reference Curve [180]

There are two other important observations for the obtained constant pressure volume specific heat capacity data. One is that constant pressure volume specific heat capacity is higher at higher temperatures before phase transformation taking place. The other observation is that at around 1000°C, the constant pressure volume specific heat capacity reached a peak point and then decreased sharply. This is associated with the exothermal phase transformation from ordered to disordered status occurring within the

vanadium carbide structure. Debye temperature is not reported for this material system so far [187].

In the laser flash method, the derivation of thermal diffusivity and constant pressure volume specific heat capacity, are based on the measurement of the rising temperature on the back surface of a sample caused by a pulsed laser beam on the sample's front surface. The measurement is performed at each temperature point and the thermal conductivity at each temperature is calculated by using the following equation:

$$k_{tc} = \alpha_{TD} C_{pV}$$
 Equation 36

where  $k_{tc}$  is the thermal conductivity,  $\alpha_{TD}$  is the thermal diffusivity,  $\rho$  is the processed specimen density,  $C_{pV}$  is the constant pressure volume specific heat capacity.

The thermal diffusivity is given by the following equation:

$$\alpha_{TD} = 0.1388 \frac{L^2}{t_{\frac{1}{2}}}$$
 Equation 37

where  $\alpha_{TD}$  is the thermal diffusivity, *L* is the thickness of the sample,  $t_{1/2}$  is the time of the half maximum (the time for the rear surface temperature to reach 50% of its maximum value).

The constant pressure volume specific heat capacity  $C_{pV}$  is given by the following equation:

$$C_{pV} = \frac{\rho Q}{\Delta T \cdot M}$$
 Equation 38

where  $\rho$  is the material density, Q represents the energy of the pulsed laser beam, which can be determined by comparing the maximum value of the temperature rise with that of a reference temperature, M is the mass of the processed specimen, and  $\Delta T$  is the maximum value of the temperature rise.

By multiplying thermal diffusivity with constant pressure volume specific heat capacity, thermal conductivity was calculated and plotted in Figure 79.



Figure 79. Thermal Conductivity versus Temperature for SPS-fabricated VC Pellets with Different Relative Density

Thermal conductivity was found to increase with higher relative density due to the reduction of voids in the processed specimens, and with higher temperature due to the larger excited atom population. Similarly to constant pressure volume specific heat capacity, the thermal conductivity is strongly dependent on relative density of the specimen, which can be manipulated through adjustment of the SPS processing parameters. However, if different parameters are used to achieve the same density, no measurable difference in thermal conductivity is observed.

# 6.4 Simulation of Vanadium Carbide Powder Consolidation

The same MSPD approach is applied to VC system to determine the strain rate sensitivity from Equation 27.

By using the determined strain rate sensitivity value, the RHS of Equation 28 is plotted against the reciprocal of temperature in the following figure, and the data is fitted by linear equation.



Figure 80. RHS of Equation 28 Plotted Against the Reciprocal of Absolute Temperature for Vanadium Carbide Powder with Mean Particle Size of 10 μm, Processed in SPS, under 75 MPa, Temperature Ranges from 850°C (1150 K) to 1400°C (1673 K), by 100°C/min Heating Rate.

The slope and the intercept from the straight line in the above figure are used to calculate the material power law creep frequency factor and apparent power law creep activation energy for vanadium carbide powder, and the results are listed in Table 12.

 Table 12. Determined Material Power Law Parameters for Vanadium Carbide

The determined strain rate sensitivity for vanadium carbide powder processed by SPS corresponds to glide controlled creep [159] [160].

By substituting the above determined material parameters into Equation 17 to solve for the porosity (or relative density) under the homogeneous heating assumption, the following prediction for relative density versus time can be obtained. By comparing the simulation prediction and the experimental results, R-square of 99.7% has been achieved.



Figure 81. Experiment and Simulation Temperature Profiles, and Relative Density Evolution with for 10  $\mu$ m Vanadium Carbide Powder SPS at 1400°C (1673 K) by 100°C/min Heating Rate, under 75 MPa ( $R^2 = 99.7\%$ )

The simulation prediction of grains size evolution with time is plotted in the following figure. This is the solution of Equation 16 under homogeneous heating condition.



Figure 82. Grain Size and Temperature Evolution with Time for 10 μm Vanadium Carbide Powder SPS at 1400°C (1673 K) by 100°C/min Heating Rate, under 75 MPa

The grain size simulation prediction result for the same previous SPS processing condition is plotted with relative density in the following figure. It is found that the grain size follows the power growth as the open pores start to close, which is consistent with other many literature reports on the grain size versus relative density relationship [168]. This is also consistent with the microstructure characterization results presented previously.



Figure 83. Grain Size Evolution with Relative Density for 10 μm Vanadium Carbide Powder SPS at 1400°C (1673 K) by 100°C/min Heating Rate, under 75 MPa

The calculations are conducted for the same heating condition but under different mechanical uniaxial stresses ranging from 20 MPa to 80 MPa, the plots are shown in the following figure to demonstrate the effect of mechanical pressure on vanadium carbide powder densification in SPS.



Figure 84. Loading Stress Effects on Consolidation of 10 μm Vanadium Carbide Powder at 1400°C (1673 K) by 100°C/min Heating Rate

As can be observed, the higher the mechanical pressure is, the higher the predicted relative density. However, the improvement extent of relative density decays at higher mechanical pressures. This reflects the nonlinear densification behavior of vanadium carbide powder with respect the mechanical pressure.

Another consolidation mapping calculation has been done to study the vanadium carbide powder densification behavior under isothermal conditions with different temperature and mechanical uniaxial stress combinations. The curved green surface is the solution of densification constitutive equation while the flat purple surface is the desired porosity for fuel pellet which is 25%. The cut between these two surfaces shows the boundary contour on which the temperature and uniaxial mechanical pressure combination dwelling for 30 min can deliver the 25% porosity structure with isothermal dwelling (given the 41.2% initial porosity).



Figure 85. Consolidation Mapping for Vanadium Carbide Powder with 10 μm Mean Particle Size, 41.2% Initial Porosity, with 30 min Holding. (Green curved surface is the porosity solution surface for different temperature and uniaxial mechanical pressure, Purple flat plane is the desired porosity (25%) for fuel pellet porous structure)

Based on the above mapped consolidation contour, the proper temperature and uniaxial mechanical pressure can be selected to deliver the desired 25% porosity. Optimization can be done accordingly.

Fully coupled FEM simulation analysis has also been performed for SPS processing of vanadium carbide powder. The basic mechanical, electrical and thermal properties of vanadium carbide are employed by using the handbook reported data (as listed in Chapter 5). The power law creep material parameters are based on the determined value from Table 12.



Figure 86. Von Mises Stress Distribution and the Tooling - Specimen Deformation for 10 μm Vanadium Carbide Powder, SPS at 1400°C (1673 K) by 100°C/min Heating Rate under Uniaxial Loading Stress 75 MPa, at 3000 s during Dwelling (stress color scale ranges from 0 to 117 MPa)

As can be seen from the above figure, the stress concentrations are located in the die wall in contact with the specimen and the corner edges of graphite punch. These predictions are consistent with the observations in the experiments in qualitative perspective at least. Those locations are where tooling damages happened most of the time.



Figure 87. Electric Current Density Distribution and the Tooling – Specimen Deformation for 10  $\mu$ m Vanadium Carbide Powder, SPS at 1400°C (1673 K) by 100°C/min Heating Rate under Uniaxial Loading Stress 75 MPa, at 2640 s during Dwelling (electric current density color scale ranges from  $1.6 \text{ A/m}^2$  to  $1.0 \times 10^6 \text{ A/m}^2$ )

The above figure shows the electric current density distribution and the tooling – specimen deformation during SPS for vanadium carbide experiment. High electric current density is predicted to be concentrated at the punch (due to the small cross sectional area). This is consistent with experimental observation that the graphite punch is the red and hottest component throughout the setup. For this vanadium carbide SPS particular case, the electric current density is also high within the specimen. This can be attributed to the high electrical conductivity of vanadium carbide (higher than graphite), which makes the specimen, rather than the graphite die, a major electrical current conduction channel for the SPS tooling-specimen setup. Therefore the heating mechanism for this SPS setup is dominated by Joule heat generated in-situ within the specimen leading to high efficiency heating.

## 6.5 Discussion

The sintered vanadium carbide surrogate pellets show desirable relative densities as listed in Table 11. The achieved density covers the range between 57.5 to 84.3% (consolidated from the loose powder packing density of 34.1%). It is noticed that if the sintering temperature is not higher than 1100°C, the achieved densification will not be larger than 10% regardless of the applied mechanical pressure (maximum allowable for the specific graphite tooling SPS device) and holding time. Therefore, 1100°C is identified as the threshold temperature for SPS hot consolidation of the studied vanadium mono-carbide powder.

Since vanadium carbide has higher melting temperature and mechanical moduli than uranium carbide [178], the SPS conditions utilized in the current research should be powerful enough to consolidate the uranium carbide powder or kernel into fuel pellets with the desired density. Regarding the vanadium carbide material, its excellent thermal and electrical properties at high temperatures make it very attractive for further exploration. The conducted research shows that, if the high end of the SPS temperature capability is used, it should be feasible to consolidate vanadium carbide into near fully dense bulk materials for more advanced applications, such as electrodes for high temperature and corrosive environment, or the core module components of thermoelectric conversion systems [181].

XRD analysis reveals that the characteristic room temperature phase of the SPSprocessed vanadium carbide specimens is the same as of the starting vanadium carbide powder. However, it is probable that an ordered to disordered phase transformation takes place at around 1000°C [180]. More studies of the vanadium carbide thermal dynamic properties are necessary to understand the high temperature consolidation behavior better.

The investigated mechanical properties of the processed vanadium carbide specimens included the measurements of the transverse rupture strength (TRS) and hardness. This is the first time that the TRS results are reported for binder-free vanadium carbide bulk material with different relative densities. Comparing to the 97% near fully dense binder-free tantalum carbide TRS of 372 MPa [102], the measured porous structure properties look promising. Regarding the hardness, the 75.7% relative density pellet specimen achieved the hardness of 64% of the fully dense vanadium carbide. Overall, the SPS is found to have very good potential for producing binder-free mono-carbide porous structures.

The thermal properties of SPS-processed vanadium carbide pellets were found to be dependent on the relative density (see Figure 78 and Figure 79). The constant pressure volume specific heat capacity for all the processed specimens shows a sharp spike at temperature around 1000°C, which is an indication of high temperature phase change with a potential order to disorder transformation [180]. Both the constant pressure volume specific heat capacity and thermal conductivity are found to be higher at higher temperatures.

## 6.6 Conclusions of Vanadium Carbide Powder Consolidation by SPS

This work represents the first report of the bulk consolidation of a vanadium mono-carbide powder material and of the processed specimens' measured mechanical and thermal properties. The major findings can be summarized as follows:

- a. SPS demonstrated capability to consolidate VC powder pellets up to a wide range of final densities (57.5 to 84.3%), and the final density can be controlled through SPS process temperature, pressure or time, while the conventional dilatometer sintering is incapable to achieve any densification with three hours long holding at the maximum possible sintering temperature 1550°C (limited by the device material). The identified SPS consolidation threshold temperature is at 1100°C.
- b. The initial powder agglomerates of very fine particles collapsed and were condensed more without observable grain growth under SPS consolidation regimes.

- c. An improved approach to determine the transverse rupture strength for porous materials has been introduced by taking into consideration the Poisson's ratio dependence on porosity.
- d. The obtained mechanical properties of the processed vanadium carbide specimens include: transverse rupture strength of 171 MPa at 75.7% relative density, and hardness of HRA 84 at 79.4% relative density.
- e. Different processing conditions used to achieve the same density do not yield an identifiable difference in constant pressure volume specific heat capacity and thermal conductivity. The achieved highest thermal conductivity is measured for the pellet of 84.3% relative density, with assessed values from 15 W/[m•°C] at 100°C to 26 W/[m•°C] at 1000°C.
- f. The processed VC powder pellets retained high permeability of 0.6 Darcy up to 72% density, which is as expected.

The overall study results show good potential for SPS to consolidate monocarbide kernels or powders with broad ranges of needed density.

# **Chapter 7** General Conclusions

### 7.1 Conclusions with Respect to Research Objectives

- (1) Analysis of power law creep based mass transfer mechanisms during spark plasma sintering
- a. Constitutive models revision and formulation for spark plasma sintering have been completed.
- b. Fundamental experiment design and conduction: the novel fundamental experiments have been designed and conducted, and the constitutive material parameters including strain rate sensitivity exponent, power law creep activation energy, and material power law creep frequency factor have been determined for copper and vanadium carbide powder.
- c. An analytical solution has been derived, and the calculation results are consistent with experimental data. The densification conditions based on the rigid die uniaxial densification boundary condition has been mapped for copper and vanadium carbide powder.

- d. The first comprehensive FEM simulation framework for SPS has been established: enabled the spatial distribution analysis for relative density, grain size, electric current density, temperature and stress throughout the SPS tooling and specimen.
- e. Densification mechanisms have been analyzed for copper and vanadium carbide processed by SPS. The dislocation climb controlled creep was found to be the dominant densification mechanism for copper, and the dislocation glide controlled creep was found to be the dominant densification mechanism for vanadium carbide.
- (2) Fabrication of functionally structured carbide:
- a. The experiments demonstrate the SPS potential for the consolidation of porous monocarbides. While conventional sintering failed to produce strong specimens at the comparable level of temperatures (as shown for VC powder specimens) and the conventional hot pressing required a comparatively long time of processing, SPS is capable of consolidating VC powder in short periods of processing time. Although the grain size retention possibility and advantage of SPS are still to be analyzed, the shorter processing time of SPS should render higher productivity and energy efficiency than conventional hot consolidation technologies. The typical time reduction in SPS compared to the conventional hot pressing is about 50%.

- b. The carbide pellets had the desired porosity (about 25%) and strength (larger than 60 MPa) for nuclear fuel application by using properly selected SPS processing conditions. The TRS had linear dependence on specimen's relative density for vanadium carbide pellets.
- c. Thermal conductivity was found to increase with the increase of relative density, while the constant pressure volume specific heat capacity was found to increase with the increase of relative density. Gas permeability was also measured for vanadium carbide pellets processed by SPS. It was found that gas permeability drops as the relative density increases.
- d. Optimization of the fabrication process has been enabled based on the fundamental study results from experiments, modeling, and simulation.
- (3) Other Conclusions
- a. Electric current was found not to affect the consolidation directly; instead it affects the consolidation by generating different temperature distributions within the tooling and specimen.
- b. For non-conductive materials the SPS has similar consolidation behavior as hot press.

c. For conductive materials, the SPS temperature measurement usually underestimates the actual specimen temperature indicating an arbitrary lower consolidation temperature than reality. However, the high electric current density at the inter particle necks heat and soften the local region first leading to accelerated densification. This leads to a reduced power law creep activation energy determined from macroscopic model.

### 7.2 Scientific and Engineering Novelties

This work successfully incorporated the power law creep theory for the deformation of fully-dense materials in the framework of the continuum theory of sintering and coupled them with an innovative grain growth model. It also developed a novel multi-step pressure dilatometry approach to determine the porous material power law creep constitutive parameters. This work successfully coupled consolidation, grain growth, mechanical, electrical, and thermal constitutive relationships for spark plasma sintering. Matches up to  $R^2$  of 99.7% between the finite element modeling - simulation predictions and experimental data occurred in this work. The fundamental analysis

capability developed by this work is applied to the proposed guide for optimizing the fabrication of functionally structured mono-carbide.

# 7.3 Recommended Future Work

- (1) Analyzing the sensitivity of the models' dependence on material parameters and processing parameters will help to improve the reliability and robustness of the entire modeling and simulation framework developed for spark plasma sintering process.
- (2) Implementation of a proportional-integral-derivative controller algorithm for the simulation framework will be desirable for enabling real time control simulation and optimization for spark plasma sintering process.

## **Appendix A. Equipment Measurement Validation and Calibration**

Calibration is a very important key step to make sure that the measurement is valid and result interpretation is meaningful.

For spark plasma sintering device particularly, there are multiple control parameters working together to complete one consolidation process. The input parameters include voltage, programmed hydraulic load, programmed temperature, and evacuated chamber pressure, while the output parameters include electric current, measured temperature, measured load, and z-axis displacement.

In automatic mode, the temperature and load profiles are set by the controllers first, and then the proportional-integral-derivative (PID) controller adjusts the input voltage and hydraulic load according to the temperature reading from thermocouple or pyrometer and the load reading from load-cell to achieve the programed temperature and load profiles.

In manual mode, the input power (which is the product of the voltage and electric current) and input load are controlled by manual knobs respectively. The measured

temperature and measured load are the ultimate output information for the user to make controlling decisions and then take actions accordingly.

Among all of the controlling parameters introduced above, it is the temperature and load which directly affect the consolidation or densification results during spark plasma sintering process.

### A.1 Temperature Measurement Validation

Temperature validation procedure is introduced first. Spark plasma sintering system has two temperature measurement options. For temperature below 1000°C, a bendable K-type thermocouple (NCF600, Chino, Japan) is used for temperature measurement by inserting it into the thermocouple hole in the middle of the graphite die surface. For temperature above 1000°C, a radiation pyrometer is required for temperature measurement by focusing it on the surface of the tooling (could be on the thermocouple hole as well). However, the pyrometer cannot measure temperatures lower than 570°C.

#### - Thermocouple and pyrometer calibration

For the K-type thermocouple, no information that is more accurate can be obtained besides the reading of its direct measurement; therefore, a brand new thermocouple temperature reading (calibrated by the manufacturer) is used as the reference true temperature ( $\pm 2.2^{\circ}$ C, or 0.75%).

For the pyrometer instrument, the reported standard deviation in the temperature range between 600 to 1500°C is  $\pm 0.5\%$  of reading  $\pm 1$  digit; in the temperature range of 1500 to 2000°C is  $\pm 1\%$  of reading  $\pm 1$  digit; and in the temperature range from 2000 to 3000°C is  $\pm 2\%$  of reading  $\pm 1$  digit. Repeatability is 1°C of reading  $\pm 1$  digit.

For the temperature calibration in this study, a brand new calibrated K-type thermocouple was installed and used to calibrate the pyrometer temperature reading in the range between 600 to 1000°C.

As shown in the Figure 27, the pyrometer focus point was selected on the equivalent spot of the thermocouple hole (2 mm diameter, 5 mm depth) to minimize the temperature gradient effects. The I85 graphite tooling material has emissivity of 0.85.

The dynamic temperature comparison results from the pyrometer and thermocouple readings are plotted in the following figure. This plot shows the temperature range between 600°C to 1000°C which is the overlapping regime between pyrometer and thermocouple. The heating rate used for this calibration test was 50°C/min.



Figure A. 1. Pyrometer vs. Thermocouple Temperature Calibration Results during Heating Ramp at 50°C/min

The discrepancy reading shows larger gap up to 62°C higher in pyrometer than thermocouple reading at low temperature 700°C. The gap decreases gradually as temperature increases. At 1000°C reading for thermocouple, the pyrometer was 22°C higher (+ 2.2%).

The static or equilibrium temperature comparison results from the pyrometer and thermocouple readings were plotted in the following figure. This plot shows the readings from both pyrometer and thermocouple during SPS dwelling at 1000°C starting from 0 second to 60 sec after reaching the set temperature at 50°C/min heating rate. As can be observed, right after reaching 1000°C, the pyrometer and thermocouple had close

readings with pyrometer showing 22°C higher temperature. However, the discrepancy became larger due to overheating effect (a systematic delay from the PID controller). At 30 seconds, the pyrometer showed a temperature reading 74°C higher than thermocouple reading. As times passed by, the discrepancy was reduced to 31°C by the compensation from lowered input electric power imposed by PID controller.



Figure A. 2. Pyrometer and Thermocouple Temperature Calibration during 1000°C (1273K) Isothermal Dwelling

#### **A.2 Load Calibration**

Loading stress calibration procedure is introduced next: the minimum required load is 3.0 kN for the Dr. Sinter 515 SPS, and the maximum load capacity is 50.0 kN. Calibration for the loading stress was conducted by inserting a standard calibrated load cell (RLC C6, Mettler Toledo AG, Switzerland) between the hydraulic driven electrode heads, then the chamber was closed and the load was applied by the hydraulic system going through the entire capability range in December  $12^{\text{th}} 2012$  (within  $\pm$  one year when this study was conducted). The load readings were generated from the standard load cell and the SPS machine built in load gauge simultaneously, and the results are listed in Table A.1.

	Load Cell	SPS Load	Delta-Load	Delta-Sigma
Minimum Load	3.4	3.04	-10.6%	-2.0
	5.0	5.28	5.6%	1.6
	10.0	10.15	1.5%	0.8
	15.0	15.31	2.1%	1.8
	20.0	20.05	0.3%	0.3
	25.0	24.97	-0.1%	-0.2
	30.0	30.09	0.3%	0.5
	35.0	35.14	0.4%	0.8
	40.0	39.80	-0.5%	-1.1
	45.0	44.90	-0.2%	-0.6
	50.0	50.01	0.0%	0.1
Maximum Load	50.1	50.14	0.1%	0.2
Back-Force*	3.3	3.10	-6.1%	-1.1
Maximum Registration*	50.30	Mean	-0.6%	0.1
Sensitivity Registration*	2.42	Stdev	3.9%	1.1

Table A.1. Load Calibration Table (Pressure Sigma is Calculated for 15 mm Diameter Punch)

Note: \*Back-Force is the minimum load measurable to the load cell;

\*Maximum registration is the maximum load measurable to the load cell;

\*Sensitivity registration is the load cell reading deviation range from the true value.

After plotting the above data into the diagram below, it is found that the variances of SPS load gauge reading from calibrated load cell reading fall in to the range between - 10.6% to 5.6%. These variances correspond to the stress reading difference on 15 mm diameter punch of -2.0 MPa to 1.6 MPa. The large variances were concentrated at low load range from 3.4 kN to 5.0 kN. At the load at 10.0 kN and above, the variances became much smaller ranging from - 0.5% to 2.1%. The average variance standard deviation is  $\pm 3.9\%$  (or  $\pm 1.1$  MPa for 15 mm diameter punch).



Figure A. 3. Relative Offset Reading of SPS Load from the Calibrated Load Cell True Reading

#### A.3 Measurement Error Discussion

Temperature validation:

During heating ramp, at 50°C/min, the temperature reading variances between the pyrometer and thermocouple are between 2.2% to 6.2% for Celsius temperature unit system (variances are higher at low temperature).

During isothermal dwelling at 1000°C, the temperature reading variances between the pyrometer and thermocouple are between 2.2% to 7.2% for Celsius temperature unit system (variances are higher at overheating stage).
These variances need to be taken into consideration when calculating the material parameters from experimental results. It is also found that the temperature measurement by thermocouple cannot be simply replaced by pyrometer measurement; a systematic adjustment coefficient needs to be determined for different temperatures and heating modes (automatic or manual), especially at low temperature range.

For copper experiments, where the peak sintering temperature was lower than 1000°C, the as measured thermocouple temperatures were used for calculations of this study. For vanadium carbide experiments, where the sintering temperature was higher than 1400°C, the as measured pyrometer temperatures were used for calculations of this study.

Loading stress calibration:

For 15 mm diameter graphite punch, the loading stress variance is about  $\pm$  1.1 MPa which is less than 5% of the typically used SPS loading stress ( $\geq$  20 MPa). Therefore, the SPS displayed loads were directly used for calculations in this study.

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