Flash cold sintering of Nb$_2$O$_5$: polarity and electrolyte effects

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ABSTRACT

We report on a novel consolidation technique based on the combination of a liquid (cold sintering) and electricity (flash sintering). The evolution of hydrogen from electrolysis of the solvent triggered the Flash Cold Sintering (FCS) event without need for external heating. Electrochemical effects were pronounced in the presence of acetic acid solution as the electrolyte had an increased conductivity compared to pure water. By adjusting the acetic acid molar concentration to 0.5 M and by inverting the polarity during FCS a 5 mm diameter 0.8 mm thick Nb$_2$O$_5$ sample was evenly sintered up to 99% in 100 s at a temperature as low as 350°C. Conventional sintered counterparts achieved a 95% relative density when dwelled for 240 min at 1400°C. The inherent complexity of the proposed FCS approach resulted in enhanced densification and weakly translucent samples.

1. Introduction

Nb$_2$O$_5$, is a functional ceramic material commonly employed in the form of a coating for electrochemical, electrochromic and optical applications. Nb$_2$O$_5$ coating is widely used to enhance the creep and wear resistance of glasses [1]. On the other side, Nb$_2$O$_5$ - nH$_2$O suits acid-catalyzed reactions [2–4]. Nb$_2$O$_5$ also finds applications in chemical sensor [5–7], energy storage [8,9] and batteries [10,11] due to its large permittivity, wide band gap (3.53–3.9 eV) and low electrical conductivity. The electrochromic characteristics of Nb$_2$O$_5$ are controlled by the insertion of Li$^+$ governing its reversible coloration from brown to blue.

Only a few attempts have been reported on the consolidation of Nb$_2$O$_5$ bulks using conventional sintering. So, it is not surprising that emerging consolidation techniques, like flash sintering and cold sintering, have not been attempted. Flash sintering (FS) was originally developed by Cologna et al. [12] to consolidate zirconia in a few seconds (<5 s). The most accepted FS mechanisms involve Joule heating, electrochemical effects [13,14] and nucleation of Frenkel pairs [15,16]. Because its high heating rate –10$^{4}$°C/min [17] and short processing times it has attracted a lot of attention and it has been applied to several ceramic systems. However, a typical limitations of FS is the formation of hot spots. In particular, uneven consolidation is exacerbated under a high voltage exceeding 100 V. Therefore, it is of primary importance to lower down both the FS voltage and furnace temperature.

On the other hand, the cold sintering process (CSP) is based on a transient liquid-phase sintering and it was first proposed by Guo et al. [18] where the synergic role of a solvent and pressure (≈300–500 MPa) enables consolidation at temperatures as low as 300°C. The CSP includes several mechanisms: facilitated particle rearrangement, hydroplasticity (plasticity enhanced by presence of a liquid), dissolution-precipitation and evaporation of the liquid. CSP is a low temperature and low energy-consuming technique fairly and it has been applied to several inorganic and hybrid materials including conductors [19,20], semiconductors [21–23], nanocrystalline ceramics [24], functional ceramics (i.e. electroceramics, thermoelectrics, ferroelectrics, solid-state-battery, piezoelectrics [25]). Due to the short life of the steel dies, the technique is hardly scalable to sample size exceeding 2 cm diameter, especially when using a pressure exceeding 300 MPa. Hence, reduction in the processing pressure is highly desirable.

The ambition of this work is to combine together FS and CSP [26] in order to surpass the limitations of both techniques [27]: i) reduce operating voltage from 100 V for FS to 20 V for FCS; ii) and lower the CSP pressure by a factor of 10. The comparison with conventional sintering of Nb$_2$O$_5$ allowed to pin down peculiarities of the newly developed technique.

2. Experimental procedures

Alfa Aesar 99.9% pure Nb$_2$O$_5$ powder with average particle size of 0.5°μm was used in this study. The experimental procedure includes four steps (see Figure 1): i) Mixing: the raw powder was pre-mixed
Figure 1. Four steps layout of the proposed methodology to investigate flash cold sintering of Nb$_2$O$_5$.

with a different solvent, either water or a weak acetic acid solution (i.e. 30% wt. water or 30% wt. and 0.5 mol/L acetic acid), in a plastic vial using a vortex mixer (XH-C) for 15 min to form a sticky paste. Using a trial-and-error approach, we attempted FCS using several solid/liquid fractions. It was found that 30% wt. was the most suitable one. Below 30% wt. loading the FCS even was not reproducible, loading exceeding 30% wt. resulted in a low viscosity paste easily expelled from the punches/die assembly; ii) FCS treatment: the paste (= 0.15 g) was then loaded inside a hollow alumina tube (inner diameter = 5 mm, outer diameter = 8 mm, length = 25 mm, purity >99%) and pressed between two stainless steel punches connected to a computer controlled bipolar power supply (SOYI-30100DM, purchased from Shanghai Soyi Power Co., Ltd., China). Two 99.99% pure Mo sheets (thickness = 1 mm) were placed between the steel punches and the paste. A K-type thermocouple was inserted through a 0.5 mm hole. For clarity see schematic proposed in Figure 1; iii) Annealing: the FCSed sample was placed into a conventional furnace at 800°C, heating rate of 10°C/min for 60 min; iv) Analyzing and testing: the FCSed sample was cut and the cross-section was inspected before and after annealing using an Optical microscope (USB camera 500A) and an XRD machine (Rigaku Smartlab) and a SEM (FESEM-F50).

The voltage current and temperature were recorded using a data logging system (National Instrument NI9775). To avoid the paste being squeezed out of the tube, the uniaxial pressure of 20 MPa was gradually applied. For comparison, green bodies for conventional sintering were prepared using a 13 mm diameter steel die using 0.5 g Nb$_2$O$_5$ powder. Conventional sintering was carried out at temperature of 1100, 1200, 1300, 1400°C with variable dwelling time 30, 60, 120, 240 min. After sintering, the cross-section was polished and thermally etched at 1200°C for 60 min.

3. Results and discussion

In order to produce dense and evenly FCSed material more than 50 samples were prepared using the setup shown in Figure 1. In summary, as illustrated in Figure 2, the inherent FCS mechanisms were captured by interrupting the process at different stages. As shown in Figure 3, electrolyte (i.e. water or acetic acid solution) and current waveform (i.e., DC vs bipolar control) were adjusted to identify their contributions.

Preliminary experiments were carried using dry powder. As expected, no current (i.e. heating/consolidation) passing across the powder even under a voltage of 200 V. The addition of water resulted in the well-known water electrolysis reactions:

\[ 2H_2O \rightleftharpoons 2H^+ + 2OH^- \]  \hspace{1cm} (1)

\[ \text{Cathode: } 2H^+ + 2e^- = H_2(g) \]  \hspace{1cm} (2)

\[ \text{Anode: } 4OH^- - 4e^- = O_2(g) + 2H_2O \]  \hspace{1cm} (3)

For comparison, during flash sintering under a DC field, an analogous electrochemical reaction within the material has been reported by several researchers [24,25]. The equilibrium between lattice oxygen (O$_{\text{latt}}^\delta$), oxygen vacancies (v$_\delta$), electrons (e$^-$) and oxygen followed:

\[ O_{\text{latt}}^\delta \leftrightarrow v_\delta + 1/2O_2(g) + 2e^- \]  \hspace{1cm} (4)

\[ \delta v_\delta + Nb_2O_5 + 2\delta e^- \rightarrow Nb_2O_{5-\delta} + 2O^\delta \]  \hspace{1cm} (5)
As a result of the electrochemical reduction (see equation (5)), the blackening started at the cathode moving toward the anode region. The latter is experimentally visualized in Figure 1(b) by interrupting the FCS process at different time intervals and confirming the electrochemical reduction. The interaction solid liquid and electric field is rather complex and dynamic (i.e. rapid evolving in time). The interpretation of the phenomenon using a thermodynamic equilibrium approach (i.e. Ellingham or Pourbaix diagrams) remains rather challenging. Further work is still needed to clarify these aspects, it is clear that the H\textsubscript{2} gas evolution (Eq. 2) and the electrochemical reduction (Eq. 5) acted synergically to reduce the starting oxide. The Nb\textsubscript{2}O\textsubscript{5} reduction was also confirmed by the electrical data suggesting an unusual spike in electrical conductivity after 30 s (Figure 2(a)). The directional polarity effect resulted in uneven blackening (Figure 2(b) and 3(b)) and predictable microstructure heterogeneities.

FCS of Nb\textsubscript{2}O\textsubscript{5} was attempted using water under 60 V DC (see Figure 3) and a 0.5 M acetic acid solution under 30 V DC. In theory, the theoretical threshold for water electrolysis is as low as 1.23 V; however a voltage as high as 60 V was needed to trigger the FCS event and produce enough heating, such a high voltage was likely to form an electric arc and undesired cracking of the sample. Instead, when using acetic acid 0.5 mol/L with a conductivity of \~10\textsuperscript{-2} S/m (significantly higher than deionized water \leq 10\textsuperscript{-6} S/m) the FCS voltage was lowered to 30 V. The rational to use acetic acid as an electrolyte accounted for: i) acetic acid had increased conductivity in comparison to water; ii) the acetic acid, as an organic acid, was fairly easy to removed without causing any contamination and residuals in specimen; iii) Excessive acetic acid concentration up to 2 M resulted in too high conductivity and ultrarapid FCS event causing current concentration and uneven sintered bodies as shown in FigureS1.

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**Figure 2.** (a) Voltage and current profiles recorded during FCS of niobium oxide; (b) photographs of cross section of samples obtained at different stages under a DC field (30 V, 20 A) using a 0.5 mol/L acetic acid solution. Note the preferential reduction and blackening at the cathode.
In order to mitigate the uneven blackening, polarity inversion proposed in Figure 2(c) was attempted. The irreversible electrochemical reduction on both sides of the specimen is a prerequisite for an even current flow and homogenous densification. As expected, by periodically reversing polarity, the Nb$_2$O$_5$ was reduced on both sides confirming a more homogenous reduction when comparing the insets of Figure 3(c) and (b). Under direct current, the blackening became apparent at the cathode and the reduction propagated toward the anode resulting in heterogeneous samples. Conversely, the

Figure 3. Current, voltage and current profiles recorded during FCS of Nb$_2$O$_5$ using (a) 30 wt% distilled water (b) 0.5 mol/L acetic acid solution 30 wt% under 30 V DC mode; (c) 0.5 mol/L acetic acid solution by reversing polarity of 20 V (d) temperature measured by K-type thermal couple using parameters described in (c). Note the difference in applied voltage for the different electrolytes.

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Figure 4. Density plot against furnace temperature for conventional sintered materials with variable soaking time (30, 60, 120, 240 minutes) along with FCSed samples processed at room temperature. Insets showing the photographs of annealed FCSed sample and counterpart processed at 1400°C using conventional approach.
electrochemical reduction was more controlled by reversing the polarity so that both sides of the sample were reduced. The FCS event resulted in several simultaneous phenomena: electrolysis of water, Joule heating, evaporation of water and consolidation of the specimen. Further work is needed to fully understand the FCS mechanisms, our findings support the significance of hydrogen evolution (Eq. 2) during the FCS incubation. The latter seems consistent with the observations of Raj et al. [28] suggesting that Joule heating is a necessary but not a sufficient condition to ignite a flash sintering event. Figure 3(c, d) refer to the sample and the peak temperature recorded using a K-type thermocouple as low as 350°C.

Figures 4, 5 propose a comparison between the samples processed using FCS and conventional sintering. In the best case, for conventionally sintered samples, a 95% relative density was obtained at 1400°C. In conventional sintering, the density significantly increased by raising the temperature above 1300°C. Interestingly, a density of 99% was obtained by using acetic acid solution (Figure 3(c)) in just 100 s discharge. For comparison, a relative density limited to 70% was obtained for samples FCSed using water (Figure 2(a)).

Another remarkable achievement is the drop in temperature (Figure 3(d)) ~ 350°C significantly lower than the 1400°C required in conventional sintering where pores are clearly visible in Figure 5(b). To compensate the oxygen vacancies produced during FCS process, the samples heat up to 800°C, obviously blackened coloration of the samples disappeared (see Figure S1). Surprisingly, unlike conventional sintered samples, FCSed ones were weakly translucent (Figure 4) confirming the high level of densification. The XRD pattern in Fig. S3 also confirmed the unchanged purity of processed materials respect to the starting powder.

4. Conclusions

The new developed Flash Cold Sintering (FCS) allowed near instantaneous consolidation of Nb2O5 in the presence of a 0.5 M acetic acid solution. The technique surpasses some of the limitations of both Flash Sintering (FS) and Cold Sintering Process (CSP): i) reduce voltage from 100 V for FS to 20 V for FCS; ii) and lower the CSP pressure by a factor of 10. Homogenous and nearly fully dense samples (RD:99%) were obtained by controlling both the electrochemical effects (liquid/solid interfaces) and by inverting polarity. Compared to the conventional sintering carried out at 1400°C for 240 min (RD:95%), FCS lowered significantly the processing temperature down to 350°C. As a proof of the enhanced densification promoted by FCS, the resulting samples were weakly translucent.

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References
[1] González-Zavala P, Calderón-Olvera RM, Muhl S, et al. Niobium oxide coatings increase the creep and wear resistance of glass. Mater Lett. 2020;277:128308.
[2] Hiyoshi M, Lee B, Lu D, et al. Supermicroporous niobium oxide as an acid catalyst. Catal Lett. 2004;98(4):181–186.
[3] Tamai T, Haneda M, Fujitani T, et al. Promotive effect of Nb2O5 on the catalytic activity of Ir/SiO2 for NO reduction with CO under oxygen-rich conditions. Catal Commun. 2007;8(6):885–888.
[4] Shishido T, Miyatake T, Teramura K, et al. Mechanism of Photooxidation of Alcohol over Nb 2 O 5. J Phys Chem C. 2009;113(43):18713–18718.
[5] Ab Kadir R, Rani RA, Alsaif MMY, et al. Optical Gas sensing properties of Nanoporous Nb 2 O 5 films. ACS Appl Mater Interfaces. 2015;7(8):4751–4758.
[6] Kadir RA, Rani RA, Zoolfakar AS, et al. Nb2O5 Schottky based ethanol vapour sensors: effect of metallic catalysts. Sens Actuators B Chem. 2014;202:74–82.
[7] Cvelbar U, Mozeič M. Behaviour of oxygen atoms near the surface of nanostructured Nb 2 O 5. J Phys D Appl Phys. 2007;40(8):2300–2303.
[8] Kulkī K, Ritala M, Leskelä M. Development of Dielectric properties of niobium oxide, tantalum oxide, and aluminum oxide based Nanolayered materials. J Electrochem Soc. 2001;148(2):F35.
[9] Augustyn V, Come J, Lowe MA, et al. High-rate electrochemical energy storage through Li+ intercalation pseudocapacitance. Nat Mater. 2013;12(6):518–522.
[10] Kim JW, Augustyn V, Dunn B. The effect of crystallinity on the rapid pseudocapacitive response of Nb 2 O 5. Adv Energy Mater. 2012;2(1):141–148.
[11] Matylikskaya VA, Bock W, Kolbesen BO. Nitridation of niobium oxide films by rapid thermal processing. Anal Bioanal Chem. 2008;390(6):1507–1515.
[12] Cologna M, Rashkova B, Raj R. Flash sintering of nanograin zirconia in <5 s at 850°C. J Am Ceram Soc. 2010;93:3556–3559.
[13] Biesuz M, Pinter L, Saunders T, et al. Investigation of electrochemical, optical and thermal effects during flash sintering of 8YSZ. Materials (Basel). 2018;11(7):1214.
[14] Janek J. Electrochemical blackening of yttria-stabilized zirconia morphology, stability of the moving reaction front. Solid State Ion. 1999;116(3-4):181–195.
[15] Naik KS, Sglavo VM, Raj R. Flash sintering as a nucleation phenomenon and a model thereof. J Eur Ceram Soc. 2014;34(15):4063–4067.
[16] Francis JSC, Cologna M, Raj R. Particle size effects in flash sintering. J Eur Ceram Soc. 2012;32(12):3129–3136.
[17] Grasso S, Sakkya Y, Rendtorff N, et al. Modeling of the temperature distribution of flash sintered zirconia. J Ceram Soc. Japan. 2011;119(1386):144–146.
[18] Guo J, Guo H, Baker AL, et al. Cold sintering: a paradigm shift for processing and integration of ceramics. Angew Chem Int Educ. 2016;55(38):11457–11461.
[19] Charoensuk T, Sukkha U, Kolodiazhnyi T, et al. Enhancing the densification of ceria ceramic at low temperature via the cold sintering assisted two-step sintering process. Ceram Int. 2018;44:554–557.
[20] Leng H, Huang J, Nie J, et al. Cold sintering and ionic conductivities of Na3.256Mg0.128Zr1.872Si2PO12 solid electrolytes. J Power Sources. 2018;391:170–179.
[21] Funahashi S, Guo J, Guo H, et al. Demonstration of the cold sintering process study for the densification and grain growth of ZnO ceramics. J Am Ceram Soc. 2017;100(2):546–553.
[22] Liu JA, Li CH, Shan JJ, et al. Preparation of high-density InGaZnO4 target by the assistance of cold sintering. Mater Sci Semicond Process. 2018;84:17–23.
[23] Medri V, Servadei F, Bendoni R, et al. Nano-tomacroporous TiO2 (anatase) by cold sintering process. J Eur Ceram Soc. 2019;39(7):2453–2462.
[24] Nur K, Mishra TP, Silva DA JGP, et al. Influence of powder characteristics on cold sintering of nano-sized ZnO with density above 99 %. J Eur Ceram Soc. 2021;41(4):2648–2662.
[25] Details Q, A theoretical analysis of cold sintering Mattia Biesuz, Gianmarco Taveri, Andrew I. Duff, Eugene Olevsky, Degui Zhu, Chunfeng Hu, A theoretical analysis of cold sintering, Advances in Applied Ceramics. 2020;119:75–89.
[26] Biesuz M, Grasso S, Sglavo VM. What’s new in ceramics sintering? A short report on the latest trends and future prospects. Curr Opin Solid State Mater Sci Internet. 2020 cited 2020 Oct 8;24(5):100868.
[27] Kermani M, Biesuz M, Dong J, et al. Flash cold sintering: combining water and electricity. J Eur Ceram Soc. 2020;40(15):6266–6271.
[28] Raj R, Chan H. Analysis of the power density at the onset of flash sintering. J Am Ceram Soc. 2016;99:3226–3232.