SPARK PLASMA SINTERING OF AGGLOMERATED VANADIUM CARBIDE POWDER

Wei Li^a, Eugene A. Olevsky^{*,a,b,c}, Oleg L. Khasanov^{b,c},
Christina A. Back^d, Oleg Izhvanov^d, Jonas Opperman^d, Hesham E. Khalifa^d

^aMechanical Engineering Department, San Diego State University
5500 Campanile Drive, San Diego, CA 92182-1326, USA

^bEngineering Physics University, Moscow, 115409, Russia

^cNational Research Tomsk Polytechnic University, Tomsk, 634050 Russia

^dGeneral Atomics, 3550 General Atomics Court, San Diego, CA 92121 USA

ABSTRACT

Spark plasma sintering (SPS) is an emerging powder consolidating technique which promises high potential capabilities to process refractory ceramics with properties previously unattainable. As the first step in studying the applicability of this technique to the processing of tailored ceramic structures, the validity of SPS to consolidate refractory carbides with controllable porosity is investigated. Vanadium carbide (V_8C_7) is chosen as a studied material. The structure, thermal and mechanical properties of the V_8C_7 powder pellets produced by SPS are analyzed and discussed in the paper. **The attained properties of the processed ceramic material are in particular suitable for applications where high electrical conductivity and strength at high melting temperatures, low thermal conductivity and low thermal expansion coefficient are needed.**

Keywords: Vanadium carbide; spark plasma sintering; thermal and mechanical properties

*Corresponding author email: eolevsky@mail.sdsu.edu

1. Introduction

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. Use of conventional consolidation techniques to achieve these goals presents challenges. Refractory carbide materials are difficult to consolidate because of their high melting temperatures. In addition, long dwell times at high temperatures, which are typically necessary to consolidate powders, tend to produce larger grains, - a disadvantage for various applications where mechanical properties of the final products are important. Furthermore, consolidation techniques are more commonly developed to reduce porosity by using additives and binders to facilitate densification, which would generally be detrimental for further performance of the produced components.

The emerging spark plasma sintering technology looks promising for the fabrication of stable porous ceramic structures [1,2]. More effective densification over conventional sintering 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 at inter-particle contacts.

Processing of vanadium carbide powder has been analyzed only to a limited extent, although this material possesses a number of useful refractory and resistive properties. Most of research works related to consolidation of VC by pressing and sintering utilized it as a complementary material only [3-13].

An interesting application is the employment of vanadium carbide (V_8C_7) as a surrogate material for uranium carbide to investigate the potential of spark

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5 plasma sintering as a hot consolidation technique to densify the carbide fuel
6 pellets. Spark plasma sintering devices are now starting to find applications for
7 fabrication of nuclear fuels. Recent publications have focused on UO_2 [14].
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11 For nuclear applications, a fuel pellet that efficiently vents fission gases may
12 be expected to have a significant (20-30%) fraction of connected pores in the fuel
13 material to allow fission products to escape from the fuel pellet to a plenum in the
14 fuel rod where the gases can then be removed [15] . However, any porous fuel
15 pellet must have sufficient strength to withstand manufacturing operations and in-
16 service thermal stresses without losing its integrity. One example of a pellet
17 microstructure arrangement being explored for a gas-cooled fast reactor called
18 “the Energy Multiplier Module, EM^2 ”, is a bi-porous structure formed by sintering
19 spherical fuel kernels (see Figure 1) [16]. This structure would have a fuel kernel
20 internal porosity and inter-kernel porosity with controlled, connected flow paths
21 for the fission product gases to escape. The inter-particle pores would provide
22 void volume for the accommodation of the fuel swelling by creep. The target
23 porosity for this pellet is around 25%. To remain intact over the lifetime of the fuel,
24 the pellet must sustain thermal stresses of the order of 60 MPa according to
25 calculations [16]. Since material strength is highly temperature dependent, high
26 thermal conductivity is required to maintain the structure temperature within the
27 designed limit for strength retention purposes. Typical fuel structure requires
28 thermal conductivity above 3 W/(m·K) at 800°C operation temperature [17]. The
29 basic desired properties for carbide-based nuclear fuel pellet according to
30 General Atomics’ design [16] are summarized in Table 1.
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Study of surrogate material processing is very important for nuclear related materials such as uranium carbide, because a well selected surrogate can significantly reduce the environmental impact and cost during the development stage while still obtaining meaningful results for the actual fuel fabrication [18,19].

V_8C_7 has exactly the same cubic-cF8 crystal structure, $Fm\bar{3}m$ No. 225 space group, as UC, and thus shares similar mechanical properties that affect consolidation. In addition, the melting temperature of V_8C_7 is the closest amongst all the refractory carbides to that of UC, - an important consideration when studying the sintering behavior. The physical properties of vanadium carbide are summarized in Table 2 [20-25]. It should be also noted that, according to the reported property summary for vanadium carbide (Table 2) and comparing it to typical metal based materials (such as aluminum, copper, and silver-based etc.), vanadium carbide has low thermal conductivity and thermal expansion coefficient, but high electrical conductivity and ultra-high melting temperature. In particular, the higher melting temperature and lower electrical conductivity, relative to that of UC, make it a good candidate for assessing an upper boundary temperature necessary for consolidation of UC by SPS.

The advantage of SPS has been demonstrated by a paper that reported free sintering results for the same vanadium carbide powder used in the present study [26]. In that study, a green vanadium carbide pellet was cold pressed up to 52% relative density, and then consolidated using a 10°C/min heating rate up to 1550°C (maximum allowable alumina tube-based dilatometer temperature) followed by a 3 hours dwell time in vacuum (10 Pa). Under these temperatures, significantly lower than the respective melting temperature, the final sintered

density was not changed at all from the density obtained under cold pressing. The authors found that it was impossible to densify binder-free vanadium carbide by conventional sintering at the above-mentioned temperature of 1550°C [26].

In the present paper, spark plasma sintering is evaluated in terms of its efficiency to consolidate carbide materials, create porous structures, and achieve sufficient product strength. In addition to the advantageous densification effects mentioned above, SPS is also selected as a processing technique because it has demonstrated the potential to reduce fabrication time, retain small grain size, and create structures with higher strength due to the enhanced SPS neck-growth kinetics.

~~The present paper is organized as follows. Section 2 describes the materials, processing and testing in the framework of the conducted research to successfully consolidate additive-free (binder-free) vanadium carbide. In Section 3, the results of the characterization of the density, microstructure, and composition phases of the vanadium carbide pellets processed by SPS, porosity, and permeability are provided. The measured physical properties including transverse rupture strength, hardness, volume specific constant pressure heat capacity, and thermal conductivity are also reported in Section 3. Section 4 includes the overall discussion of the research results.~~

2. Materials and Experimentation

2.1 Materials Processed by Spark-Plasma Sintering

For these studies, raw material having a nominal particle size similar to that expected for the fuel kernels was obtained from the vendor Changsha Asian

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5 Light Economic Trade Co., Ltd. Its powder characteristics are reported in Table
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7 3. After processing by the vendor, which included dry milling in a WC-Co
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9 container by WC balls, the vanadium carbide (V_8C_7) was a mixture of powder
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11 ranging in size from 5 to 10 μm and of agglomerated irregular particles roughly
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13 200 to 300 μm in size (see Figure 2).
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17 A laser diffraction particle size and image analyzer (S3500SI, Microtrac,
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19 Nikkiso, Japan) was used to characterize the particle size distribution for different
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21 powders. The laser used in the micro-size detector had a wavelength of 405 nm.
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23 10% of nonionic hydrophilic surfactant Triton X100 was added to the deionized
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25 water to disperse the powders effectively and then test them in the wet mode.
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27 Before the powder entering into the laser chamber, further dispersion by
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29 ultrasonic vibration at 40 Watts for 60 seconds was applied to guarantee
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31 obtaining the accurate particle size distribution. The particle size distribution
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33 measurement results are shown in Figure 3.
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39 The material composition was identified by both combustion and X-Ray
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41 diffraction (XRD) methods. Combustion analysis measured oxygen content of
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43 0.16 wt.%. X-Ray fluorescent analysis revealed Ti, Fe, Ni, Ge, Ca, Al impurities
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45 at the level from 0.1 to 0.3wt.%. To determine the characteristic phase after
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47 sintering, X-ray diffraction (Panalytical, XPert Pro MRD) was performed on the
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49 pellets. The XRD analysis was performed using the following configuration:
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51 copper target, K-Alpha band (1.54 $\text{\AA}$), and generator setting of 40 mA at 45 kV.
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53 These measurements identified the phase of the vanadium carbide powder to be
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55 a stoichiometry of V_8C_7 . The results are plotted in Figure 4.
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2.2 Consolidation of Vanadium Carbide Powder

Experiments were performed using a spark-plasma sintering apparatus (Dr. Sinter 515 SPS, Fuji Electronics Industrial Co, Ltd., Japan) with pulse duration of 3.3 ms. A machine 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. First the ball-milled powder mixture was prepared in pellet form with a tap density of 1.97 g/cm³ (34%). Pellets of 15 mm in diameter and 4.00 gram in mass were then placed 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 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 sequence 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 dwelling during 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 dwelling time, the current was shut down, yielding a cooling rate of about 300°C from T_F 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 afterwards.

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5 The tooling and the pellet configuration are shown in Figure 5. The
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7 temperature was measured by an optical pyrometer focused on the surface of
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9 the graphite die and automatically regulated from 580°C up to the final sintering
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11 temperatures of 1100, 1200, 1300 or 1400°C.
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14 The experiments were performed over specified ranges of pressures and
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16 temperatures to determine the relationship between porosity and processing
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18 conditions.
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21 22 23 24 *2.3 Characterization of Processed Specimens*

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26 The characterization of the spark-plasma sintered vanadium carbide pellets
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28 consisted of the density measurements, microstructural analysis using Scanning
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30 Electron Microscopy (SEM), the determination of characteristic phases using
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32 XRD, porosity measurement by pycnometry, mechanical properties'
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34 measurements including transverse rupture strength and scale A Rockwell
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36 hardness, thermal properties' measurements including constant pressure specific
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38 heat capacity and thermal conductivity .
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42 Since the porosity of the processed pellets was relatively high (>8%), the
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44 Archimedean immersion method was difficult to apply. The density of the
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46 vanadium carbide pellet specimens was measured by geometry method
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48 (accurate for a regular cylindrical pellet specimen shape). The pellet specimens
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50 were weighed three times on a high accuracy scale (resolution ± 0.0001 g); the
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52 diameter and height of the cylindrical pellet specimens were measured at three
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54 different locations; and the average density was calculated accordingly.
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For the microstructural observations using SEM, the pellet surfaces were polished with successively smaller grinding medium down to 0.04 µm of colloidal silica. Grain boundary relief was produced by deep etching of V₈C₇ pellet in the mixed HCl-HNO₃-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 obtained and the average grain size was estimated from each micrograph by the line intercept method [27]. In some cases the electron backscatter diffraction was used to confirm the measured grain size.

2.4 Mechanical Property Measurement

To test the mechanical strength of porous structures, a customized Transverse Rupture Strength (TRS) procedure based on the modified ASTM C1499-09 Standard [28] was developed. 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 [29]. 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:

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

where σ_{TRS} is the equivalent TRS value in MPa, F is the load in N, ν 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 [30]:

$$\nu_p = \frac{2 - 3\theta}{4 - 3\theta} \quad \text{Equation 2}$$

where ν_p is the Poisson's ratio for a porous material, θ 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 [31] (normalized to show the dependence on porosity) is employed:

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

where R_N is the relative or normalized Poisson's ratio, ν_{pi} is the Poisson's ratio for incompressible isotropic materials (equal to 0.5). Then the actual Poisson's ratio for a porous material with a compressible substance material can be calculated as:

$$\nu = \nu_0 R_N = 2\nu_0 \left(\frac{2 - 3\theta}{4 - 3\theta} \right) \quad \text{Equation 4}$$

where ν_0 is the Poisson's ratio for fully dense bulk materials, and ν is the general material Poisson's ratio that is used for the transverse rupture strength calculation.

2.5 Thermal Properties' Measurement

Vanadium Carbide constant pressure specific heat capacity and thermal conductivity were measured using Netzsch Differential Scanning Calorimeter

(DSC) 404 F1 Pegasus and Laser Thermal Flash Analyzer (LTFA) 427, respectively. The measurements were performed on various V_8C_7 specimens processed under different SPS conditions. The constant pressure specific heat capacity was determined by the differential ratio method using a sapphire standard. The constant pressure specific heat capacity data were used along with the thermal diffusivity data to determine thermal conductivity. All thermal analysis measurements have been conducted between room temperature and 1100°C in argon atmosphere.

There are two other important observations for the obtained constant pressure heat capacity data. One is that constant pressure specific heat capacity is higher at higher temperatures before phase transformation takes place. The other observation is that at around 1000°C, the constant pressure heat capacity reached a peak point and then decreased sharply. This is associated with the exothermal phase transformation from ordered to disordered state occurring within the vanadium carbide structure. Debye temperature is not reported for this material system so far [32].

In the laser flash method, the derivation of thermal diffusivity and constant pressure 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:

$$k_{tc} = \alpha \rho C_p \quad \text{Equation 5}$$

where k_{tc} is the thermal conductivity, α is the thermal diffusivity, ρ is the processed specimen density, C_p is the constant pressure specific heat capacity.

The thermal diffusivity is given by the following equation:

$$\alpha = 0.1388 \frac{L^2}{t_{\frac{1}{2}}} \quad \text{Equation 6}$$

where α 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 specific heat capacity C_p determined by DSC, is given by the following equation:

$$C_p = \frac{m_{Standard}}{m_{Sample}} \cdot \left(\frac{Q_{Sample} - Q_{Baseline}}{Q_{Standard} - Q_{Baseline}} \right) \cdot C_{p,Standard} \quad \text{Equation 7}$$

where m is the mass, Q represents the energy of the DSC measured heat, and $C_{p,Standard}$ is the constant pressure specific heat capacity for the standard reference (in this study, sapphire was used).

Measurement results for porosity, permeability, mechanical and thermal properties and data are described in Section 3.

3. Processed Vanadium Carbide Pellets' Characterization Results

3.1 Structure Characterization Results

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 4.

Figure 6 shows an example of the sintering curves for two different pressures at the 1100°C consolidation temperature. As can be observed, there is softening and then a roughly linear densification after 600 seconds (with temperature of about 1100°C). Figure 7 shows the densification kinetics for the 60 MPa runs. For every 100°C increment in temperature, a relative increase of 3.5-4% in density occurs. The data from Table 4 are selectively plotted in the form of a diagram (see Figure 8) to further explore the trend of the consolidated relative density dependence on temperature, pressure, and dwelling time. It is observed that higher temperature, longer dwelling time and higher mechanical stress generally produce specimens with higher relative density, as expected.

Figure 9 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 μm without significant growth for low to high density specimens. However, the reduction of the pore size is obvious as seen in Figure 9. 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 ($\pm 10 \mu\text{m}$) comparing to the starting powder ($\pm 100 \mu\text{m}$) indicating no bimodal distribution characteristics.

In some SEM images, deep etching did not clearly reveal detailed grain structure, as in Figure 10 (a), so electron backscatter diffraction (EBSD) technique was used as a cross check. Figure 10 (a) and (b) show a comparison of the same surface area of the sample consolidated at 1300°C, 60MPa, for 30

min, with 79.8% relative density, characterized by SEM and EBSD technique, respectively. Different colors reflect transition from grain to grain and make grain size calculations easier. As it can be seen, EBSD images confirm grain size to be within scattering range of 8-12 μm .

XRD analysis was used to determine the characteristic phases before and after SPS processing. Figure 11 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 dwelling time.

The crystal structure characteristic peaks for the powder and the consolidated pellet match very well indicating that the SPS process did not change the vanadium carbide powder dominant 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 heat capacity data (see Figure 16) and of the phase diagram reported in Ref. [8] indicate that there is a phase transformation from ordered to disordered structure around 1000°C. However, measurements show that after cooling to room temperature, the sintered pellet returns to its original phase composition.

Porosity in the structure consists of two types, open porosity and closed porosity. Pycnometer [33] was used to measure the closed porosity of the porous structure, and volumetric method was used to measure and calculate the total porosity.

Total Porosity = 100% - Relative Density = Open Porosity + Close Porosity
With the equation above, one can determine the fraction of open porosity within total porosity [34]. The correlation between open porosity and relative density is

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5 plotted in Figure 12. The data are available only for relatively low density range
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7 (60 to 65%). In this range, open porosity contributes up to 90% of the total
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9 porosity.
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12 Air was used as the pressurization gas to measure the permeability. The
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14 permeability test was conducted in the differential pressure range from 0 up to
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16 100 kPa.
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19 The average permeability versus different relative density is plotted in Figure
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21 13. The permeability of porous structure drops as the relative density increases.
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23 Still, at density of 72%, the permeability is as high as 0.6 Darcy.
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26 27 28 *3.2 Mechanical and Thermal Property Measurement Results* 29

30 31 *3.2.1 Mechanical Properties of Processed Specimens* 32

33 The mechanical properties for selected pellets are plotted in Figure 14. In this
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35 graph, the data on four additional vanadium carbide pellets processed by
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37 traditional hot pressing are also included for comparison to cross check the TRS
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39 dependence on relative density. These hot pressing pellets data were obtained
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41 with the following processing parameters: peak temperature of 1400°C, heating
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43 rate of 14°C/min, uniaxial pressure of 20, 26 or 28 MPa, and dwelling time of 30
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45 min.
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50 It is found that higher TRS strength and hardness are associated with higher
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52 relative density. The TRS of vanadium carbide pellets is found to have a linear
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54 dependence on relative density.
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57 The processed specimens were polished to 1000 grit SiC paper surface finish
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59 for conducting the hardness measurements.
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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 (120° diamond cone), 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 15). Bulk vanadium carbide hardness is 2800 VHN25 (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.

3.2.2 Thermal Properties of Processed Specimens

Constant pressure specific heat capacity was found to increase with increasing relative density (see Figure 16). 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 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 specific heat capacity.

By multiplying thermal diffusivity with constant pressure specific heat capacity, thermal conductivity was calculated and plotted in Figure 17.

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 heat capacity, the thermal conductivity is strongly dependent on density, which can be manipulated through adjustment of the SPS processing parameters. However, when different parameters are used to achieve the same density, no measurable difference in thermal conductivity was observed.

4. Discussion

The sintered vanadium carbide specimens show desirable relative densities as listed in Table 4. 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 hot consolidation temperature is not higher than 1100°C, the achieved densification will not be larger than 10% regardless of the applied mechanical pressure and dwelling time (maximum allowable for the specific graphite tooling and SPS device). Therefore, 1100°C is identified as the threshold temperature for SPS hot consolidation of the studied vanadium carbide powder.

Since vanadium carbide has higher melting temperature and mechanical moduli than uranium carbide [22], 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

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5 should be feasible to consolidate vanadium carbide into near fully dense bulk
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7 materials for more advanced applications, such as electrodes for high
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9 temperature and corrosive environment and the core module components of
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11 thermoelectric conversion systems [35].
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14 XRD analysis reveals that the characteristic phase of the SPS-processed
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16 vanadium carbide specimens is the same as of the starting vanadium carbide
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18 powder. However, this does not mean there is no reversible phase
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20 transformation at high temperatures.
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23 The investigated mechanical properties of the processed vanadium carbide
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25 specimens included the measurements of the transverse rupture strength (TRS)
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27 and hardness. This is the first time that the TRS results are reported for binder-
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29 free vanadium carbide bulk material with different relative density levels.
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31 Comparing to the 97% near fully dense binder-free tantalum carbide TRS of 372
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33 MPa [36], the measured porous structure properties look promising. Regarding
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35 the hardness, the 75.7% relative density pellet specimen achieved the hardness
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37 at 64% of the fully dense vanadium carbide value. Overall the SPS is found to
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39 have very good potential for producing binder-free carbide porous structures.
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45 The thermal properties of SPS-processed vanadium carbide pellets were
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47 found to be dependent on the relative density (see Figure 16 and Figure 17). The
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49 constant pressure specific heat capacity for all the processed specimens show a
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51 sharp spike at temperature around 1000°C, which is an indication of high
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53 temperature phase change with a potential order to disorder transformation [24].
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55 Both the constant pressure specific heat capacity and thermal conductivity are
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57 found to be higher at higher temperatures. The phase transformation leads to
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stoichiometry change from V_8C_7 to VC_y (with y in the range of 0.66 to 0.88). The impacts of the associated material property changes due to this phase transformation are very difficult to predict due to the lack of reported or measured high temperature treatment results. The challenge is associated not only with the complexity and metastable structure of the carbide at high temperatures, but also with the significant difficulties and high costs of test setups for elevated temperature treatments [37]. However, it is worth noticing that the exothermic phase transformation may cause carbon precipitation from carbide structure and increase the temperature within the structure temporarily, which may possibly compromise the strength of the fabricated materials.

Overall, by considering the requirements for a potential carbide fuel pellet, the SPS conditions which can render surrogate structures with satisfactory properties are summarized in Table 5.

5. Conclusions

This paper represents the first report of the bulk consolidation of a vanadium 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 vanadium carbide powder specimens 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 during three hours long processing. The identified SPS consolidation threshold temperature is at 1100°C.

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5 b. The initial powder agglomerates of very fine particles collapsed and were
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7 condensed without observable grain growth under SPS consolidation regimes.
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10 c. An improved approach to determine the transverse rupture strength for
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12 porous materials has been introduced by taking into consideration the
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14 Poisson's ratio dependence on porosity.
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17 d. The obtained mechanical properties of the processed vanadium carbide
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19 specimens include: transverse rupture strength of 171 MPa at 75.7% relative
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21 density, and hardness of HRA 84 at 79.4% relative density.
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24 e. Different processing conditions used to achieve the same density do not yield
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26 an identifiable difference in constant pressure specific heat capacity and
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28 thermal conductivity. The achieved highest thermal conductivity is for pellets
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30 of 84.3% relative density, with assessed values from 15 W/[m•°C] at 100°C to
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32 26 W/[m•°C] at 1000°C.
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36 Overall, this study shows that SPS can consolidate a refractory carbide
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38 powder with controllable final porosity. Generally, the high electrical conductivity
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40 and ultra-high melting temperature of vanadium carbide can make it very suitable
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42 as a high temperature conductor, especially for the applications in the thermo-
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44 electric conversion systems [35].
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48 For application to nuclear fuels, the successful consolidation of vanadium
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50 carbide with densities spanning the range of 58 to 84%, provides high confidence
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52 that uranium carbide can be also consolidated with controlled porosity. The
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54 objectives to produce refractory carbide porous (75% of the theoretical density)
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56 ceramic structure with sufficient (60 MPa) mechanical strength and high fraction
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58 of open porosity, while retaining average grains size and stoichiometry of the
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original agglomerated powder, were achieved. Also, the measured 0.6 Darcy value of permeability allows for a pressure drop that is orders of magnitude better than that needed for the venting of fission gas in an EM² reactor fuel pellet. Obtaining these results at temperatures 44 to 54% of the melting temperature would eliminate the need for costly processing in high temperature (> 2000°C) furnaces.

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TABLE CAPTIONS

Table 1. Desired Basic Properties for Carbide Based Nuclear Fuel Pellet According to General Atomics Design

Table 2. Vanadium Carbide and Uranium Carbide Physical Properties at 25oC: Comparison20-,21,22,23,24,25

Table 3. Vanadium Carbide Powder Characteristics

Table 4. SPS Consolidation Results for VC Powder Processed with 100°C/min Heating Rate

Table 5. Satisfactory SPS Consolidation Parameters and Obtained Surrogate Properties

Table 1. Desired Basic Properties for Carbide Based Nuclear Fuel Pellet According to General Atomics Design

Key Property	Range
Porosity	20% to 30%
Strength at about 800°C	> 60 MPa
Thermal conductivity at about 800°C	> 13.8 W/(m.K)

Table 2. Vanadium Carbide and Uranium Carbide Physical Properties at 25°C: Comparison²⁰⁻²⁵

Property \ Material	Unit	Vanadium Carbide	Uranium Carbide
Chemical Formula		V ₈ C ₇	UC
Crystal Structure		cubic, cF8	cubic, cF8
Space Group		Fm $\bar{3}$ m, No. 225	Fm $\bar{3}$ m, 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 ³ /K]	3.058	2.753
Heat Capacity - Mole	[J/mol/K]	33	51
Thermal Conductivity	[W/m/K]	39	19
CTE	[10 ⁻⁶ /K]	7.20	0.12
Melting Temperature	[K]	3083	2660
Electrical Conductivity	[μΩ/cm]	37	60

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Table 3. Vanadium Carbide Powder Characteristics

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

Table 4. SPS Consolidation Results for VC Powder Processed with 100°C/min Heating Rate

Temperature [°C]	Stress [MPa]	Time [min]	Relative Density ($\pm 0.5\%$)
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%
	60	10	75.0%
		15	77.2%
		30	79.5%
	75	10	79.2%
1400	20	5	69.7%
	60	10	80.1%
	75	30	84.3%

Table 5. Satisfactory SPS Consolidation Parameters and Obtained Surrogate Properties

Property \ Density and SPS	Density 70.2% 1200°C, 5 min 60 MPa	Density 75.0% 1300°C, 10 min 60 MPa	Density 77.2% 1300°C, 15 min 60 MPa	Density 79.2% 1300°C, 10 min 75 MPa	Density 79.5% 1300°C, 30 min 60 MPa	Density 80.1% 1400°C, 60 min 10 MPa
Porosity at 25°C, 1 atm	29.8%	25.0%	22.8%	20.8%	20.5%	19.9%
Extrapolated Open Porosity at 25°C, 1 atm	26.7%	22.4%	20.4%	18.6%	18.4%	17.8%
Extrapolated Permeability at 25°C [Darcy]	0.0069	0.0043	0.0034	0.0028	0.0027	0.0026
TRS @ 25°C [MPa]	112	164	188	209	213	219
Extrapolated Hardness at 25°C, 1 atm	72	81	79	77	77	76
Extrapolated Heat Capacity at 800°C, 1 atm [J/(cc.K)]	3.51	3.66	3.73	3.79	3.80	3.82
Extrapolated Thermal Conductivity at 800°C, 1 atm [W/(m.K)]	15.8	16.0	16.4	17.2	17.3	17.7

FIGURE CAPTIONS

Figure 1. Schematic of EM2 Fuel in Which the UC Fuel is Formed by Sintering of Spherical Kernels

Figure 2. Agglomerated Vanadium Carbide Powder, (a) 100X-Scale Bar 500 μm ; (b) 5000X-Scale Bar 10 μm ; (c) 1000X-Scale Bar 50 μm

Figure 3. Vanadium Carbide Powder Particle Size Distribution

Figure 4. XRD Scanning of Vanadium Carbide Powder (V8C7 Ref. Code 00-023-1468)

Figure 5. SPS Tooling and Pellet Configurations, Interfaces between Pellet, Punches, and Die Wrapping with a Layer of Graphite Foil of 0.40 mm (Drawn in Scale)

Figure 6. Relative Density vs. Temperature for 1100°C Consolidation Temperature with Corresponding Fracture Surfaces

Figure 7. Densification Kinetics for 60 MPa

Figure 8. Relative Density versus (a) Temperature, (b) Pressure, and (c) Time for SPS Processed Vanadium Carbide Pellets

Figure 9. 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

Figure 10. Cross Sectional Surface of 1300°C, 60 MPa, 30 min - with 79.8% Density; (a) by SEM; (b) by Electron Backscatter Diffraction

Figure 11. Vanadium Carbide 84.3% Dense Pellet and Powder XRD Scanning Results Comparison

Figure 12. Open Porosity versus Relative Density for SPS-fabricated VC Pellets

Figure 13. Permeability versus Relative Density for SPS VC Pellets

Figure 14. Transverse Rupture Strength (TRS) versus Relative Density for SPS VC Pellet and Literature Reported TRS for TaC Specimen [36]

Figure 15. Scale A Rockwell Hardness versus Relative Density for SPS-produced Vanadium Carbide Pellet

Figure 16. Constant Pressure Specific Heat Capacity versus Temperature for SPS-fabricated Vanadium Carbide Pellets with Different Relative Density and the Bulk Vanadium Carbide Reference Curve [24]

Figure 17. Thermal Conductivity versus Temperature for SPS-fabricated
Vanadium Carbide Pellets with Different Relative Density

Figure 1. Schematic of EM² Fuel in Which the UC Fuel is Formed by Sintering of Spherical Kernels

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