

Manufacture of Porous Electrically Conductive Ceramics

Chris R. Bowen*, Vaia Adamaki, Tony Thomas

Materials Research Centre, Department of Mechanical Engineering,
University of Bath, Bath, United Kingdom
c.r.bowen@bath.ac.uk

Abstract - This paper describes approaches to manufacture porous conductive ceramic materials which include the production of Magnéli based ceramic materials which are formed via carbo-thermal reduction of titania with a fugitive binder; by combining the sintering and reduction heat treatment it was possible to generate porosity at the ceramic surface to achieve a high surface area. The fabrication of macro-porous Ti_2AlC will also be described via a polymer foam replication technique; in this case the sintering profile and processing methods are adapted to reduce defects generated by the burn-out stage of the polymer phase. Applications for such porous electrical conductive ceramics include sensors, high surface area substrates, as an electrode material and energy harvesting.

Keywords: Ceramics, Porosity, Conductive, Sintering, Microstructure, Conductivity.

1. Introduction

The creation of ceramic porous materials with desired properties and microstructure are generating increasing interest with one reason being the relative ease in which the porous structure can be manufactured in response to the application requirements; a good example is the development of high-temperature ceramic filters (Schwartzwalder et al, 1963). Other examples of foams include porous ceramics for water purification (Imhot et al., 1999) and porous hydroxyapatite bioceramics as a bone graft substitute (Padilla et al., 2005). Porous ceramics are of interest where the application environment demands a resistance to high temperatures, thermal shock resistance, corrosion resistance and thermal insulation (Borchardt et al., 2012). Some of the techniques developed for creating porous ceramics include (i) foaming of the aqueous ceramic suspension, (ii) foam replication and (iii) pyrolysis of fugitive species.

In this paper we consider the manufacture of porous ceramics that are *electrically* conductive. These materials are of interest for a number of applications such as sensors or energy applications; examples include corrosion resistant electrodes with high surface area, sensing elements in a hostile environment, or as a conductive substrate. The first section of the paper will discuss the manufacture of Magnéli ceramics with relatively small pore sizes (less than $100\mu\text{m}$) and pores concentrated at the surface, such materials and pore geometries are of interest for applications such as redox batteries or as a chemical sensing electrode (Adamaki et al., 2014). The second section will describe the formation of macro-porous ceramics from MAX phase ceramics; these materials have metallic-like conductivity and potential applications are as a conductive substrate for microbial fuel cells (Thorne et al., 2011) or a catalyst support (Hu et al., 2012).

2. Development of Porous Magnéli Samples

TiO_2 has been studied in detail and used in a variety of technological applications such as in paints and food as a white pigment, orthopaedic and dental implants, catalyst supports (Chen et al., 2003), photo-catalysis, photo-splitting of water, dye-sensitised solar cells and gas-sensing. While stoichiometric TiO_2 has a low electrical conductivity of typically 10^{-10} S/m, it is well known that electrical conductivity can be significantly increased by heat-treating the oxide at a high temperature in a reducing atmosphere (Hayfield, 2002). The reduction process leads to the formation of sub-stoichiometric titanium oxides of the general formula $\text{Ti}_n\text{O}_{2n-1}$ (with $3 < n < 10$), known as Magnéli phases. In non-stoichiometric titanium

dioxide, TiO_{2-x} , with a low x ($0 < x < 0.10$), the dominant point defects in the structure consist of Ti^{3+} and Ti^{4+} interstitials and oxygen vacancies. However the Magnéli phases ($x=0.10-0.34$) are characterised by extended planar defects and crystallographic shear planes which vary according to the oxygen deficiency. Due to their high electrical conductivity and chemical resistance, Magnéli phases are of interest in a variety of applications, which include cathodic protection, batteries, catalyst support for fuel cells as well as their potential use in the treatment of aqueous waste and contaminated water (Hayfield, 2002). In order to increase surface area and create a more intimate contact with the surrounding environment the introduction of porosity is of interest; clearly the formation of open porosity or porosity at the material surface is beneficial here. To form the Magnéli phases, TiO_2 powder (PI-KEM, 99.5%, $0.3 \mu\text{m}$ particle size, specific surface area $7.49 \text{ m}^2/\text{g}$) was sintered and reduced through a carbo-thermal process performed in a tubular furnace; details of processing *dense* Magnéli materials have been reported with exaggerated grain growth during the reduction process (Regonini et al., 2011; Regonini et al., 2012; Adamaki et al., 2014). In order to achieve high surface area to meet the requirements for applications such as battery electrodes, this manufacturing process is aimed at achieving a high porosity and limit grain growth. The electrical conductivity should be as high as possible for the above applications, so the heat treatment for sintering and carbo-thermal reduction was at a maximum of 1300°C to create the most conductive phase, namely Ti_4O_7 . Green body tablets were prepared using an organic binder (polyethylene glycol-PEG 8000) and various concentrations of organic binder were employed in order to achieve high porosity; the binder is burnt out during heat treatment to leave behind residual porosity. The TiO_2 mixes were prepared with 2.5, 5, 7.5, 10, 20 and 50wt.% binder to create a range of porosity levels. A slurry was created with the addition of distilled water (1ml per 1g of powder) and ball milled for 24h which was then dried and the resulting powder sieved through a $45\mu\text{m}$ mesh. TiO_2 tablets were formed by dry cold pressing, applying a pressure of $\sim 250\text{MPa}$ ($\sim 20\text{kN}$ over an area of 1cm^2). Previous work (Adamaki et al., 2014) had shown that using a ‘two-step’ heating treatment, namely sintering of TiO_2 in air at 1300°C and an additional heat treatment to form Magnéli phases by carbo-thermal reduction at 1300°C led to excessive grain growth. In order to prevent such large grain growth a ‘one-step’ preparation method was employed whereby both sintering and carbo-thermal reduction stages were combined into one process in a tubular furnace with carbon black powder under constant argon flow. The heating profile is an initial slow heating at $60^\circ\text{C}/\text{hr}$ to 400°C and dwell for 3hrs to burn out the binder; followed by heating at $120^\circ\text{C}/\text{hr}$ to 1300°C and a dwell for 1hr for sintering and reduction and then cooling of $150^\circ\text{C}/\text{hr}$ to room temperature. At higher binder contents ($>20\text{wt.}\%$) the heating profile was changed with a slow heating of $60^\circ\text{C}/\text{hr}$ to 400°C , a dwell for 3hrs, a heating at $40^\circ\text{C}/\text{hr}$ to 1300°C and a dwell for 1hr and then cooling of $150^\circ\text{C}/\text{hr}$ to room temperature; this lower heating rate enables the highly porous green body to maintain a volume similar to the initial pressed ‘green’ bodies.

Density and the apparent porosity of the sintered materials were measured according to the BS EN623-2:1993 standard. Table 1 compares the density and the porosity measurements for all the materials prepared for the ‘one-step’ preparation method with increasing content of binder. The properties of the dense material, prepared with 2.5%wt binder, using a ‘two-step’ preparation are also included; in this case the carbo-thermal reduction takes place after sintering the TiO_2 in air to high density.

Table 1. Density measurements of porous of porous bulk samples.

Batch No	wt% binder	Theoretical density (g.cm^{-3})	Bulk density (g.cm^{-3})	Apparent solid porosity (%)	%Theoretical density
Two-Step dense samples	2.5	4.3	4.19 ± 0.03	0.17 ± 0.17	97.41 ± 0.63
1	2.5	4.3	4.00 ± 0.02	3.02 ± 0.34	93.07 ± 0.58
2	5	4.3	4.01 ± 0.03	2.87 ± 0.44	93.31 ± 0.64
3	7.5	4.3	3.75 ± 0.09	5.62 ± 2.09	87.28 ± 2.08
4	10	4.3	3.94 ± 0.04	1.78 ± 0.53	91.63 ± 0.93
5	20	4.3	2.88 ± 0.06	7.68 ± 2.70	66.92 ± 1.51
6	50	4.3	1.45 ± 0.03	64.92 ± 0.69	33.87 ± 0.77

There is an increase in porosity with added binder that reaches a maximum of 64.9% with 50wt.% binder; therefore these samples would be better suited for applications that require a high surface area such as electrodes. All material compositions were examined using JEOL6480LV Scanning Electron Microscope (SEM) and the images were analysed using the ImageJ software in order to determine accurately the porosity and grain size. The images in Figure 1 present a plan and a cross-section view of the dense material containing 2.5%wt binder, prepared with the 'two-step' (Figure 1a) and 'one-step' process (Figure 1 b-d); it is interesting to note that the combination of both sintering and carbo-thermal reduction into 'one-step' leads to significant porosity at the ceramic surface (Figure 1c,d). Figure 2 shows the plan and cross-section view of selected porous Magnéli phases tablets prepared with the 'one-step' process. The effect of the binder content on the porosity of the tablets is apparent in terms of the increase in porosity (as in Table 1).

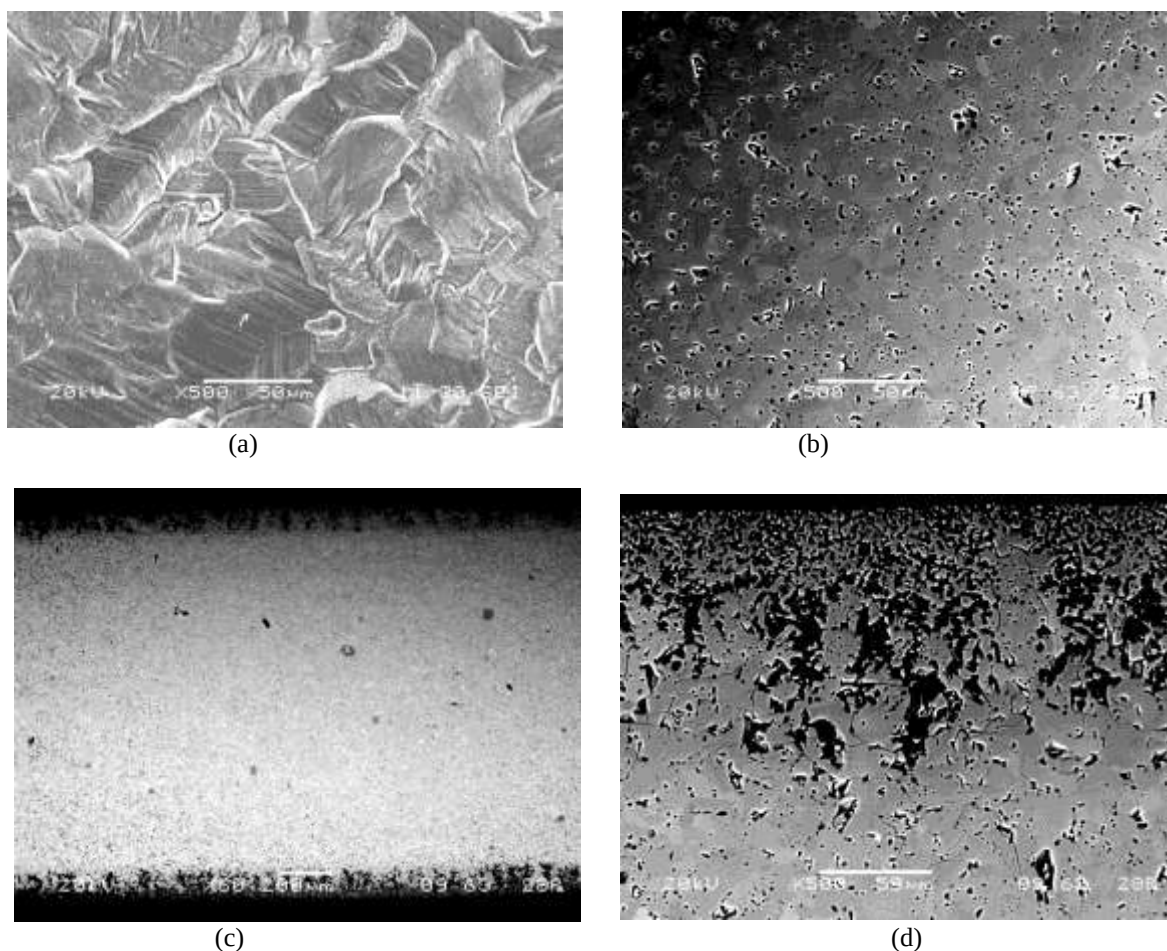


Fig. 1. SEM images of Magnéli phases tablets with 2.5%wt binder prepared with two-step (a) and one-step (b,c,d) process.

The grain size of the samples with 2.5%wt binder prepared with the 'two-step'(Figure 1a) and the 'one-step' (Figure 1b) preparation method are 98.94µm and 13.69µm respectively, this is due to the Magnéli ceramic prepared with the two-step preparation method being subjected to two separate heat treatments at 1300°C. An additional conclusion is that as the content of binder increases the grain size decreases significantly, even though the heat treatment time and temperature is the same. Pores in a material are essentially defects in the structure and due to the Zener pinning effects, if of a high enough proportion, can prevent grain growth. X-ray diffraction spectrums in Figure 3 show the nature of the Magnéli phases formed which show that the Magnéli phases are present in all the samples. The presence

of Ti_4O_7 which is the most conductive phase is more clear (16.8° , 20.7° , 23.5°) at high porosities; possibly due to the higher surface area which enhances the carbo-thermal reduction process.

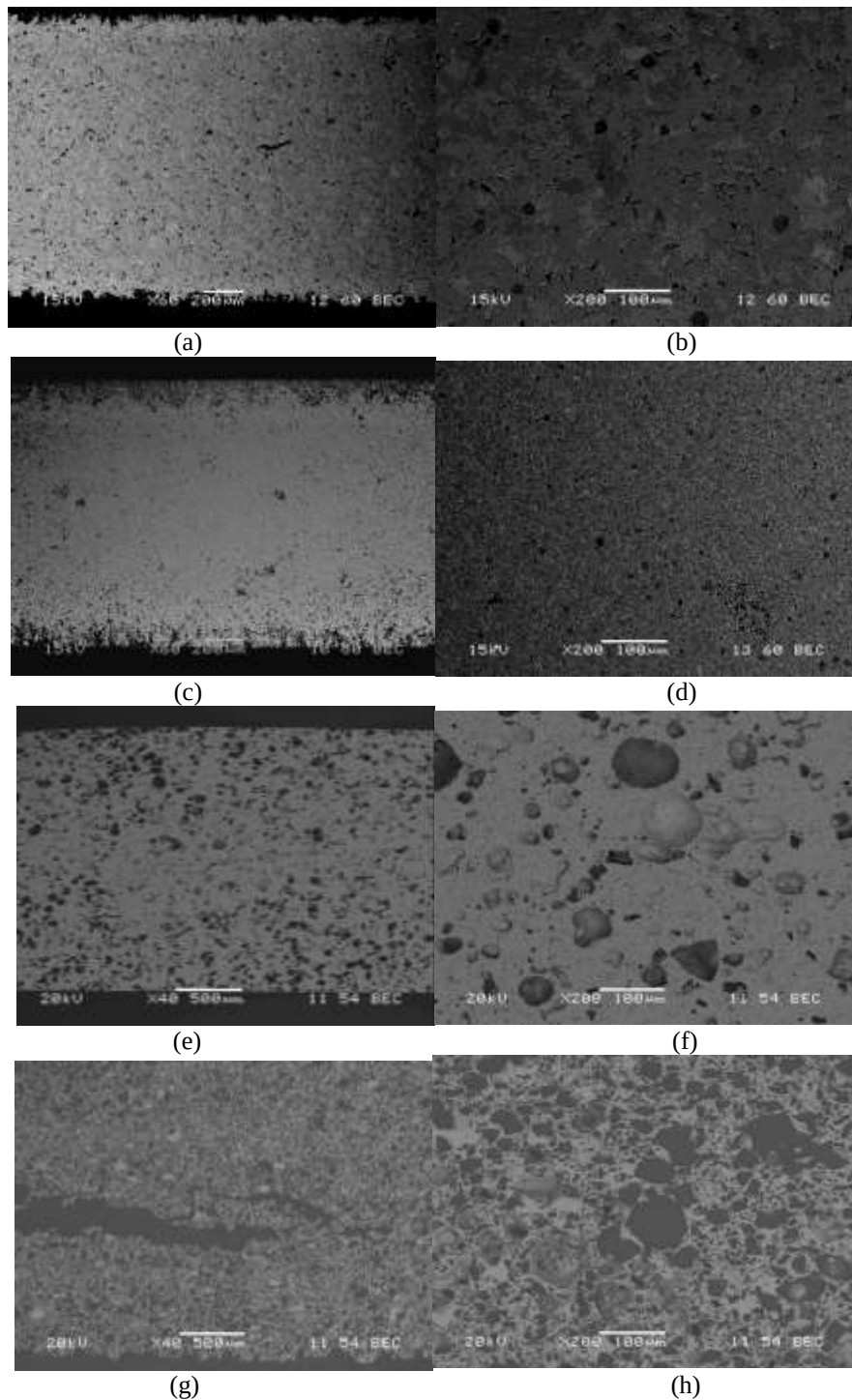


Fig. 2. SEM images of the Magnéli phases tablets prepared with one-step process with (a,b) 5%wt binder; (c,d) 7.5%wt binder (e,f) 20%wt binder and (g,h) 50%wt binder.

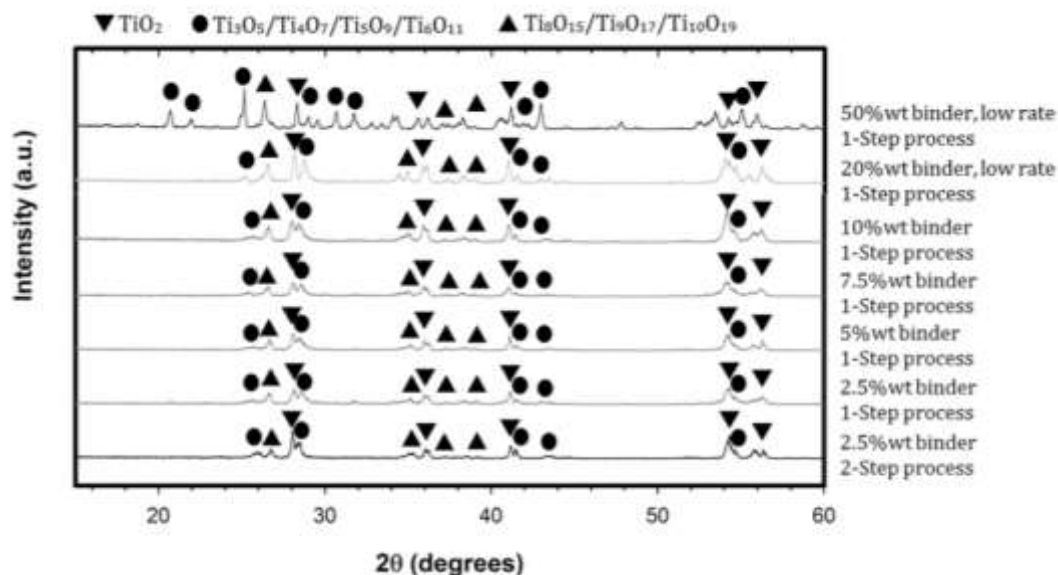


Fig. 3. XRD patterns for all the batches with various percentages of binder.

3. Macro-porous MAX Phase Ceramics

While the addition of a fugitive binder phase introduces pores of typically less than 100 μ m in size in some cases there is a need for larger pores; for example, for high gas permeability (Hu et al, 2012). In this case the foam replication method is a suitable approach. The MAX-phases are a class of ductile material group with the general molecular formula $M_{n+1}AX_n$ ($n = 1, 2$, or 3), where M is an early transition element, A is an element from group 13 or 14 of the periodic table such as Al, C, B, Ga, Ge, Sn, Pb and Si and X is either a nitride or carbide (Barsoum et al, 2001). Porous MAX phase are of interest for mechanical damping (Hu et al, 2012), catalyst supports and microbial fuel cells (Borchardt et al. 2012).

To manufacture macro-porous conductive ceramics, commercially available Ti_2AlC ("Maxthal 211 engineering ceramic material") from Kanthal was used as the ceramic powder source with a 90% particle size distribution of 20 μ m particles, with the remainder being a mixture of 2 μ m and 8 μ m particles. Poly(ethylenglycol) with an average molecular number of 380-420 from Sigma Aldrich was used (2 wt% of the ceramic powder) as the plasticizer and binder to obtain a high flow of the slip solution for easy coating of a polyurethane foam. Dispex GA40 from Ciba AG (1.2 wt% of the ceramic powder) was used as an anti settling agent to suspend the ceramic particles in the solution during the foam replication process. Methyl cellulose from Sigma Aldrich (2.4 wt% of the ceramic powder) was used as a thickening agent to increase the viscosity of the slip without affecting the solid loading (defined in this paper as the wt.% of ceramic employed). The above-mentioned chemicals was mixed in distilled water with a resistivity of 18.2M Ω cm and ball milled for 36 hours. Polyurethane foam ("Reticulated vitreous carbon foam" from Duocel) of 10 ppi (pores per inch) was used as the synthetic replica template in this work; tailoring the nature of the polymer foam can obviously be used to tune the pore size of the final ceramic. Once dried the impregnated foams were sintered in a tube furnace using an Argon atmosphere. The sintering profile in Figure 4a was optimized to produce a MAX phase ceramic (Ti_2AlC); for example a shorter dwell at 1300 $^{\circ}$ C for 3hrs (rather than 5hrs in Figure 4a) produced a large amount of excess TiC. Figure 4b shows and XRD of the final sintered material showing Ti_2AlC with some TiC present for the optimum heating profile. The heating profile in Figure 4a also minimised the production of defects during the burn out stage of the polymer foam; without a slow initial heating and dwell at 200 $^{\circ}$ C, the burn out of the polymer foam produced defects in the struts of the foam.

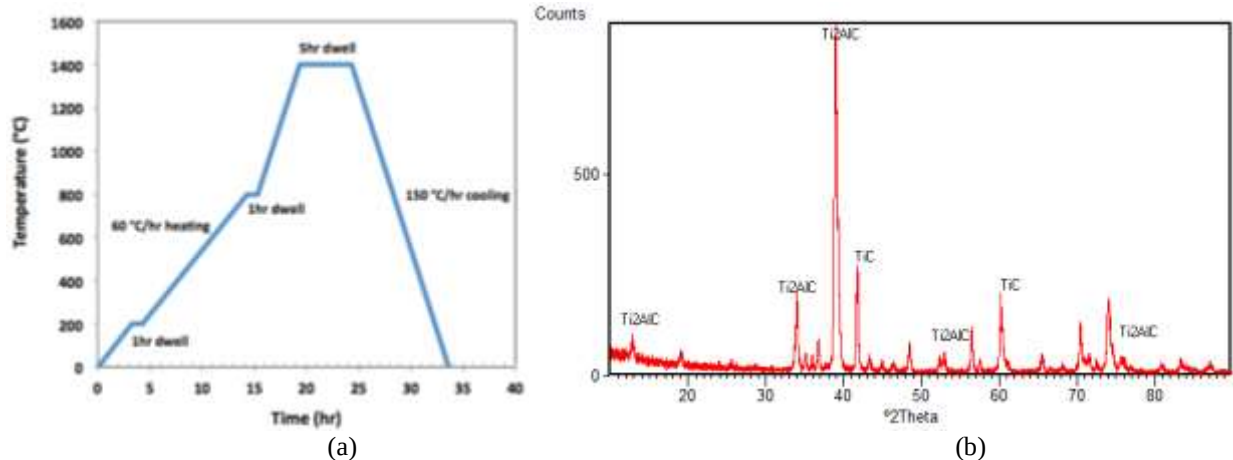


Fig. 4. (a) sintering condition introducing pyrolysis stage for minimising the defects in porous ceramic and reducing TiC formation (b) typical XRD data of porous ceramic prepared using temperature curve.

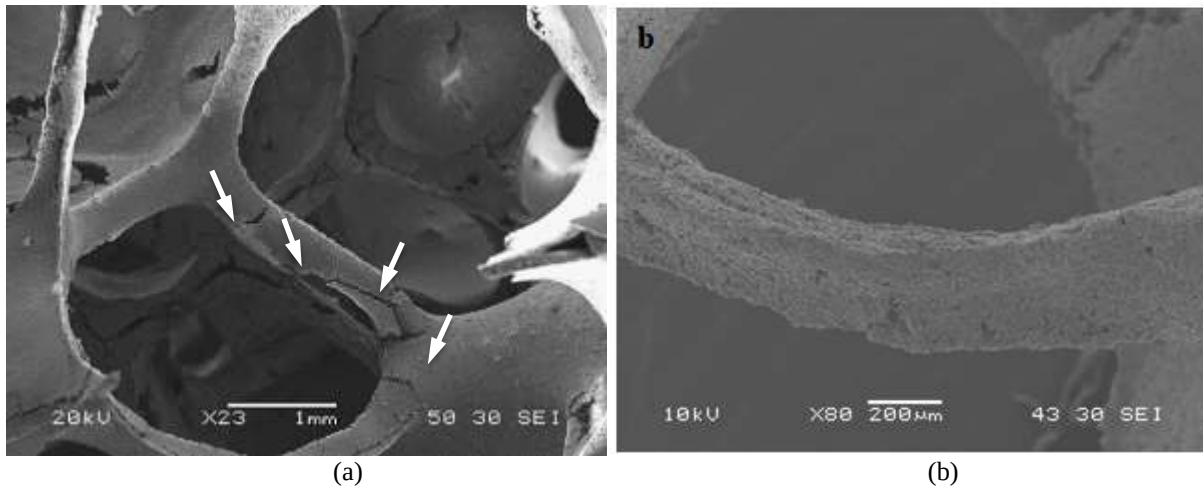


Fig. 5. SEM of cracks formed along struts for samples prepared (a) without slow cooling to burn out polymer foam (b) with slow cooling as in Figure 4a.

Figure 5a shows the SEM images of the struts where it can be observed that the struts contain a number of defects in the form of cracks. The formation of crack has are a result of the burn-out of gases produced during the decomposition of the polyurethane foam at elevated temperature. The pyrolysis stage of slow heating at the early stages of the heat treatment (Figure 4a) was introduced in the sintering temperature to help control the decomposition rate of the foam so there is a more gradual outgassing of the foam during heat treatment and sintering; this leads to reduced frequency of defects in the final sintered foam material (Figure 5b). Nevertheless the use of a coated polymer foam which is burnt-out is a processes that will inherently produce defects; for example the centre of the ceramic struts will always contain porosity since this is the location of the original foam. These defects can be observed in Figure 6a, which is an optical micrograph of a fracture surface of a Ti_2AlC foam where internal porosity in the struts is present. Nevertheless, by careful control of slip-viscosity and heat treatment it is possible to produce high porosity macro-porous material as shown in Figure 5b. Compressive strength in typically less than 0.5MPa due to the presence of defects.

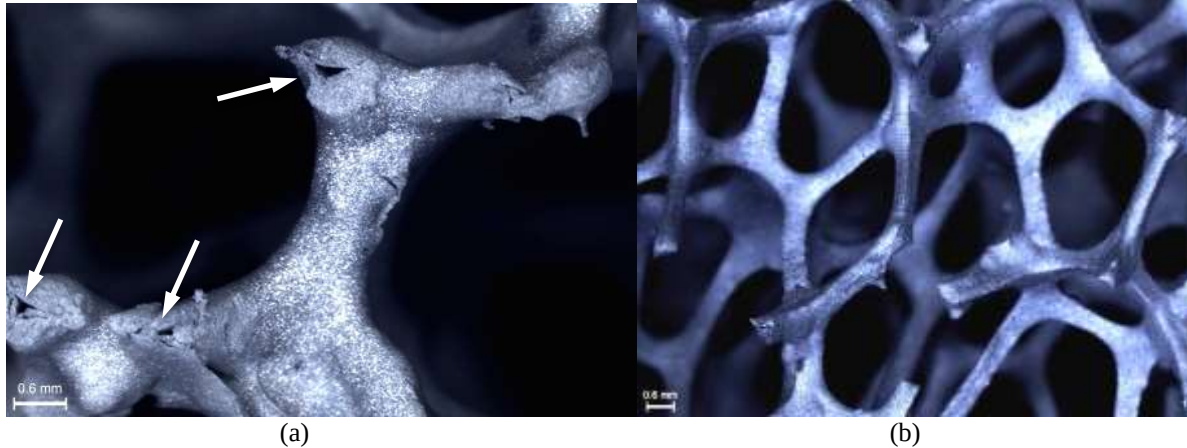


Fig. 6. (a) Optical image showing a non-uniform (variable strut thickness) coating obtained viscous slip (b) Optical image showing a uniform coating on sintered porous ceramic.

Since it is evident that the majority of the cracks are formed during the decomposition of the polyurethane foam, an approach to improve the properties and reduce the size and frequency of defects is to re-coat the sintered ceramic foam; this approach does not remove the internal porosity within the ceramic struts but heals pores on the ceramic strut surface and increases the amount of ceramic at the strut. In this method a single coated sintered MAX phase sample is used as the template (ceramic precursor) to make a porous Ti_2AlC ceramic. The single coated samples are recoated with a slightly lower viscosity slip and subjected to vacuum of 1 bar pressure for 5 minutes to ensure that the recoated slip is absorbed into the cracks of the ceramic foam. The re-coated ceramic is then re-sintered using the profile of Figure 4a. This approach minimising the cracks and also to ensure any entrapped air bubble is removed and ensure pores are open.

Figure 7 is an SEM image of the sample prepared using the double coating in vacuum technique; the surface of the strut is fairly smooth, compared to the other samples in Figure 6a. Some defects in the form of cracks are formed during the shrinkage of the sample during sintering process. Compression test revealed that the strength is increased from less than 0.5MPa for a single stage coating to 3MPa by the two stage process.

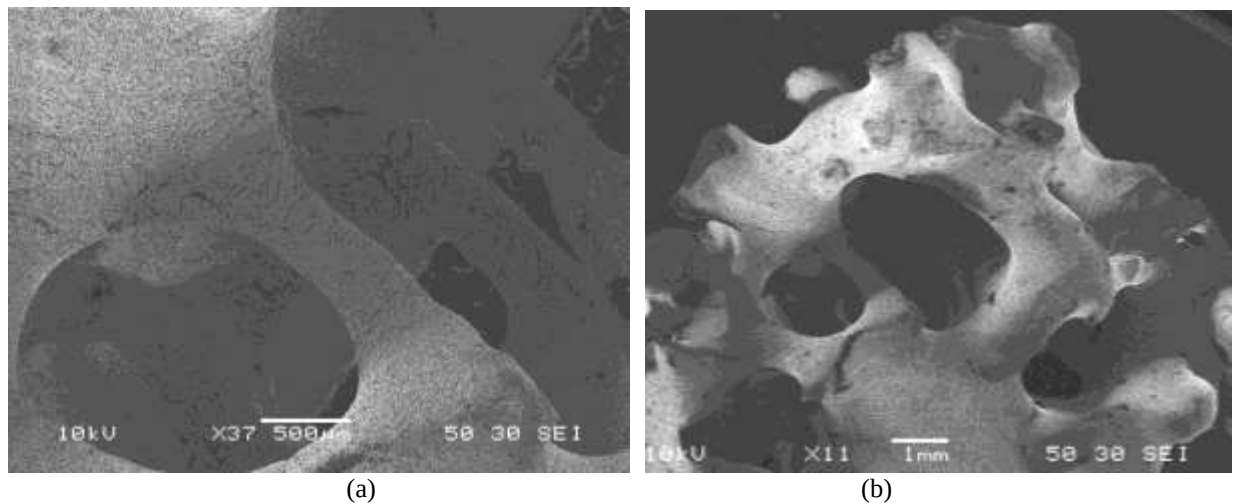


Fig. 7. SEM image of double ceramic sample after sintering. (a) image showing individual strut surface. (b) image showing various strut with lower number of defects.

4. Conclusions

This paper has shown that it is possible to produce a range of porosity in electrically conductive ceramic materials for a variety of applications. For Magnéli based materials it is possible to develop porosity by the burn out of excess binder at various weight fractions. Based on a 'one-step' sintering profile to reduce the titania to Magnéli via carbo-thermal reduction it is also possible to create a high level of porosity at the surface of the ceramic. Macro-porous ceramics can also be produced using a foam replication technique; as demonstrated using Ti_2AlC . The sintering profile, slip viscosity and use of multiple coating stages can be used to reduce the defect density and mechanical strength of such materials as a result of the burn out of the foam replica. Such materials are of interest in energy harvesting, sensing, catalyst supports and as electrode materials.

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