DENSIFICATION OF ZIRCONIUM NITRIDE BY SPARK PLASMA SINTERING AND HIGH VOLTAGE ELECTRIC DISCHARGE CONSOLIDATION: A COMPARATIVE ANALYSIS

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ABSTRACT

The densification behavior of zirconium nitride powder is investigated for various temperature and pressure conditions imposed by spark plasma sintering and high voltage electric discharge consolidation techniques. The crystal structure, chemical composition, porosity, and grain size of the powders and processed specimens are analyzed by X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The outcomes of the two considered consolidation techniques are comparatively assessed. Vickers micro-hardness of the processed ZrN specimens is investigated, and hardness dependence on porosity is analyzed. The densification mechanism of ZrN consolidated by spark plasma sintering is revealed by applying the constitutive equation of the continuum theory of sintering, and it turns out to be a similar mechanism to hot pressing. Application of the sintering constitutive equations shows that the mechanism of ZrN densification by high voltage electric discharge consolidation method depends on the magnitude of the applied voltage.

Keywords: Zirconium Nitride, Spark Plasma Sintering, Field-Assisted Sintering, High Voltage Electric Discharge Consolidation

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1. Introduction

Zirconium nitride (ZrN) is a material that has been attracting increasing attention over the last decades, due to the combination of excellent thermal, mechanical and electrical properties, even though there are significant difficulties in its synthesis and processing methodologies. In particular, mechanical strength of ZrN retained at high temperatures and chemical inertness, with the exception of a limited tendency to oxidize [1, 2], render it a suitable material for a variety of applications, such as coatings for thermal barrier layers and tooling setups for material processing. Another application is as a model material for the highly radioactive materials used in nuclear reactors: for fuel pellets (UN) [3, 4], as an inert matrix for actinide fuels [5-7] or as an additive for PuN pellets, with which it can form a solid solution [8, 9]. However, it is difficult to obtain ZrN fully dense bodies due to ZrN high melting temperature (2980°C), low self-diffusion coefficient ($\sim 0.026 \text{ m}^2/\text{s}$ at 2400~2600°C), strong covalent bonding [10], and the existence of an oxide layer (ZrO₂) on the surface of the starting powders.

A few studies report on the consolidation of ZrN powders by sintering or hot pressing (HP), which demonstrated that these methods were not suitable for forming dense, mechanically robust materials [11, 12]. The best result for sintering in a high purity nitrogen atmosphere at $\sim 2000^\circ\text{C}$ for one hour was 95% relative density with a submicron-sized microstructure [11]. For the hot isostatic pressing (HIP) procedure, 99% relative density was obtained, which required spherical shape powders and a pre-sintering stage of cold pressing (250 MPa), followed by 2 hours of HIP at a temperature of 1950°C and pressure of 195 MPa [13].

Presently, more efficient ZrN consolidation methodologies are needed; and promising solutions may be in the more modern electric current-assisted sintering techniques, such as spark plasma sintering (SPS) and high voltage electric discharge consolidation (HVEDC).

SPS is a low-voltage field-assisted sintering method that utilizes an electric current for consolidation of powders under elevated temperature and pressure. A powder specimen placed in an electrically conductive die is subjected to an external pressure applied by electrically conductive punches,

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4 and the specimen temperature is controlled by Joule heating generated in the die-punch tooling and in the
5 specimen itself, if it is made of an electrically conductive powder material. In comparison with
6 conventional sintering methods, the main advantages of the SPS are lower processing temperature, higher
7 heating rates and shorter holding times – the factors, which usually enable grain size retention [14-18].
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13 In HVEDC, a single pulse of electric current flows through the source powder, leading to an ultra-
14 intense energy release inside the powder volume, which is sufficient to allow consolidation up to high
15 density levels for a variety of materials. The high-voltage discharge (up to 30 kV), obtained by a capacitor
16 bank and released with an extremely short pulse (the pulse length is increase with the applied voltage: 500
17 ~ 1300 μ s for 1.5 ~ 5 kV), creates a significant current density passing through a powder compact, while
18 an external pressure is being applied. As a result, an ultra-rapid temperature increase is attained at the
19 contact points between powder particles and almost instantaneous micro-welding occurs during the
20 electric discharge. Because of such short sintering times, densification is accompanied only by minimal
21 changes in the microstructure, a factor of merit when aiming at achieving high mechanical strength
22 characteristics. During the last decade, this method has attracted growing interest and detailed review can
23 be found in elsewhere [19].
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38 In the past, the mechanical and thermo-electrical characteristics of SPS-processed ZrN samples
39 have been investigated and formulated as functions of porosity and temperature [20, 21]. Some more
40 specific analyses of SPS studied the influence of a boron nitride wrapping of powder specimens [22] and
41 the treatment of W/ZrN composites [23]. An absence of the modeling-aided analysis of the densification
42 kinetics in these previously conducted studies should be noted. Also, the densification behavior of pure
43 ZrN and the corresponding mechanical properties has not been reported, and there are no reports on
44 HVEDC processed ZrN materials.
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54 In the present study, the sinterability and final mechanical properties of the two commercial ZrN
55 powders processed through the two different field-assisted sintering methods (SPS and HVEDC) have
56 been tested and compared. With fixed holding time and heating rate, a systematic densification map of
57 SPS ZrN was built. Also, the influence of high pressure by double die SPS setup was evaluated. A
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constitutive model of powder hot pressing (based on the continuum theory of sintering [24]) was subsequently applied to the obtained experimental results for the description of the densification kinetics during both SPS and HVEDC.

2. Materials and processing methods

2.1 Materials investigated

Two ZrN powders (Face centered cubic, Fm3m) were employed for this study, one produced by Sigma Aldrich (SA) and the other by Alfa Aesar (AA). The main powder utilized for the consolidation by both SPS and HVEDC was AA, while SA was utilized for the SPS processing only, in order to compare the behavior of slightly different materials when undergoing this type of electric field-assisted technology.

The powder data are reported in Table 1. The powder morphology and size (Fig. 1) were observed using the scanning electron microscope (SEM) (FEI Quanta 450, USA). The SA powder particles show sharp edges and the absence of agglomeration, while the AA powders are well-rounded, almost spherical particles with a tendency to form agglomerates. The particle size was derived by manual measurements of 90 particles for each powder, resulting in an average value of $6.71 \pm 0.5 \mu\text{m}$ for SA and $6.02 \pm 0.42 \mu\text{m}$ for AA, as shown in Fig. 2.

The crystal structure and lattice parameters were evaluated by X-ray diffraction (XRD) (Bruker D-8 diffractometer, MA, USA), utilizing CuK_α radiation at room temperature. In Fig. 3, measured and reference ZrN (ICSD collection code # 167851)[25] XRD diffracted plot was drawn by hollow circle and solid line respectively. Also, dashed line shows the intensity difference between the measured and reference peak. Diffracted (h,k,l) planes are shown on the top of each peak. From the XRD data, in Fig. 3, the cubic NaCl-type structure dominates, however oxide impurities were found in both powders. Comparing these results with the zirconium oxide peak locations shown in Fig. 3 (a) and (b), the SA powder has oxide in the Zr_3O form (ICSD Collection code # 88320) [26], while AA includes ZrO_2 (ICSD Collection code # 66781) [27]. The lattice parameter for the two powders was found to be 0.4563 nm, a value close to what reported in the literature (0.457 nm) [25].

From energy-dispersive X-ray spectroscopy (EDS) (Oxford Instruments, UK) analysis, a different oxygen content was detected between the two powders: 8.72% for SA and 13.03% for AA, even though the two powders have almost analogous non-stoichiometric compositions, *i.e.* $\text{ZrN}_{0.86}$ and $\text{ZrN}_{0.87}$, respectively, when atomic % of each powder by the EDS converges to composition. AA also showed the presence of hafnium in amount $< 3\%$.

2.2 Spark plasma sintering processing regimes

The SPS system utilized was a Dr. Sinter SPSS-515 (SPS Syntex Inc., Japan), with a tooling setup generally constituted by Isocarb Graphite I-85 (Electrodes Inc., CA), except for the selection of silicon carbide for a specific application, as described later.

Fig. 4a shows a schematic diagram of the tooling setup assembly and Fig. 4b shows a photograph of the setup, located in the SPS chamber, before an experimental procedure was run.

Two different pressure conditions were selected. For low-pressure (< 90 MPa) experiments, 3.76 g of powder was placed into a 15.4 mm-diameter graphite die and compressed between two 20 mm-long graphite punches. For the high-pressure (> 90 MPa) experiments, a double die setup was used [28]. In this case, the tooling additionally had an internal 7 mm-diameter graphite die and two SiC 7 mm-high punches. This double die setup contained 0.82 g of powder.

A 0.2 mm-thick graphite paper wrapped the powder to prevent adhesion and contamination between the specimen and the tooling. A carbon felt layer, surrounding the graphite die, was used to reduce heat loss. An optical pyrometer (IR-AHS2, Chino, Japan) was used to detect the temperature of the graphite die.

For the SA powders, the measured green densities of the powder compacts were $\sim 57\%$, 59% and 66% , for the pre-SPS cold compaction at 30 MPa, 60 MPa and 120 MPa, respectively. The sintering regime consisted of heating at $100^\circ\text{C}/\text{min}$ from room temperature to the maximum temperature (1400, 1500, 1600 or 1700°C) with a dwell time of 6 min as represented in Fig. 5.

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4 For the AA powders, the measured green densities of the powder compacts were ~ 47%, 62%, 63%
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6 and 64%, for the pre-SPS cold compaction at 20 MPa, 120 MPa, 150 MPa and 180 MPa, respectively.
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8 The maximum sintering temperature was set at 1700°C. A broader range of pressures, compared to the
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10 processing conditions of SA powders, was applied: 0, 20, 120, 150 and 180 MPa, while the other
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12 experimental conditions were analogous. For the free pressure-less SPS a cold compaction step with a 50
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14 MPa load was applied, reaching the green density of 49%.
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18 For both SA and AA powders, the selected pressure was applied during the entire process and was
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20 concluded within 30 minutes. The SPS machine provided a periodic sequence of 12 ms of DC pulses
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22 followed by a pause of 2 ms during the whole process. All the experiments were conducted under ~20 Pa
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27 The axial displacement of the graphite die was monitored with a position sensor imbedded in the
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29 SPS device. For each case, a control procedure was conducted by employing the tooling setup in absence
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31 of powder and imposing the same experimental conditions. Such process provided the necessary data to
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33 compensate for the expansion and shrinkage of the tooling material. For the control experiment of high-
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35 pressure SPS, three SiC punches were inserted, instead of the conventional two, because the total length
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37 of the two SiC punches used with the powders was smaller than the overall axial dimensions of the die.
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41 Once the SPS process was complete, the densified specimens were extracted from the graphite die,
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43 ground by a 75 µm diamond disk and subsequently by a series of progressively finer SiC grinding papers
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45 (36 µm, 21.8 µm and 15.3 µm). To remove the carbon paper residuals from the specimen surface the
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47 samples were dried in an oven at 120°C for 20 min.
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51 *2.2 High voltage electric discharge compaction processing regimes*

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54 As for the materials employed, the information relative to powder AA given in section 2.1 is valid
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56 in this case too and will not be reiterated.
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59 The schematic of the apparatus for HVEDC (Impulse-BM, Russia) and a photograph of this setup
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61 are shown in Fig. 6 [19]. The overall system consists of the energy storage unit, switch-board, pressure
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4 and temperature measurement systems, electric current parameters' recording system and powder material
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6 sealing registration system. The energy storage unit includes a capacitor bank with a stored energy of 75
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8 kJ, which provides an intense energy discharge to the powder compact and the charging unit. The
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10 apparatus uses a pulsed current generated by the capacitor bank, for rapid processing of the powder under
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12 constant pressure during the whole process.
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15 The tooling setup employed in the HVEDC procedures consisted of a mold and two molybdenum
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17 punches. The mold was a metal cage fixed to an insulating mullite liner with an inner diameter of 10 mm
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19 and an outer diameter of 20 mm. The consolidation of the powders was conducted at pressures of 75 MPa
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21 to 300 MPa and at a voltage of 2 kV to 4 kV. Measured green densities after applying the pre-sintering
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23 pressure ranged from 53.5% to 61.0% under pressures of 75 MPa to 300 MPa, respectively, as shown in
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31 **3. Processed specimen characterization results**

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33 Final density was evaluated, together with the role of temperature and pressure on consolidation,
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35 and the influence of porosity on the mechanical and morphological characteristics of the sintered material.
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37 The employed technologies and methodologies involved various density measurement techniques,
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39 imaging by SEM, analysis by EDS, and hardness obtained from Vickers micro-hardness testing. All
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41 measurements were taken at room temperature.
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46 *3.1. Characterization of specimens processed by SPS*

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48 *3.1.1 Sigma Aldrich powders*

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51 The relative density of the SPS specimens was evaluated by means of the Archimedes' immersion
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53 method, which required the samples to be coated with paraffin wax prior to the measurements to prevent
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55 the access to the open porosity, which resulted in a non-negligible amount of the overall porosity in
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57 several specimens.
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All the sintered specimens were fractured or etched and characterized by SEM and EDS. High quality surface was obtained by etching for a few seconds in a solution containing concentrated HF, Aqueous (49%) / HNO₃, Aqueous (70%) / H₂O₂, Aqueous (30%) with ratio of 4.5:4.5:1 respectively [29].

Vickers micro-hardness tests were performed at room temperature by applying a 1 kg load on the standard diamond indenter (M-401-H1 Hardness testing machine, Leco, Michigan). A total of 12 indents per specimen from edge to center over the sample cross-section were realized and their diagonal was measured using an optical microscope, so that the Vickers micro-hardness could be calculated as follows:

$$HV = 1.854 \frac{F}{D^2} \quad (1)$$

in which F is the load (kgf) and D is the arithmetic mean of the two diagonals (mm).

The physical and mechanical properties of the specimens are listed in Table 3, which showed that the highest values of relative density (~100%) were achieved with the SA powder at 1700°C under 120 MPa. The final relative densities of these samples are reported in Fig. 7. For a fixed value of pressure, relative density is increased with increasing maximum final temperature with the only exception of the 1700°C /120MPa case (explained below). For the temperature and pressure ranges used in this study, these are the highest relative density values attained with a commercial powder. It is worth noting that the powders were not milled and sintering agents were not used. Such relative density values are significantly higher than the 63.5% we obtained by means of high temperature vertical dilatometer (Unitherm 1161, Anter coporation, USA), with a maximum sintering temperature of 1500°C, heating rate of 10°C /min and 2-hours holding time.

One of the main influencing factors during SPS is pressure, whose significant role in powders has been widely investigated [16, 17, 28]. Quach *et al.* [28] pointed out in yttria-stabilized ZrO₂ that pressure prevails diffusional mechanisms at low temperatures, while this trend tends to be less effective once higher temperatures are reached. Analogous conclusions were reached in the present investigation. Fig. 8 plots relative density as a function of temperature. Densification is significantly enhanced when increasing pressure from 30 MPa to 60 MPa at relatively low temperatures (1400°C and 1500°C).

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4 However, a further increasing of pressure up to 120 MPa did not appear to have a noticeable influence on
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6 the relative density. A slightly lower final density was observed for 1500°C and 1700°C when increasing
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8 pressure from 60MPa to 120MPa. Including previous relative density result of 1700 °C/120 MPa in Fig. 7,
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10 such small decrease could be attributed to measurement errors in the Archimedes' method or to a
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12 discrepancy in the application of a high pressure (in this case, 120 MPa) when using SiC punches instead
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14 of the graphite components employed for the low-pressure cases. The SiC punches present lower thermal
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16 and electrical conductivity compared with those of graphite, which results in slow heat transfer to
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18 specimens compared with regular graphite punches.
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22 Fig. 9(a) shows the relative density as a function of time for a maximum temperature of 1600°C for
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24 different pressures. The 30 MPa and 60 MPa curves present the same shape, with the latter being shifted
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26 to higher values of density, while the 120 MPa case has a different shape. Even though the 120 MPa
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28 curve has the highest initial relative density, the corresponding densification rate is lower with respect to
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30 the other two cases. Such trend is confirmed by considering the temperature at which the highest
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32 densification rate (slope of the curve) is reached for the various levels of pressure. While the 30 and 60
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34 MPa curves behave as expected, with peak densification rates at 1359°C and 1290°C respectively, for the
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36 120 MPa one this peak is reached only at 1370°C. Nevertheless, in both 60 and 120 MPa cases a final
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38 relative density of ~99% is attained, according to the Archimedes' immersion method (Table 4). Fig. 9(b)
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40 - (d) shows the microstructure of the fractured specimens consolidated under different pressures of
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42 30MPa, 60MPa and 120MPa respectively. Generally, an increase of the applied pressure results in the
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44 reduction of the grain size of the specimen with the same density [28]. In our results, the 60MPa and
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46 120MPa under 1600 °C condition have similar density (~ 99%) and grain size (~24 μm) (Table 3). This
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48 may be attributed to the low thermal conductivity of the SiC punches.
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53 Fig. 10 shows the effect of the maximum sintering temperature on the relative density as a function
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55 of time under 60 MPa pressure and shows SEM fractured images of the specimens. Higher sintering
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57 temperatures lead to an augment of the final density. As a drawback, the more elevated temperatures
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59 promote the increase in grain size from 8.62 μm to 33.26 μm, as shown in the micrographs. Fig. 10(b)
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shows the presence of several open pores for a specimen with 94.55% final relative density, while solely closed porosity, with voids characterized by small dimensions and a spherical shape, is encountered in the > ~ 98%-density samples depicted in Fig. 10 (c) – (e).

Fig. 11 shows the grain size dependence on porosity of the SA specimens. The general trend is an increase in grain size with decreasing porosity, with the exception of a few data points. Finally, Vickers micro-hardness measurements were performed. This parameter's dependence on porosity for the SA specimens is shown in Fig. 12(a), revealing a strong correlation. Several previous studies measured the Vickers micro-hardness of ZrN samples consolidated by SPS [20, 22] or other techniques, such as hot pressing and hot isostatic pressing [7, 13, 30], and reported average values of Vickers micro-hardness between 1000 kgf/mm² and 1500 kgf/mm², which is in a good agreement with our data.

3.1.2 Alfa Aesar powders

Fig. 11 and Table 4 present the relationship between the porosity and grain size of the AA samples.

Fig. 13 shows the effect of pressure on relative density and also shows the images of fractured specimens sintered at 1700°C under four different pressures (20, 120, 150 and 180MPa). Relative density appears to increase with growing pressure, and this influence of pressure is more prominent than that for the SA cases (Fig. 8). It is noted that a maximum relative density of 97.42% is achieved with highest pressure (180MPa), a value that can be compared with fully dense specimens of SA powders in terms of sinterability, as shown in Table 4.

Additionally, from the analysis of the microstructure shown in Fig. 13(b)-(e), we notice that pores start to be closed at 93~97% relative density.

The Vickers micro-hardness measurements outcomes, represented in Fig. 12(b), proved that the hardness dependence on porosity is analogous to the SA case.

3.2. Characterization of specimens processed by HVEDC

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4 The relative density of the specimens processed by HVEDC was evaluated by means of hydrostatic
5 weighing in a pycnometer. It is found that the maximum specimen density of ZrN did not exceed 93%.
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8 Since the governing parameters of the HVEDC technology are pressure and voltage, the
9 densification map describing the density dependence on these two quantities was built and is pictured in
10 Fig. 14. The map is constructed by fitting the experimental data in the test parameters intervals, with an
11 error < 12%. The density of the specimens increases with the load applied in the pre-pressing stage. This
12 trend appears, nevertheless, to have an upper bound. Given a value of electric current, a densification
13 enhancement is observed up to a certain value of cold-pressing load, after which any further increase
14 affects density only slightly. Fig. 14 also shows that the dependence of the relative density on the voltage
15 is linear. The electric power is proportional to the squared voltage. If the voltage is applied for more than
16 a few seconds, the zirconium nitride specimens can reach a thermodynamically stable structure. In this
17 context we expect the ZrN relative density to depend on the squared voltage. However, the extremely
18 short duration of HVEDC processes leads to kinetically trapped structures, which renders the relative
19 density linearly dependent on the applied voltage. A raise in the electric current density that flows through
20 the powder compact leads to an increase in the density of compacts [31]. However, beyond a certain
21 critical value, the powders will release a significant amount of voltage through the matrix. Quantitatively,
22 the dependence between the energy and the voltage is complex, since the material resistance depends on
23 the relative density of the material, which evolves during processing. In general, the dependences between
24 the process energy and the instant values of system internal parameters, such as density, can be described
25 by rather complex relationships, including exponential / logarithmic terms [32, 33]. Therefore it may be
26 expected, that if explored over wider ranges of applied voltages, the relationship between the relative
27 density and the voltage may become non-linear.
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53 It should be noted also that for the completeness of the conducted analysis, it is highly desirable to
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55 configuration, the temperature of specimens could not be measured during HVEDC process due to very
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short pulse duration. Theoretically, the correlation between electric discharge parameters and the localized temperature field developed during HVEDC has been analyzed in earlier publications [19, 34].

Fig. 15 shows the typical microstructure of a sample prepared under 3kV and 175MPa for the (a)~(c) and 3kV and 200MPa for the (d). Fig. 15(a) shows that the particle size in the center does not exceed the initial values of powder particle size, which indicates an absence of grain growth, as such rapid densification process was expected to guarantee.

On the other hand, the final porosity of the compact with density $> \sim 75\%$ includes a certain amount of open porosity, primarily located in the peripheral layer (Fig. 15(b)). Having a compact core and a porous periphery may be related to a radially heterogeneous distribution of the green density. This effect is due to a gradient in the lateral pressure caused by the friction of the mold walls against the powder particles movement. The magnitude of this lateral pressure is not constant along the height of the specimen, and it has a tendency to decrease when moving from the punches to the powder, therefore causing a heterogeneous density distribution in the axial direction within the specimen.

A consequence of the uneven distribution of the lateral pressure is a lower green density at the center of the powder compact, combined with a reduced contact area among the particles, which leads to an increased electrical resistivity and therefore enhanced Joule effect and localized peak temperatures.

Apparently with a decrease in the density of electric current (at constant pressure) or the level of applied pressure (at constant current density), the size of the densified central zone is reduced and a corresponding increase in the volume occupied by the porous peripheral zone is obtained, which ultimately leads to a lower overall relative density of the specimen.

An improvement against such non-homogeneities can be reached by applying more elevated (axial) pressures, responsible for the expansion of the dense central zone. If, instead, the current density is increased, the raise in electrical power is focused on the central area. Consequently, localized heating occurs in the region that is already the most compacted, causing a grain size increase in the central zone.

When an electrical current pulse passes through the compact, the peripheral zones can be heated at a temperature relatively lower than the ones in the central part, which results in the friable structure at the

edge of specimens (Fig. 15(b)). The thickness of the porous layer was reduced by increasing the applied pressure, which can be seen by comparison between Fig. 15(b) and Fig. 15(d).

However, it should be noted that in some areas of the end pressing parts (Fig. 15(c), apparently strong energy is released after formation of the individual grains by dissociation of nitride, constituting eutectic solid solution of zirconium nitride and zirconium (large grains of Fig. 15(d)).

In order to confirm the discussion above, we checked the Vickers micro-hardness measured with a load of 1kgf. These measurements along the longitudinal direction of the samples' cross-section confirmed that the central part was endowed with the most densified material, as shown in Fig. 16(a). The internal area of the specimen exhibits micro-hardness values four times greater than the peripheral areas as shown in Fig. 16(b).

4. Discussion: processing – structure – properties correlation and modeling of densification kinetics

4.1. Processing – structure – properties correlation

The processing of SA powders resulted in higher relative densities consolidated under SPS compared to AA powders, even though they share similar properties in terms of particle size and distribution. Such behavior can be explained by considering that AA powders are more agglomerated and have higher levels of impurities ($\text{Hf} < 3\%$), which typically hamper the sinterability of this material. Another possible reason may be the higher initial oxygen content in the AA powders. The average composition was $\text{ZrN}_{0.94}\text{O}_{0.11}$ for SA and $\text{ZrN}_{0.99}\text{O}_{0.3}\text{Hf}_{0.01}$ for AA (Table 4), which can be compared with the respective initial compositions of $\text{ZrN}_{0.86}\text{O}_{0.18}$ and $\text{ZrN}_{0.87}\text{O}_{0.28}\text{Hf}_{0.01}$ (Table 1). In both cases the starting powder oxide ratio was retained, which implies that the initial oxide content affects the composition of the densified specimens.

ZrN is characterized by a broad range of non-stoichiometry (ZrN_{1-x} , $0 < x < 0.35$). The sintering of ZrN is accompanied by the release of weakly bound nitrogen [35, 36]. Interestingly, the application of high pressures makes the nitrogen ratio increase in the AA powders (Table 4). It is inferred that the cold

pressing with elevated loads prior to the SPS process renders the contact area of the particle larger, which results in reducing the amount of the open pores that act as fast diffusion paths of the dissociated nitrogen. Therefore, nitrogen dissociation is at least partially impeded by a sintering stage of cold pressing.

Both powders share the natural tendency to increase in grain size when porosity is reduced. However, for analogous porosity levels, AA specimens showed a smaller average grain size than SA (Table 4).

Concerning mechanical properties, the specimens' hardness also resulted to be dependent on porosity, as Fig. 12 shows. To evaluate the Vickers hardness of a porous material, the following equation was utilized [37]:

$$H_v(\theta) = H_{v,0} \times \exp(-b\theta) \quad (2)$$

where $H_{v,0}$ is the Vickers hardness of the fully dense material, b is a constant that depends on the applied load and θ is porosity.

By applying this equation to our hardness data we obtained b and $H_{v,0}$, which resulted to be 4.22 and 1609.96, respectively, for SA samples and 4.53 and 1633.75 for AA, revealing that the hardness dependence on porosity of the two powders is comparable. The b values are in good agreement with the literature [20].

Because of the high electric currents applied, HVEDC allows consolidation of a powder compact within a few seconds, and therefore the retention in the sintered specimens of smaller grain sizes than in the SPS cases is expected. But, interestingly, the specimens processed by the two techniques share analogous average grain sizes.

The maximum relative densities achieved in the experiments are ~93% for HVEDC, ~97% for AA SPS and ~99% for SA SPS. The lower values attained for the HVEDC cases are explainable by the presence of the porous peripheral zone, while the SPS process renders a more homogeneous microstructure.

Fig. 16(c) and (d) shows the measurements of the Vickers micro-hardness for the cross-section of the SPS-processed specimens (AA1712 and SA1403) along the longitudinal direction. Compared with Fig. 16(b), which concerns the analogous properties for the HVEDC-processed specimens, the SPS samples present a more uniform structure within the axial cross-section.

Another macro-scale effect of the non-uniformities characterizing HVEDC specimens is found in the presence of cracking and barrel-like shapes in the densified compacts. Additionally, the application of high pressures and voltages create mullite contamination in the samples. The optimal compaction conditions to prevent shape alterations and mullite contamination in the HVEDC of zirconium nitride have been identified in the application of a pressure within the 100~160MPa range and a voltage of 2~3kV, which, on the other hand, limits the final relative density to 83%.

4.2. Modeling of the densification kinetics imposed by SPS and HVEDC

Many efforts are currently dedicated to the individuation and modeling of densification mechanisms of ceramic materials under SPS conditions [32, 38-43], while equations capable of reliable describing consolidation kinetics for HVEDC procedures have not been developed.

In the present study, the constitutive equation of the continuum theory of sintering developed for hot pressing is used to analyze the effect of electric currents on densification kinetics during the SPS and HVEDC processes. Power law creep can be considered the dominant mechanism of densification of crystalline powders [44, 45].

The constitutive equation for a non-linear viscous material is [32]:

$$\sigma_z = A_m \sqrt{\frac{2(1-\theta)}{3}} \frac{(1-\theta)}{\theta} \left[\sqrt{\frac{2(1-\theta)}{3}} \frac{\dot{\theta}}{\theta} \frac{1}{(1-\theta)} \right]^m \quad (3)$$

where σ_z is the load applied (Pa), θ is porosity (dimensionless), $\dot{\theta}$ is the porosity change with time (1/s) and m is the strain-rate-sensitivity exponent. The material constant A_m (Pa·s^m), which is a function of

microstructure (principally reflecting the influences of the grain size, sub-grain size, and dislocation density), is expressed by an Arrhenius-type relationship [46, 47]:

$$A_m = A_{m0} T^m \exp\left(\frac{m\Delta H_{SD}}{RT}\right) \quad (4)$$

where A_{m0} is a material's constant ($\text{Pa}\cdot(\text{s/K})^m$), T the absolute temperature (K), ΔH_{SD} is the activation energy for self-diffusion (J/mol), and R is the gas constant (J/mol·K).

Using the Ashby creep equation [45], the sintering mechanism is related with the stress exponent n , which is the reciprocal of m . Specifically, each creep mechanism corresponds to a certain range of values of n (or m), as summarized elsewhere [32, 48]. Petrykina *et al.* [49] investigated the hot pressing of ZrN and found that the underlying creep mechanism consists in dislocation climb ($n=4\sim5$, $m=0.2\sim0.25$) and determined the activation energy for sintering as 142.26 kJ/mol [50]. Fig. 17 is a plot of the porosity evolution with time for the SA powder under 1400°C and 30 MPa during SPS. The experimental densification curve is displayed by a solid line, while the curves defined by scattered symbols represent the various fitting curves obtained by varying m and A_m . The best fitting appears to be constituted by the circles traces, corresponding to $A_m = 2085000$ ($\text{Pa}\cdot\text{s}^m$) and $m = 0.22$, indicating that the sintering mechanism of ZrN under SPS conditions is dislocation climb, analogously to the hot pressing case. It is worth mentioning that in fully dense stoichiometric uranium nitride (UN), which has the same crystallographic structure as ZrN, an analogous value for m was found [51]. Additionally, these results confirm a study conducted by Langer *et al.* [38-40], who found that the sintering mechanism for ionic conductors, semiconductors or insulating materials did not change between hot pressing and SPS.

For HVEDC, a significant aspect to be taken into account for the modeling of the process is the extreme rapidity characterizing this technique, which allows powders to be consolidated within a few seconds. A “zero-order approximation” of such technology based on its peculiarly short processing time can disregard the influence of heat on densification and, in view of the applied high pressures, can describe HVEDC as a cold pressing process.

From the constitutive equation for the cold pressing case, the following relationship can be derived [32]:

$$\sigma_z = \sigma_y \sqrt{\frac{2}{3} \frac{(1-\theta)^3}{\theta}} \quad (5)$$

where σ_y is the yield stress of the bulk material.

By substituting the experimental data on pressure and final porosity into Eq. (5), the yield stress for each condition can be calculated, as shown in Fig. 18 (a). It appears that when a low voltage is applied, Eq. (5) provides good correlations with experimental data for a constant value of the yield stress of the bulk material. Indeed, in low voltage processes the short sintering time does not allow enough time for the effect of heating to be significant, and the adoption of a cold pressing model can be considered adequate. When the voltage is increased, the high electrical currents are involved, and the consequent increased heat and/or field-related phenomena, compromise the validity of the purely plastic material assumption, inducing a pressure-dependent behavior on the “apparent yield stress.”

The constitutive equation for a non-linear viscous material, Eq. (3), was applied to the HVEDC results to determine the densification mechanism (m value). Taking the natural logarithm of Eqn. (3) and rearranging,

$$\ln \sigma_z - \frac{1}{2} \ln \frac{2}{3} \left(\frac{1-\theta}{\theta} \right) - (1-\theta) = m \left\{ \frac{1}{2} \ln \frac{2}{3} \frac{1}{\theta(1-\theta)} + \ln \dot{\theta} \right\} + \ln A_m \quad (6)$$

After inserting the average porosity rate by calculating slope and pressure given in Fig. 14 into Eq. (6), a plot can be generated to determine m and A_m , as shown in Fig. 21b. In the conventional sintering theory, the densification of a powder by means of hot pressing provides one m value that is associated with a specific sintering mechanism. However, Fig. 18(b) shows an increase of the slopes (m value) with increased voltage, if excluding the high pressure points (300MPa for 2.5kV and 225 ~ 300MPa for 3 ~4kV). Under low voltage, $m = 0$, which confirms that HVEDC acts like quasi-cold pressing. Increasing

the voltage leads to a change of the strain-rate sensitivity value m from 0 to 1, which is attributed to the increasing heat generation.

The provisional exclusion of the high pressure data was motivated by the markedly distinct behavior of our curves when shifting from low to high values of pressures, which suggested that the two pressure regimes need to be evaluated separately. It appears that the combination of high pressure and voltage during HVEDC induce a different behavior in the material with respect to those used for modeling of hot pressing. The obtained first order approximation provides an impetus for future work on refining the mechanisms underlying the novel and still rare technology of HVEDC.

5. Conclusions

A comparative study of the spark plasma sintering (SPS) and high voltage electric discharge compaction (HVEDC) methods for the consolidation of zirconium nitride (ZrN) was conducted.

SPS allows the obtainment of the highest relative densities and the formation of more uniform microstructures with respect to HVEDC. In this more successful case of SPS, two different ZrN powders were utilized, so that the significant impact of powder agglomeration and oxide content on the physical and mechanical properties of the sintered specimens could be evidenced. Sintering temperature is the critical variable, on the other hand, pressure gives serious effect only with low sintering temperature for the densification of the ZrN powder (SA). Densification of AA powder depends strongly on the pressure and, nitrogen dissociation from ZrN was reduced with increasing pressure. Specimens densified by HVEDC have porous structure at the edge and non-uniform shape.

A constitutive model of the densification behavior was proposed and verified based on the experimental data. For SPS, dislocation climb appears to control the consolidation kinetics, while a univocal underlying sintering mechanism could not be individuated for HVEDC in which modeling outcomes are strongly dependent on the applied voltage. It was found that sintering mechanism of ZrN by SPS is similar to HP, which implies that electric effect of SPS is relatively small compared with the heat effect for the densification of ZrN. Further investigation is necessary in order to perform a more detailed

analysis of HVEDC, in which the electric field effects are likely to be playing a significant role during densification.

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Table Captions

Table 1.	ZrN powders' characteristics.
Table 2.	Energy-dispersive X-ray spectroscopy results of SA and AA powders.
Table 3.	Green density of AA specimens after applying the pressure for the high voltage electric discharge consolidation.
Table 4.	Physical, chemical and mechanical properties of ZrN (SA and AA) specimens prepared by spark plasma sintering.

Figure Captions

Fig. 1.	As-received ZrN powders, (a),(b) SA and (c),(d) AA powders.
Fig. 2.	Particle size distribution of the ZrN powders, (a) SA and (b) AA powders.
Fig. 3.	X-ray diffraction results of SA (a) and AA powders (b), arrows indicate the oxide impurity positions. Zr ₃ O (a) and ZrO ₂ (b) peak location and relative intensity were shown at the bottom of each plot.
Fig. 4.	(a) Schematic representation of spark plasma sintering process, (b) spark plasma sintering machine before an experiment.
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Fig. 10.	Relative density variation with time at fixed pressure of 60MPa and scanning electron microscope image of the fracture surface of SPSed ZrN (SA) : (b) 1400 °C, (c) 1500 °C, (d) 1600 °C and (e) 1700 °C. Open and closed pores are indicated by white arrows.

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4 Fig. 11. Grain size dependence on porosity of SA and AA specimens consolidated by spark
5 plasma sintering. 1400~1700 °C, 30~120MPa for SA specimens and 1700 °C, 0~180MPa
6 for AA specimens.
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10 Fig. 12. Vickers microhardness dependence on porosity of ZrN specimens (a,b) SA, AA
11 consolidated by spark plasma sintering and (c) AA consolidated by high voltage electric
12 discharge consolidation.
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14 Fig. 13. Relative density variation with pressure at fixed maximum temperature of 1700°C (a) and
15 SEM image of (b) 20MPa, (c) 120MPa, (d) 150MPa and (e) 180MPa for the ZrN (AA)
16 consolidated by spark plasma sintering. Open and closed pores are indicated by white
17 arrows.
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20 Fig. 14. The densification map of ZrN (AA) consolidated by high voltage electric discharge
21 consolidation. The relative density of the specimens is given as a function of pressure and
22 voltage. The legend indicates the relative density.
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25 Fig. 15. Scanning electron microscope images of ZrN (AA) specimens consolidated by high
26 voltage electric discharge consolidation. (a) central and((b) and (c)) edge of the specimen
27 (3kV and 175MPa) and (d) edge of the specimen (3kV and 200MPa).
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30 Fig. 16. Vickers micro-hardness results of ZrN specimens after sectioning, (a) schematics of the
31 analyzed areas, from edge (Location 1) to center(location 3), Vickers micro-hardness plot
32 as a function of the radial position of (b) AA specimen consolidated by high voltage
33 electric discharge consolidation, (c) AA specimen consolidated by spark plasma sintering
34 and (d) SA specimen consolidated by spark plasma sintering.
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37 Fig. 17. Constitutive equation fitting of experimental porosity curves of ZrN (SA) specimen
38 (SA1403) prepared by spark plasma sintering.
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41 Fig. 18. Constitutive equation fitting of high voltage electric discharge consolidation results. (a)
42 yield stress variation with pressure and (b) m variation with voltage.
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Table 1. ZrN powders' characteristics

Name	SA*	AA**
Vendor	Sigma Aldrich	Alfa Aesar
Lot #	BCBC1256V	L27X042
Purity	≥99% (trace metals basis)	99.5% (metal basis excluding Hf), Hf<3%
Size	Particle size: $6.71 \pm 0.5 \mu\text{m}$	Particle size: $6.02 \pm 0.42 \mu\text{m}$
Melting temperature (°C)	2980	2980
Composition	$\text{ZrN}_{0.86}\text{O}_{0.18}$	$\text{ZrN}_{0.87}\text{O}_{0.28}\text{Hf}_{0.01}$

* Sintered by spark plasma sintering

** Sintered by spark plasma sintering and high voltage electric discharge consolidation

Table 2. Energy-dispersive X-ray spectroscopy results of SA and AA powders

Element	Shell	SA	AA
N	K	42.26%	40.19%
O	K	8.72%	13.03%
Zr	L	49.02%	46.26%
Hf	M	0%	0.53%

Table 3. Green density of AA specimens after applying the pressure for the high voltage electric discharge consolidation

Pressure (MPa)	75	100	125	150	175	200	225	250	275	300
Green relative density (%)	53.5	54.5	56	57	58	59	60.5	60.5	61	61

Table 4. Physical, chemical and mechanical properties of ZrN (SA and AA) specimens prepared by spark plasma sintering

Specimen	Sintering temperature (°C)	Sintering pressure (MPa)	Relative density (% , Archimedes)	Grain Size (μm)	HV1 (kgf/mm ²)	Composition (Atom %)
SA1403	1400	30	89.73	6.99	959.59	ZrN _{0.76} O _{0.10}
SA1503	1500	30	93.18	12.47	1234.02	ZrN _{0.87} O _{0.11}
SA1603	1600	30	95.36	17.59	1435.89	ZrN _{1.03} O _{0.13}
SA1703	1700	30	98.34	32.70	1413.85	ZrN _{0.88} O _{0.10}
SA1406	1400	60	94.55	8.62	1249.33	ZrN _{0.93} O _{0.11}
SA1506	1500	60	98.51	17.47	1561.46	ZrN _{0.94} O _{0.10}
SA1606	1600	60	98.94	24.67	1507.16	ZrN _{0.90} O _{0.10}
SA1706	1700	60	99.52	33.26	1528.58	ZrN _{0.88} O _{0.10}
SA1412	1400	120	96.22	9.14	1419.09	ZrN _{1.21} O _{0.14}
SA1512	1500	120	97.90	16.71	1473.06	ZrN _{0.81} O _{0.10}
SA1612	1600	120	99.12	24.09	1480.54	ZrN _{1.15} O _{0.13}
SA1712	1700	120	98.12	22.79	1498.11	ZrN _{0.89} O _{0.10}
AA1700	1700	0	54.07	-	-	-
AA1702	1700	20	75.58	3.61	546.30	ZrN _{0.82} O _{0.17} Hf _{0.01}
AA1712	1700	120	93.19	3.77	1183.6	ZrN _{0.90} O _{0.36} Hf _{0.01}
AA1715	1700	150	96.95	5.99	1446.71	ZrN _{1.06} O _{0.37} Hf _{0.01}
AA1718	1700	180	97.42	6.30	1422.46	ZrN _{1.16} O _{0.31} Hf _{0.02}

Fig. 1. As-received ZrN powders, (a),(b) SA and (c),(d) AA powders.

Fig. 2. Particle size distribution of the ZrN powders, (a) SA and (b) AA powders.

Fig. 3. X-ray diffraction results of SA (a) and AA powders (b), arrows indicate the oxide impurity positions. Zr_3O (a) and ZrO_2 (b) peak location and relative intensity were shown at the bottom of each plot.

Fig. 4. (a) Schematic representation of spark plasma sintering process, (b) spark plasma sintering machine before an experiment.

Fig. 5. Temperature regime for the consolidation of ZrN (SA) powders by spark plasma sintering process.

Fig. 6. (a) Schematic representation of high voltage electric discharge consolidation process, (b) high voltage electric discharge consolidation machine before an experiment [19].

Fig. 7. Relative density plot of ZrN (SA) specimens prepared by spark plasma sintering measured by Archimedes immersion method.

Fig. 8. Effect of the pressure on the final relative density of SPSed ZrN (SA) specimens sintered at different temperature.

Fig. 9. Relative density variation with time at fixed maximum temperature of 1600 °C and scanning electron microscope image of SPSed ZrN (SA) specimens (b) 30MPa, (c) 60MPa and (d) 120MPa.

Fig. 10. Relative density variation with time at fixed pressure of 60MPa and scanning electron microscope image of the fracture surface of SPSed ZrN (SA) : (b) 1400 °C, (c) 1500 °C, (d) 1600 °C and (e) 1700 °C. Open and closed pores are indicated by white arrows.

Fig. 11. Grain size dependence on porosity of SA and AA specimens consolidated by spark plasma sintering. 1400~1700 °C, 30~120MPa for SA specimens and 1700 °C, 0~180MPa for AA specimens.

Fig. 12. Vickers microhardness dependence on porosity of ZrN specimens (a,b) SA, AA consolidated by spark plasma sintering and (c) AA consolidated by high voltage electric discharge consolidation.

Fig. 13. Relative density variation with pressure at fixed maximum temperature of 1700°C (a) and SEM image of (b) 20MPa, (c) 120MPa, (d) 150MPa and (e) 180MPa for the ZrN (AA) consolidated by spark plasma sintering. Open and closed pores are indicated by white arrows.

Fig. 14. The densification map of ZrN (AA) consolidated by high voltage electric discharge consolidation. The relative density of the specimens is given as a function of pressure and voltage. The legend indicates the relative density.

Fig. 15. Scanning electron microscope images of ZrN (AA) specimens consolidated by high voltage electric discharge consolidation. (a) central and ((b) and (c)) edge of the specimen (3kV and 175MPa) and (d) edge of the specimen (3kV and 200MPa).

Fig. 16. Vickers micro-hardness results of ZrN specimens after sectioning, (a) schematics of the analyzed areas, from edge (Location 1) to center(location 3), Vickers micro-hardness plot as a function of the radial position of (b) AA specimen consolidated by high voltage electric discharge consolidation, (c) AA specimen consolidated by spark plasma sintering and (d) SA specimen consolidated by spark plasma sintering.

Fig. 17. Constitutive equation fitting of experimental porosity curves of ZrN (SA) specimen (SA1403) prepared by spark plasma sintering.

Fig. 18. Constitutive equation fitting of high voltage electric discharge consolidation results. (a) yield stress variation with pressure and (b) m variation with voltage.