

Imperial College London
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Ultra-High-Temperature Ceramics for Transpiration Cooling

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Abstract

Porous ultra-high-temperature ceramics (UHTCs) have been studied for their use in transpiration cooling of the leading edges of hypersonic vehicles. The envisioned design consists of a layered hybrid material: a dense UHTC substructure with channels providing coolant fluid to a partially sintered, permeable surface layer to evenly distribute coolant across the leading-edge surface.

To assess sintering during the fabrication of zirconium diboride (ZrB_2) for the surface layer, two size grades of commercially available ZrB_2 powders were heated in air to 450 – 540 °C to vary oxygen content in the powder from 0.5 – 5.3 wt%O. Monitoring of density during hot-pressing showed that densification during initial stage sintering was plastic flow, with grain boundary diffusion from 1730 °C and volume diffusion from 1850 °C. The onset of rapid densification during hot-pressing of oxidised powders was delayed until after the onset of volume diffusion and prevented entirely with 5.3 wt%O in the fine power and 2.2 wt%O in the coarse powder up to 2000 °C/ 24 MPa.

Increasing powder size increased permeability from 0.79 m² to 2.59 m² in 33 vol% porous ZrB_2 hot-pressed at 1700 °C/ 12 MPa due to an increase in pore size from 0.66 to 1.1 µm. Increased surface transport also increased pore size, allowing for permeability of 1.9×10^{-14} m² at 31 vol% porosity. The resulting reduction in pore surface area prevented further densification of the partially sintered microstructures at intended application temperatures of 2000 °C.

The elastic modulus, flexural strength, and thermal conductivity of partially sintered ZrB_2 increased linearly with density after the initial development of properties above 40 vol% porosity. Flexural strength and thermal conductivity were improved due to the expansion of inter-particle neck area when hot-pressing with oxidised powders. The elastic modulus did not depend on neck formation after initial growth, so increasing strength without an increase in elastic modulus is predicted to be beneficial to thermal shock resistance. Increasing pressure during hot-pressing aided the formation of necks between particles by plastic flow, as well as increasing density. This resulted in partially sintered ZrB_2 with 28 vol% porosity with 200 MPa flexural strength and 50 W m⁻¹ K⁻¹ thermal conductivity.

Finite element analysis (FEA) was then used to assess the effect to surface coolant flux by introducing fluid to the partially sintered layer by varying arrays of channel sizing and spacing. This showed that the overall resistance to flow of the system was reduced when using narrower channels, spaced closer together to maintain overall channel porosity. For an even surface flux, the channel spacing needed to be less than the permeable layer thickness. Experimental validation of FEA then matched the trends of reducing resistance to fluid flow with narrower channels and smaller spacing.

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Declarations

Statement of Originality

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1 Introduction

1.1 Transpiration Cooling

The recent drive to develop new hypersonic aerospace vehicles has led to an increase in research activity for the development of thermal protection systems (TPS) to meet the increased demands of hypersonic flight. These new TPS must operate at temperatures of 2000 to 2400 °C in air and be re-usable[1].

State-of-the-art thermal protection systems rely on ablation to move heat away from the leading edge[2]: thermal energy is removed by the material as it vaporises and flows away. Low curvature shapes are employed where possible to reduce the speed, and therefore friction heating from the atmosphere. Low curvature also creates a thick boundary of air between the leading edge and the high-speed flow of air around it, as shown in Figure 1.1, reducing the heat flux to the surface[3]. Where high curvature is required, ablatives are not possible to use due to requirements of shape stability[4].

The future requirements of TPS are to move away from single use, blunt, leading edges and towards a re-usable sharp edge, with tip radius in the order of 3 mm[4]. Increased curvature of the leading edge is desirable in order to have greater aerodynamic control of the vehicle. This will therefore result in thinner boundary layers, as illustrated in Figure 1.1, and higher temperatures at the leading edge[5].

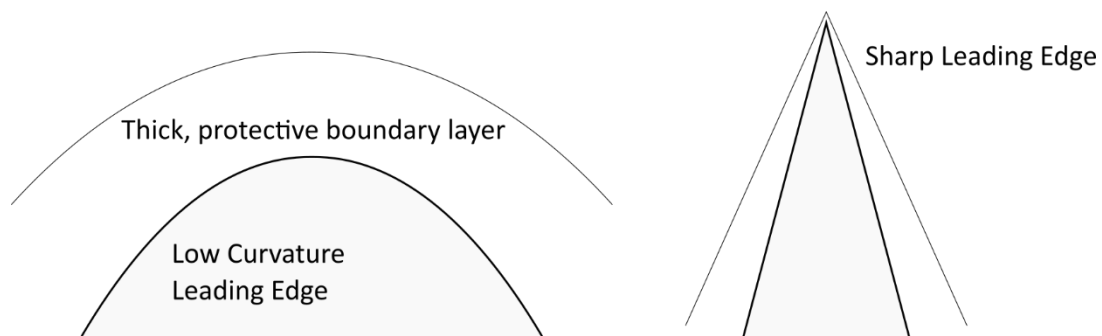


Figure 1.1 Illustration of protective boundary layer for a blunt vs. sharp leading edge.

A proposed method to achieve the greater requirements of a sharp leading edge is by using transpiration cooling[6]. This is a method of cooling by flowing an inert coolant gas through a porous, or channelled, material to cool the surface. Figure 1.2 shows a schematic of the proposed layered design of the transpiration cooled TPS; a highly porous ultra-high-temperature ceramic (UHTC) surface layer is fed coolant gas through a dense, channelled substructure which provides structural integrity and control of fluid delivery. Cooling of the material system is then achieved by three contributing factors: heat transfer from solid to coolant fluid, reduction of heat flux by expansion of boundary layers, and protection from catalytic heating by oxygen free radicals[4].

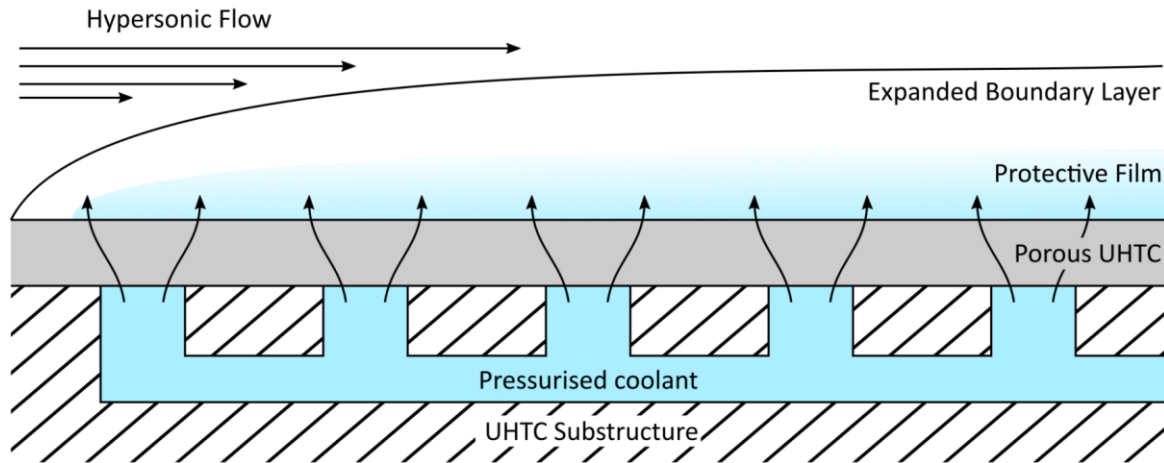


Figure 1.2 Transpiration cooling concept using ultra-high-temperature ceramics (UHTCs).

Heat is transferred from the hot material to the cool fluid, which then flows out and away from the surface, thereby lowering the temperature. This fluid layer will then act in a similar way to the boundary layer employed by blunt leading edges, reducing heat flux to the surface from the hot external atmosphere[6].

This expanded boundary layer not only reduces heat flux to the surface but also hinders the movement of oxygen free radicals from the atmosphere to the surface. These otherwise recombine on the surface exothermically (catalytic heating), further increasing the temperature[7].

The use of substructures introduces a combination of fluid flow mechanisms between channelled arrays and porous material. Therefore, one aim of this work is to develop design criteria for channelled substructures to optimise flow properties of the combined hybrid system.

1.2 Ultra-High-Temperature Ceramics

Ultra-high-temperature ceramics (UHTCs) are the lead candidate materials for novel TPS. UHTCs are somewhat arbitrarily defined as ceramics with melting temperatures above 3000 °C, but they are widely referred to as the nitrides, carbides, and borides of transition metals. Although their melting temperatures exceed the desired temperature of application, the use of UHTCs in a traditional TPS is limited by their oxidation and the lower melting temperature oxides that form during use[1], [8].

The main requirement for a UHTC surface layer is permeability, allowing the flow of coolant fluid to reach the surface while becoming evenly distributed. This means that the material used must be porous, but the bulk of research for UHTC fabrication centres around reducing porosity as it has a detrimental effect on mechanical and thermal properties[9].

One of the most well researched UHTCs is zirconium diboride (ZrB_2) and it has been identified as a promising material for transpiration cooling. It can be made porous by the method of partial sintering, but the mechanical and thermal properties are low compared to dense UHTCs[10].

UHTCs are typically consolidated from powders into a solid material by solid-state sintering, with the resultant properties dictated by the resultant microstructure. The microstructure is created as a result of a wide range of processing variables, such as powder size, purity, sintering temperature, heating rates, applied pressure, and sintering atmosphere[11].

Initial material development of porous UHTCs from previous work by Larrimbe *et al.*[10], while demonstrating effectiveness, highlighted key issues that need to be addressed; mainly low physical properties and loss of permeability with increasing density. The aim of this work, therefore, is to further explore the feasibility of using ZrB_2 as a material for transpiration cooling by developing hot-pressing methods to improve strength and thermal conductivity while maintaining permeability.

1.3 Chapter summary

The literature review in 'Chapter 2: Literature Review' of this thesis will discuss the previous work in the field of transpiration cooling, with an overview of the sintering mechanism and methods to achieve porous UHTCs. The mechanical and thermal properties of ZrB_2 are discussed, with additional focus on the effect of porosity on these properties as well as fluid flow.

'Chapter 3: Experimental Methods' details the hot-pressing methods used to create porous ZrB_2 , and measurement principle of characterisation methods used to assess porosity, permeability, and thermal and physical properties.

The first three results chapters then present the results of partial hot-pressing of ZrB_2 . Course and fine powders are used to create porous microstructures, along with variation in powder oxide content. 'Chapter 4: Porous ZrB_2 By Hot-Pressing' starts by assessing the effect of hot-pressing parameters on the porosity and permeability of as-received powders, to establish a baseline and processing conditions for further development. The effect of powder size, oxygen content, and hot-pressing temperatures on the porosity, pore morphology, and impact on permeability are then presented. Finally, this chapter will assess the stability of the porous microstructures at the intended application temperature of 2000 °C.

The mechanical and thermal properties of the porous ZrB_2 are then discussed in 'Chapter 5: Properties of Porous ZrB_2 ' With discussion of how the porosity and pore morphology impacts elastic modulus, flexural strength, thermal conductivity, and therefore the implications for thermal shock.

'Chapter 6: Densification Mechanisms of ZrB_2 ' aims to identify key sintering mechanisms involved in the formation of microstructures characterised in the previous two chapters. The density is monitored throughout hot-pressing for a range of powder size, oxygen content, and heating rates, with onset temperatures for densification compared to the literature surrounding sintering mechanisms in UHTCs.

The final results chapter, 'Chapter 7: Substructure Channel Design', then turns the attention towards dense, channelled substructures for multi-layered UHTC hybrids. Finite element analysis is used to assess the effect of varying channel size and spacing on the spread of coolant fluid through the porous surface layer, before the final overall conclusions in 'Chapter 8: Conclusions and Future work'.

2 Literature Review

The aim of this project is to develop ultra-high-temperature ceramics (UHTCs) for use in transpiration cooling systems. This requires a material that is porous to allow for fluid flow and is stable up to 2000 °C[6]. High thermal conductivity is desirable to conduct heat away from the leading edge while strength is required to withstand multiple launches and the stresses of hypersonic flight[1].

Partially sintered ZrB_2 has been demonstrated as an effective material for transpiration cooling, as shown in the plasma tunnel testing in Figure 2.1 from Ewenz Rocher *et al.*[5]. However, the high porosity required for suitable permeability means the strength and thermal conductivity are much lower than that of dense ZrB_2 [6], [10]. The first part of this literature review will therefore detail the structure, processing, and properties of ZrB_2 . Also discussed are the principles of sintering and the mechanisms that lead to the creation of porosity in partially sintered materials and the effect this has on properties.

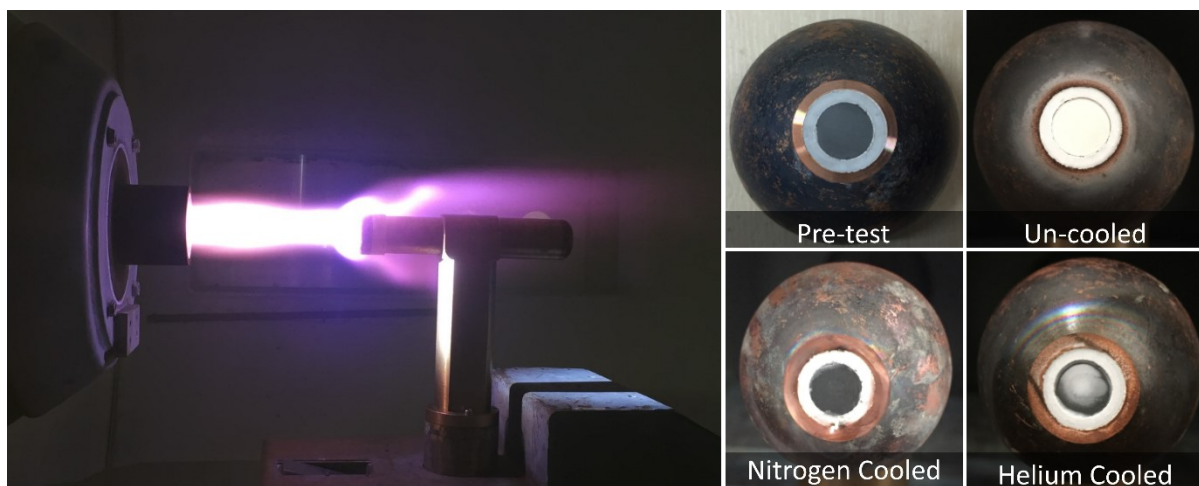


Figure 2.1 Demonstration of effective transpiration cooling at the IRS plasma tunnel adapted from Ewenz Rocher *et al.*[5]. White oxidation of the ZrB_2 surface is visible in the uncooled and He cooled cases.

The principles of fluid flow through porous materials are then discussed for both permeable materials and channelled structures as the proposed design also includes a substructure as mechanical reinforcement.

2.1 Structure and Properties of Zirconium Diboride

UHTCs are a class of material commonly defined as the ceramics with melting temperatures above 3000 °C. While there are practical issues with measuring such high melting temperature, it is widely agreed in the literature that UHTCs comprise of the borides, carbides, and nitrides of the early transition metal elements Zr, Hf, Ta, W, and Nb[12]. ZrB_2 is one of the most studied materials in this

group, while also being used previously in transpiration cooling development for hypersonic flight[5], and is therefore the focus of this work.

2.1.1 Structure

The crystal structure of ZrB_2 is primitive hexagonal, with alternating layers of zirconium and boron in the AlB_2 -type, $P6/mmm$ space group. The boron layers are arranged in rings around each zirconium atom, which are themselves arranged in a close packed arrangement as shown in Figure 2.2. Strong covalent bonds define the plane of B atoms while the Zr close packed plane is metallic, with Zr-B bonding between these layers being covalent as well as ionic from polarisation of the Zr-B covalent bonds. Typical properties of ZrB_2 are given in Table 2.1[9].

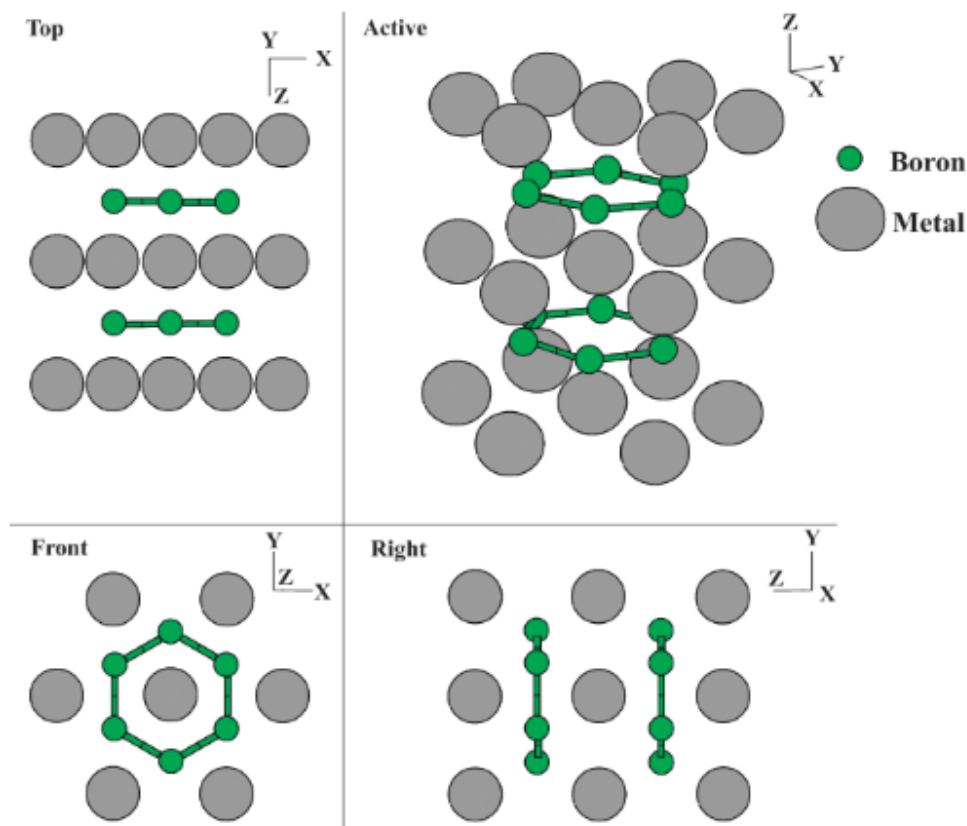


Figure 2.2 Crystal structure of ZrB_2 and other metal diborides[9].

Table 2.1 Typical properties of ZrB₂[9]

Property	Unit	Value
Crystal system space group		Hexagonal
Prototype structure		P6/mmm AlB ₂
<i>a</i>	Å	3.17
<i>c</i>	Å	3.53
Density	g/cm ³	6.099
Melting Temperature	°C	3553 ± 35 [13]
Youngs Modulus	GPa	511 ± 10 [14]
Bulk Modulus	GPa	215 [15]
Hardness	GPa	23[15]
Coefficient of Thermal Expansion	K ⁻¹	6.8 x 10 ⁻⁶ [16]
Heat Capacity at 25°C	J mol ⁻¹ K ⁻¹	48.2[17]
Electrical Conductivity	S m ⁻¹	1.0 x 10 ⁷ [18]
Thermal Conductivity	W m ⁻¹ K ⁻¹	87 - 141 (25 °C) [19]–[23]
Enthalpy of formation at 25°C	kJ	-322.6[17]
Free energy of formation at 25°C	kJ	-318.2[17]

2.1.2 Thermal Properties

Thermal expansion and thermal conductivity are key factors in the development of stress during high-temperature operation of UHTC assemblies and complex geometries[24]. Okamoto *et al.* measured thermal expansion of ZrB₂ as 6.8 x 10⁻⁶ K⁻¹ [16], with Zimmermann *et al.* later refining the definition of thermal expansion between 300 and 1675 K to equation 2.1.

$$\left(\frac{\Delta l}{l_0}\right) = -1.64 \times 10^{-3} + 4.92 \times 10^{-6}T + 1.72 \times 10^{-9}T^2 - 2.31 \times 10^{-13}T^3 \quad 2.1$$

$$\{300 \text{ K} < T < 1675 \text{ K}\}$$

ZrB₂ has high thermal and electrical conductivities. This high electrical conductivity allows for electric discharge machining of sintered bodies while high thermal conductivity is beneficial in the application of transpiration cooling, allowing rapid dispersion of heat away from the leading edge[1].

There is a wide range of values reported for thermal conductivity in pure ZrB₂, the main factors that determine the thermal conductivity being grains size, purity, and density[23]. Values typically range from 87 to 141 W m⁻¹ K⁻¹ [19]–[23], and are highest for large grains, high density, and high purity[22].

At room temperature it has been shown that electron contribution to conductivity is up to three times as great as the phonon contribution, rising to 90 % of the overall thermal conductivity above 1000 °C[21], [24], [25].

2.1.3 Mechanical Properties

Elastic modulus of ZrB₂ varies with porosity, with various models to describe this behaviour detailed in ‘Chapter 2.3.1: Elastic Modulus’. Experimental data from literature for the elastic modulus of ZrB₂ processed without sintering aids is shown in Figure 2.3a, with Neuman and Hilmas collating a wide range of elastic modulus data to determine an estimate for the intrinsic elastic modulus of ZrB₂ of 511 ± 10 GPa[14]. First principles calculations of elastic modulus by Zang *et al.* calculated 520 GPa[26], with single crystal measurements by Okamoto *et al.* used to calculate the polycrystalline elastic modulus of ZrB₂ to be 525 GPa[27], both in good agreement with the experimental data.

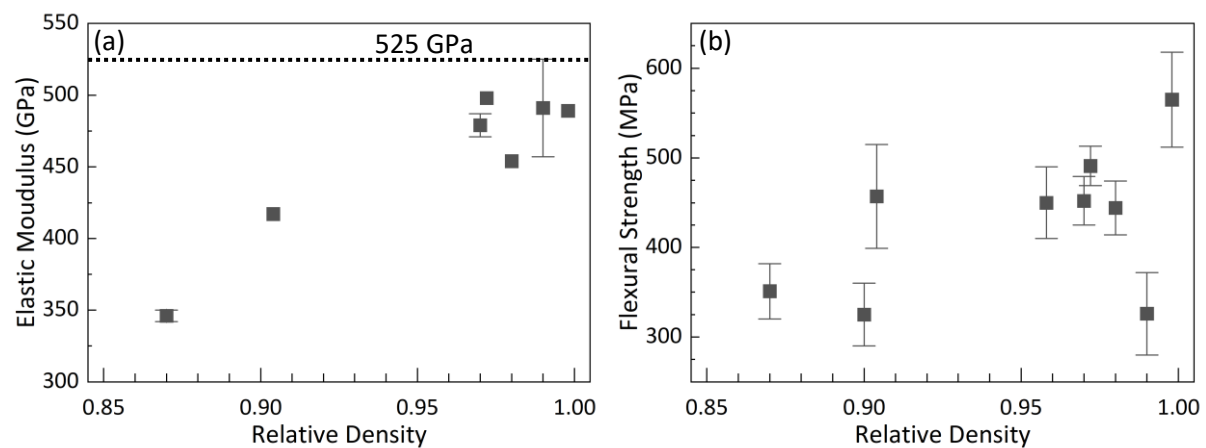


Figure 2.3 Literature data for ZrB₂ when sintered without sintering aids. (a) Elastic modulus with intrinsic modulus as determined by Okamoto *et al.* marked at 525 GPa. (b) Flexural strength [14], [18], [28]–[44].

The room temperature strength of ZrB₂ follows an inverse square root relationship with grain size ($D^{-1/2}$)[14]. This type of relationship is typical of dense ceramics where the largest critical flaw is the grains themselves. Strength ranges from > 600 MPa when grains sizes in the order of 3 μm[45] but can fall below 300 MPa with grains > 50 μm[14]. Porosity also plays a significant role in the strength of ZrB₂ as large pores can replace large grains as the critical flaw, a further overview of the effects of porosity on strength in ceramics is detailed in ‘Chapter 2.3.2: Strength’. Figure 2.3b shows a collection of literature data for ZrB₂ hot-pressed without sintering additives, with strengths typically above 400 MPa for > 95 % dense ZrB₂[14].

There are limited studies into the strength and creep behaviour of UHTCs above 1600 °C, most of these focusing on composites of ZrB₂ and silicon carbide (SiC) due to increased oxidation resistance[46]. There is evidence to show that methods for improving room temperature strength do not apply at

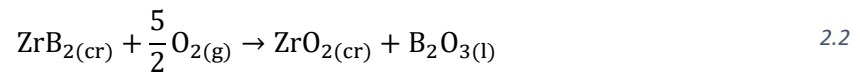
higher temperatures. Trends in the literature show even ZrB₂-SiC composites that retain strength of 500 – 700 MPa at 1000 °C, dramatically reduce to 200 – 340 MPa by 1500 °C[47].

Strength retention up to 1000 °C in ZrB₂-SiC has been attributed to the formation of silica glass, filling surface defects that would otherwise initiate failure. While the later loss of strength is largely due to grain growth and softening of amorphous grain boundary phases[48]–[50].

More recently, Silvestroni *et al.* have hot-pressed ZrB₂-SiC-WC composites which obtained a maximum flexural strength of 800 MPa at 1800 °C and remained as high as 660 MPa at temperatures up to 2100 °C [47]. The retention of strength was attributed to WC shells pinning grain growth and lack of amorphous regions at grain boundaries. The drop above 1800 °C is explained by growth of SiC flaws and eutectic liquid formation[47].

2.1.4 Oxidation

Oxidation of ZrB₂ in air starts at temperatures around 400 °C, forming B₂O₃ and ZrO₂ by the following reaction[51]:



The oxide forms a protective layer, oxidation becoming a diffusion limited process up to 1100-1200 °C. The oxide scale is made up of an outer glassy layer of B₂O₃ and a porous inner layer of ZrO₂ filled with B₂O₃[52]. This leads to a parabolic rate of oxidation to be expected from diffusion limited oxidation.

Above 1200 °C the B₂O₃ scale begins to evaporate, leading to diffusion limited oxidation through ever shrinking boria channels between ZrO₂. Parthasarathy *et al.* modelled the oxidation from 1000 °C to 1800 °C, showing only above 1850 °C will the boria evaporate as fast as it is formed, with the remaining porous ZrO₂ not offering effective protection from further oxidation[53]. Oxidation resistance can be improved with the addition of SiC to form a SiO₂ glass scale, which offers additional protection up to 1700 °C. At temperatures above 1800 °C the porous ZrO₂ has been shown to recrystallise, forming a dense subscale that can provide protection from further oxidation[46].

2.2 Sintering

The densification of ZrB₂ powder to a monolithic ceramic is difficult because of its high melting point, strong covalent bonds, and low self-diffusion rates. These factors generally mean that temperatures greater than 1800 °C are required for densification[54]. Pressure can be applied to assist densification, a process known as hot-pressing. Typical pressures applied to achieve dense ZrB₂ are 30 – 50 MPa, usually with sintering aids to promote densification, however the porous ZrB₂ made for the plasma

tunnel testing for transpiration cooling[5] was hot-pressed at 1700 °C and 12 MPa[6], [10]. This section will therefore cover the general principles of sintering as they apply to ZrB_2 , particularly surrounding competing mechanisms that aid and prevent densification to achieve a porous material.

2.2.1 Sintering Mechanisms

Sintering is the process that joins solid ceramic powder particles together, the driving force for which is the reduction in interfacial energy. This reduction in energy can be achieved by reducing the free surface area of the particles by coarsening, or by replacing solid-vapour interfaces with solid-solid grain boundaries by densification, as shown in Figure 2.4. Generally, a combination of the two processes will occur, densification will cause a shrinkage as porosity is eliminated, with coarsening continuing to grow grains at elevated temperatures[55].

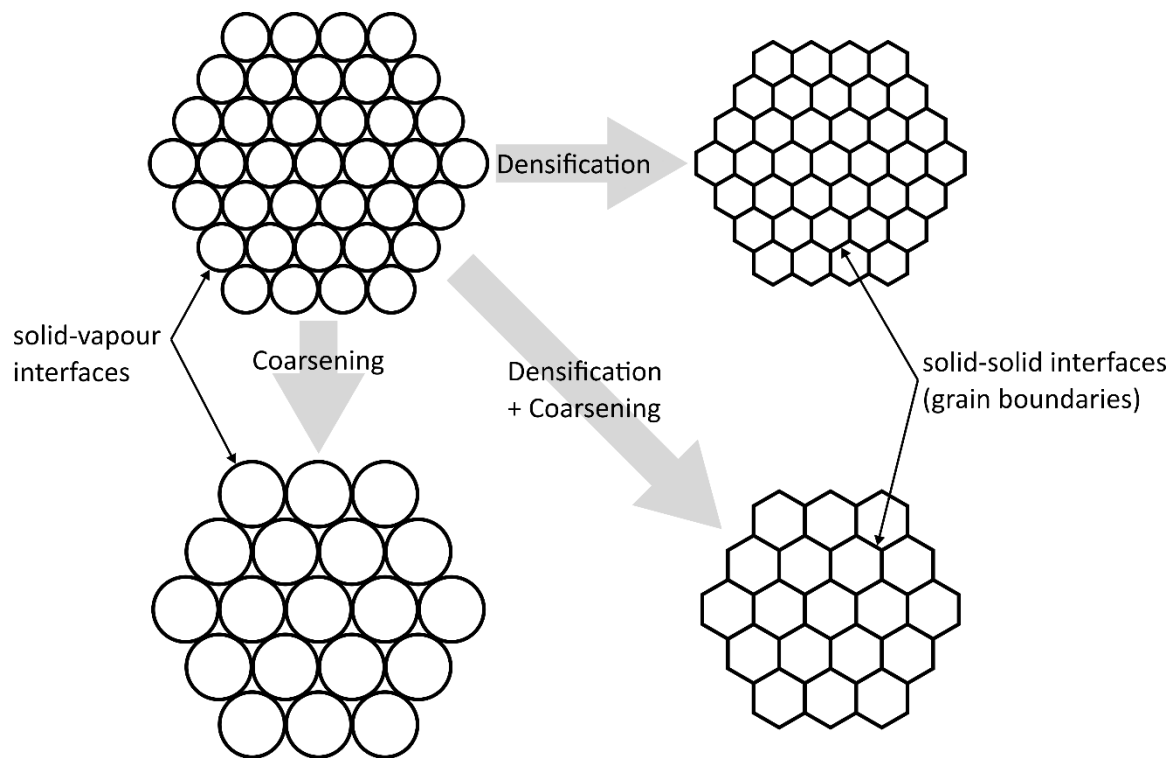


Figure 2.4 Interfacial energy reduction by coarsening and densification, adapted from Kang[56].

There are six main sintering mechanisms that contribute to coarsening and densification, each is illustrated in Figure 2.5. Coarsening occurs by surface mass transport mechanisms and will not cause any global shrinkage.

The first of these surface transport mechanisms is evaporation-condensation, this reduces the solid-vapour interface by moving atoms towards the inter-particle necks through the vapour phase. Evaporation occurs preferentially from convex and flat surfaces, while condensation is preferential at concave surfaces between particles where the vapour pressure is below equilibrium[55].

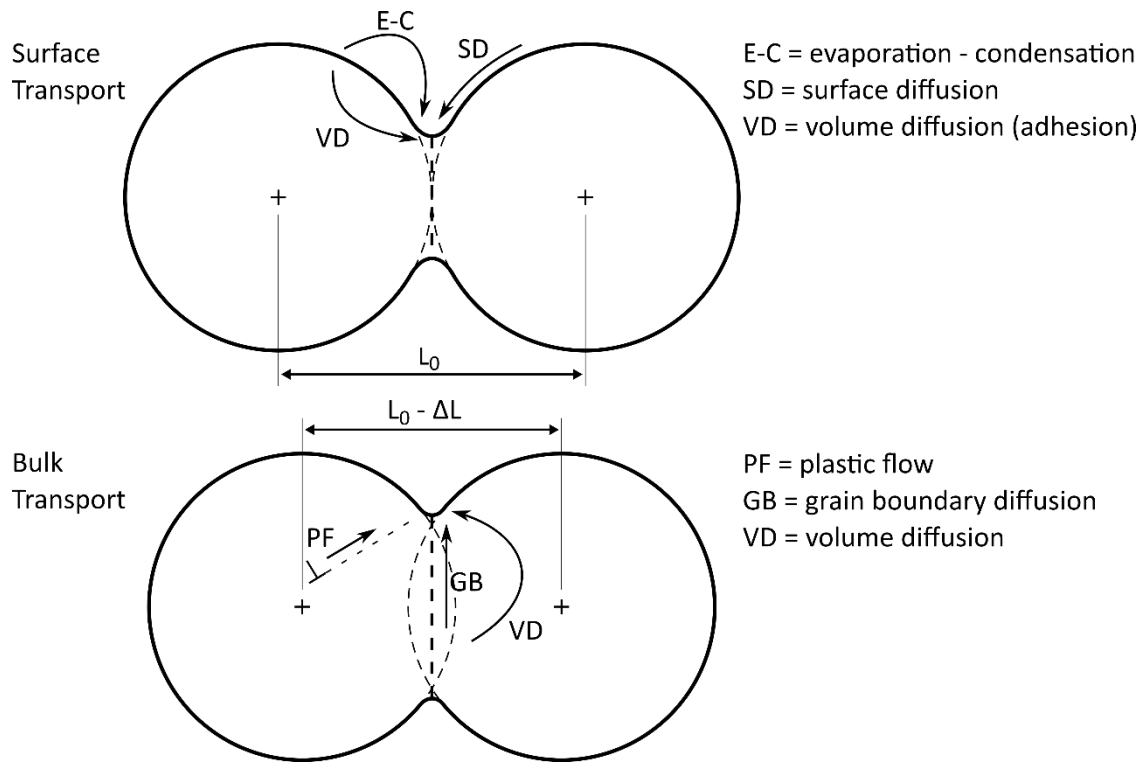


Figure 2.5 Schematic for the six surface and bulk transport mechanisms for sintering adapted from German[57].

The second surface transport mechanism is surface diffusion. Surface diffusion relies on movement of atoms between defects in the surface of the crystalline solid particle. The process of surface diffusion requires an atom to break away from a defect site, it will then move randomly across the surface until re-attaching at another surface defect. The greater the curvature of the surface the greater the concentration of defects and so the greater activity of both break away and reattachment from surface diffusion. This leads to a general movement of atoms from low to high curvature areas along surface curvature gradients[55].

Baik and Becher showed the contribution of oxides to surface transport in TiB_2 [58]. Evaporation-condensation of boria (B_2O_3) was responsible for coarsening between 1400 – 1700 °C, while titanium oxides (TiO_x) increased surface diffusivity between 1700 – 2050 °C. This effect translates to ZrB_2 , where preventing the role of oxides in surface transport is considered essential for pressureless densification[31], methods for which are discussed in the following section on sintering techniques.

Both these surface transport mechanisms are thermally activated, with an activation energy associated with the breaking of bonds required for vaporisation for evaporation-condensation and the breaking of bonds at a surface defect for surface diffusion. As such, they increase in activity with increasing temperature. They are both driven by curvature, so as they progress to reduce surface curvature and the available surface area is consumed by densification, the role of surface mass transport is diminished. Figure 2.6 shows the effect of surface diffusion to increase neck size and

create stable pores, resulting in a uniform surface curvature that has no curvature gradient to drive surface diffusion.

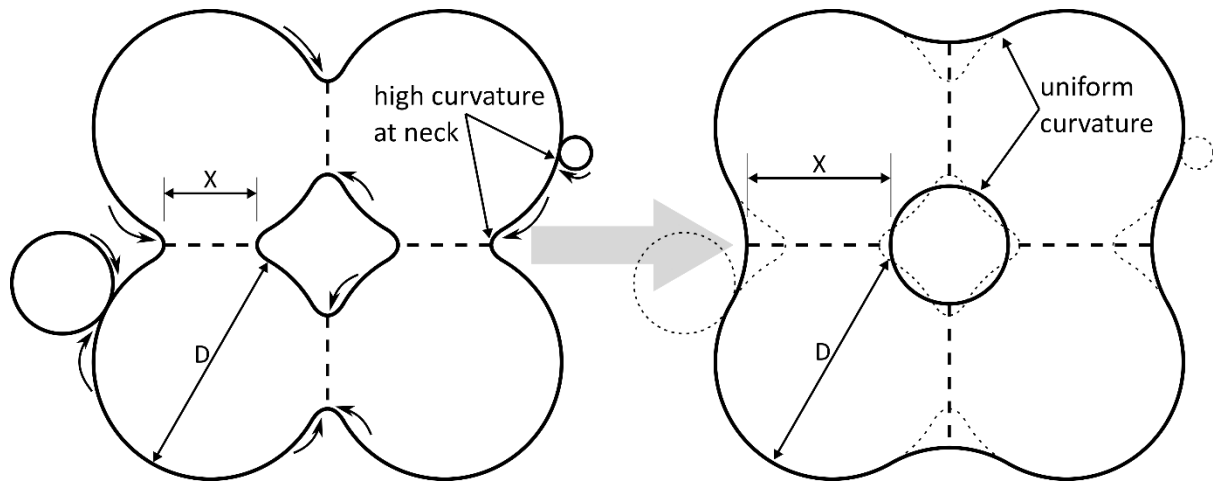


Figure 2.6 Coarsening by surface transport mechanisms. Mass transport is motivated by local curvature gradients, from high to low curvature until small grains are absorbed and the surface has a uniform curvature. X is the neck width and D the grain size.

Volume diffusion can act as both surface transport and bulk transport, depending on if mass is transported from the grain boundary or from the particle surface. In either case, mass is moved through the atomic lattice towards the sinter bond between particles. Where mass moves through the lattice from the grain boundary to the sinter bond at the surface of the particle neck, densification and shrinkage occur as atoms are moved away from the space between particle centres to the neck. The direction of mass transport is dictated by the vacancy concentrations within the grain. Vacancy concentration is high at surfaces with high concave curvature, the highest curvature usually being the neck surface at the sinter bond, so mass flows into this area[55].

Grain boundary diffusion typically has an activation energy greater than surface diffusion but lower than volume diffusion, due to the high defect concentration at the grain boundary compared to the bulk lattice. The grain boundary diffusion contribution to sintering depends on the grain boundary area per unit volume, which is inversely proportional to grain size. The mass transport for grain boundary diffusion is essentially the same for volume diffusion, with mass moving opposite to the vacancy diffusion away from the interparticle neck, using the grain boundary as a fast diffusion pathway with low activation energy. This movement of mass towards the surface at the particle neck causes pile up, or hillocks, of mass which can be redistributed across the particle surface by surface diffusion[59].

ZrB₂ is considered to have an onset temperature for densification at 1750 °C[29], with grain boundary and volume diffusion active above 1800 °C[60]. Increasing the temperature will increase the speed of both grain boundary and volume diffusion. This means that once either mechanism is active the

densification rate will increase as temperature is increased. Lonergan *et al.* studied densification rates in reaction hot-pressed ZrB_2 , finding the densification rates increased faster above 2000 °C. This suggests that below 2000 °C grain boundary diffusion is the dominant mechanism for densification, and above 2000 °C volume diffusion is the faster mechanism[61].

Plastic flow is the movement of dislocations, more commonly associated with deformation in metals, and can occur by climb or glide mechanisms. Densification by climb occurs by the flow of vacancies from high vacancy concentration at inter-particle necks, annihilating at dislocations, causing dislocation climb as the dislocation moves to an adjacent slip plane. Dislocation glide occurs when the local stress exceeds the required flow stress of a dislocation at the current temperature. This stress arises from the surface curvature, with negative (compressive) stresses arising from concave surfaces such as particle necks, and positive (tensile) stresses from the particle surface. This results in a stress gradient that drives dislocation glide towards the neck, reducing the curvature and stress gradient. The high curvature at the start of sintering gives rise to the highest stress gradients, therefore plastic flow is most active during neck growth. The process is sufficiently rapid once the energy requirement is met for dislocation movement, by increasing temperature or applied load, that the effect is limited to the first minutes of sintering and is negligible during the final stages[55].

2.2.2 Stages of Sintering

Sintering of powders into a monolithic ceramic is typically described as four stages, each with a different combination of coarsening and densification mechanisms, as outlined in Table 2.2. The first stage is adhesion, with powder particles forming contacts with weak Van de Waals forces at random orientations. As certain orientations have a lower interfacial energy, particles will rotate towards this orientation if possible and increase packing density.

Next is the initial-stage sintering, where necks are formed between particles by a combination of all sintering mechanisms, leading to minimal amounts of densification, while there is a significant reduction in surface area by surface mass transport mechanisms. As detailed above, surface transport acts to move mass along local curvature gradients, widening the inter-particle necks but without significant increases in grain size, as demonstrated in Figure 2.6. Densification at this stage occurs by plastic flow due to the high sintering stress from curvature gradients at this early stage of sintering[62].

The greatest amount of densification then occurs during the intermediate stage of sintering. The activation of grain boundary and volume diffusion mechanisms leads to rapid densification, grain growth, and pore rounding. The degree to which densification occurs largely depends on the surface area remaining after initial stage sintering, which will be greatly reduced in surface curvature, the energy of which can be reduced by replacement with grain boundaries by densification[55].

Table 2.2 Stage of sintering, adapted from German [55].

Stage	Process	Surface Area loss	Densification	Coarsening
Adhesion/ Rearrangement/ Packing	Contact formation	Minimal	None	None
Initial	Neck growth	Up to 50%	Slight	Minimal
Intermediate	Pore rounding and elongation	Near total loss of open porosity	Significant	Increase in grain and pore size
Final	Pore closure, final densification	Negligible	Slow, minimal	Extensive grain and pore growth

Neuman *et al.* showed that peak densification rates occurred around 60 % relative density and 1954 °C in ZrB₂ when hot-pressed at 32 MPa, heating at 50 °C/ min[63]. The density of 60 % coincides with the expected transition from initial to intermediate stage sintering.

The rate of densification then slows as the surface area from open porosity is nearly completely removed, leaving little driving force for further densification. This stage of sintering is termed final stage sintering and sees pores close, while coarsening at this stage causes grain and pore growth as interfacial energy is reduced, with minimal further densification[55]. The goal of many ZrB₂ studies is to produce fine grain structures, so grain growth in this stage is undesirable. However, as this work aims to create a porous ZrB₂ product, the processes which create the porous network during the initial stage are the focus.

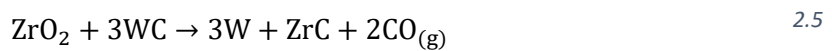
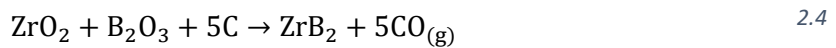
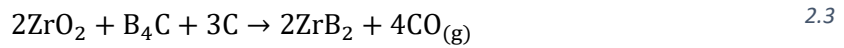
2.2.3 ZrB₂ Sintering Techniques

Common methods for densifying ZrB₂ include pressureless sintering (PS), hot-pressing (HP), and spark plasma sintering (SPS). Development of sintering methods generally centre around promoting densification while suppressing coarsening. The various approaches to achieving high density ZrB₂ involve reducing powder size and oxygen content, as well as procedural changes such as increasing heating rates and applied pressures[64].

The use of ultra-fine powders drastically increases the solid-vapour surface area and curvature. Such powders are typically made by reactive methods and can be produced in advance of sintering[65], or *in situ* during sintering in processes such as reactive hot-pressing (RHP)[61], [66].

The particle size can also be reduced mechanically by high energy milling. This can have a combined effect of reducing particle size while increasing the surface defect concentration, further increasing the driving force for densification[67]. However, milling increases the oxide content of the powder as the new surface area, created with a reduction in particle size, oxidises. This increased oxide contamination will disrupt densification by coarsening if the oxide is not removed[68].

Surface oxides in ZrB₂ promote surface transport which remove the driving force for densification[69]. Removal of oxides at the surface of ZrB₂ particles is therefore the topic of much research into improving the sinter-ability of ZrB₂ [9], [70]. Common sintering additives to reduce oxide impurities are B₄C[68], [71], C[71]–[73], and incidental WC[68] from milling[32]. Oxides react with sintering additives to predominately produce ZrB₂ and CO_(g), with ZrC and W also possible, as per reactions 2.3 - 2.6.



Pressureless sintering is favourable in some instances as it allows for near-net shape manufacturing, but typically requires temperatures > 2100 °C for densification of ZrB₂, with hold times of several hours[31]. The use of sintering additives in pressureless sintering reduces the effects of coarsening by surface transport, with Zhang *et al.* showing that the addition of boron carbide can allow for sintering of > 98 % relative density as low as 1850 °C[68].

Applying external pressure by hot-pressing also reduces the temperatures and times required for full densification of ZrB₂ compared to pressureless sintering but can only produce flat samples[74]. Pressures of 32 – 50 MPa are typical of ZrB₂ hot-pressing methods, and reduction of powder particle size by milling combined with the use of sintering aids is common to achieve high density products [61], [66], [69], [73], [75].

The onset of densification during hot-pressing is 1750 °C, with temperatures of > 1850 °C required for full densification by hot-pressing [29]. While this temperature requirement is comparable to pressureless sintering, the time required is greatly reduced, with hold times of tens of minutes rather than hours. Less time at high temperature results in a smaller grain structure and greater strength[69].

Fast heating rates can also be employed to reduce the time spent coarsening without densification in low temperature regions. Hot-pressing typically uses heating rates of 10 – 50 °C/ min, with faster heating rates associated with smaller grain sizes and stronger products[75]. Spark plasma sintering can directly heat the ZrB₂ powder, and die, by passing a current between the two rams, rather than heating via radiation/ convection from nearby graphite elements. This allows for heating rates up to 430 °C/ min, and full density can be achieved in just 3 minutes hold at 1900 °C[76]. The reduced

exposure time to elevated temperatures produces even finer grain sizes with improved strength, while pulsing a current directly through the sample is thought to assist with the reduction of oxide impurities at lower temperatures[69].

2.2.4 Porous ZrB₂

There are many different methods for achieving porosity in ceramic materials. The technique used to create pores varies depending on the size of pore and volume fraction of porosity desired, as well as the morphology of pore required for each specific application. While fully dense materials are desired for high strength, pores can be desirable in ceramics as a means of reducing density of components or to add function such as permeability as for filtration. The application of transpiration cooling requires an open porous network within a UHTC to flow coolant fluid through.

Previous works in manufacturing porous UHTCs are limited, and mainly focus on reducing the weight of components. Porous ZrB₂ has been created previously by ice templating, creating an array of unidirectional pores, which are then connected by secondary globular pores[77]. Du *et al.* also used ice templating to create ZrB₂-SiC with 5 μm pore size, with the aim of reducing density of ZrB₂ structures[78].

Medri *et al.* also aimed to reduce the density of ZrB₂ with sandwich structures, using replica templates and direct foaming techniques to create ZrB₂ sponges up to 70 vol% porosity capped with a dense slipcast layer[79].

Traditional UHTC sintering aims to produce high density products. Sintering at lower temperatures and pressures will result in a porous material, not allowing for densification means powder particles will fuse but leave a porous network between particles as illustrated in Figure 2.6. Partially sintered ZrB₂ has been created by low temperature results of studies attempting to achieve near full density, generally held as an example of the poor sinter-ability of ZrB₂ without sintering aids. The density and method of these studies are shown in Figure 2.7[10], [69], [76].

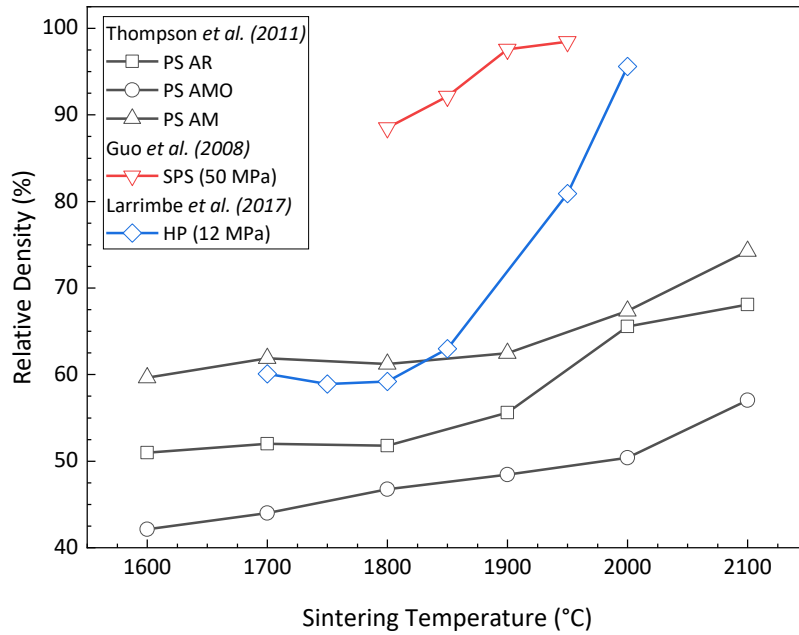


Figure 2.7 Relative density of sintered ZrB_2 without sintering aids from various studies. Thompson *et al.* [69] sintered ZrB_2 by pressureless sintering (PS) for 2 hours at each target temperature from both as-received (AR) and attrition milled (AM) powder using Co-bonded WC milling media, AM powder was then oxidised to 8.2wt% O (AMO). Guo *et al.* [76] used attrition milled powder with SiC milling media for spark plasma sintering (SPS), heating at 300 °C/min and holding for 3 minutes under 50 MPa load. Larrimbe *et al.* [10] hot-pressed (HP) AR ZrB_2 powder for 15 minutes at 12 MPa.

Pressureless sintering by Thompson *et al.* with oxidised powders resulted in the highest porosity, with more than 40 vol% porosity after holding at 2100 °C for 2 hours [69]. Larrimbe *et al.* produced 40 vol% porous ZrB_2 by hot-pressing as it was found to be stronger than pressureless sintering at equal porosity [10]. This material was then characterised by Ifti *et al.* for permeability [6] before successful testing of transpiration cooling in a plasma tunnel [5].

Spark plasma sintering is shown to produce the densest product, with high pressures and heating rates resulting in just 10 vol% porosity when sintering at 1800 °C [76]. However, while studying the effect of porosity on thermal conductivity, Yuan *et al.* made ZrB_2 with relative density from 0.62 to 0.79 by a two-step spark plasma sintering-reaction sintering (SPS-RS) process [42].

Porous ceramics made by partial sintering typically have very fine porosity in the size range of the sintered powder, the random nature of partial fusion of powder particles creating thin, tortuous pore pathways with high internal surface area. The porosity can be controlled by the extent to which densification can occur, commonly controlled by varying temperature and time, or by altering factors affecting densification discussed above [80].

2.3 Effect of Porosity on Properties

The effect of porosity on the physical properties while partial sintering has been studied extensively for alumina, but there is limited data specific to UHTCs. This section, therefore, will summarise the models associated with the effect of porosity on partially sintered ceramics and the observed trends and models.

There are many properties of ceramics that do not depend on porosity, mainly those that depend solely on atomic bonding. The main properties that are independent of porosity are lattice parameter/unit cell volume, melting/ boiling temperatures, ablation energy, emissivity, and thermal expansion[80].

2.3.1 Elastic Modulus

There are many different models for the effect of porosity on elastic behaviour of ceramics, with varying degrees of complexity and number of coefficients depending on the morphology of the pores being considered. The simplest model for properties in a porous material is the rule of mixtures, which considers the pores to be a phase where $E = 0$ [81].

$$E = E_0(1 - \phi) \quad 2.7$$

Where:

- E = Elastic modulus of the porous material
- E_0 = Intrinsic elastic modulus of the fully dense material
- ϕ = Volume fraction porosity

Models for elastic modulus of porous ceramics can also be derived from the geometry of the solid phase surrounding open pores, as described by Gibson and Ashby according to the definition in Figure 2.8[82].

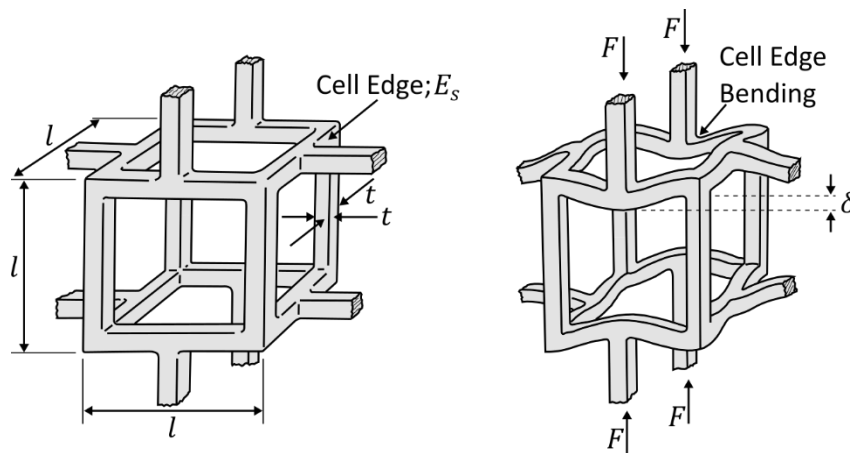


Figure 2.8 Open cell model for elastic modulus adapted from Gibson and Ashby[82] for a material with elastic modulus, E_s , with cell edge length, l , edge thickness, t , bending with a displacement, δ , under load, F .

The second moment of area, I , of the cell is related to the porosity and edge length, l , of the material by[82];

$$(1 - \phi) \propto \left(\frac{t}{l}\right)^2 \quad 2.8$$

$$I \propto t^4 \quad 2.9$$

To yield;

$$(1 - \phi)^2 \propto \frac{I}{l^4} \quad 2.10$$

The deflection, δ , is proportional to the applied force, F , and intrinsic elastic modulus of the edge material, E_s , by[83];

$$\delta = \frac{Fl^3}{E_s I} \quad 2.11$$

The stress, σ , and strain, ε , on the cell structure are represented by;

$$\sigma \propto \frac{F}{l^2} \quad 2.12$$

$$\varepsilon \propto \frac{\delta}{l} \quad 2.13$$

Combining with 2.11 therefore yields the elastic modulus of the porous material, E^* , by;

$$E^* = \frac{\sigma}{\varepsilon} \propto \frac{\delta E_s I}{l^5} \cdot \frac{l}{\delta} \equiv \frac{E_s I}{l^4} \quad 2.14$$

Which by substituting equation 2.10 simplifies to;

$$\frac{E^*}{E_s} \approx (1 - \phi)^2 \quad 2.15$$

This result matches experimental results of many cellular ceramics but fails to accurately predict the measured elastic modulus of partially sintered ceramics.

Many empirical and derived models have been developed to match the observed behaviours. Linearity in semi-log and log-log plots of elastic modulus vs. porosity lend themselves to exponential relationships. Equation 2.16 fit well to semi-log data, with a coefficient, b , for the gradient. This model was later derived through strain analysis by Anderson[84]. Log-log relationships can be fitted to equation 2.17, with coefficients A and n and have been modelled on the principle of minimum solid area[85]. Other commonly used models for elastic modulus with porosity are Spriggs equation (2.18) and Hasselman's equation (2.19) based on mechanical analysis with spherical pores[80].

$$\frac{E}{E_0} = e^{-b\phi} \quad 2.16$$

$$\frac{E}{E_0} = 1 - A\phi^n \quad 2.17$$

$$E = E_0(1 - h\phi) \quad 2.18$$

$$E = E_0 \left[1 + \frac{A\phi}{1 - (A + 1)\phi} \right] \quad 2.19$$

These models match well to ceramics with spherical pores but are mainly empirical in nature and do not contain any boundary condition for when $\phi = 1, E = 0$. To improve upon these models Phani and Niyogi derived equation 2.20 to describe the complete loss of elastic properties at a critical porosity $\phi = \phi_c$ [86];

$$\frac{E}{E_0} = \left(1 - \frac{\phi}{\phi_c} \right)^n \quad 2.20$$

This boundary condition is particularly relevant to partially sintered ceramics, as the porous microstructure develops from a powder compact that cannot withstand any loading[87]. However, rather than this exponential increase from a critical density, Lam *et al.*[87] observed the development of elastic modulus in alumina powder compacts to be linear from this initial onset of densification at ρ_0 up to full density according to equation 2.21.

$$\frac{E}{E_0} = \left(\frac{\rho - \rho_0}{1 - \rho_0} \right) = \left(1 - \frac{\phi}{\phi_c} \right) \quad 2.21$$

At the on-set of sintering, neck growth between powder particles is responsible for a rapid increase in mechanical properties for very little increase in density and does not lead to densification. This increase in properties without increase in density is not captured by equation 2.21, leading Hardy and Green[88] to propose an additional term E' to be the elastic modulus after the initial increase without densification at ϕ_c , equation 2.22.

$$\frac{E - E'}{E_0 - E'} = \left(\frac{\rho - \rho_0}{1 - \rho_0} \right) = \left(1 - \frac{\phi}{\phi_c} \right) \quad 2.22$$

This relationship, while empirical in nature, has held up to comparison with a wide range of both experimental data[89]–[91] and modelling[90], [92] of partially sintered materials.

2.3.2 Strength

The strength of a porous ceramic develops in a similar way to the elastic modulus when sintering from a porous green body. There is a rapid increase in strength for very little increase in density, attributed to the formation of necks between powder particles by surface diffusion[93]. The Weibull modulus of partially sintered alumina has been shown to be consistent from the green body up to close to theoretical density, suggesting that the strength of a partially sintered material with porosity > 8 vol% is determined by the flaws resulting from the initial powder packing and neck development in the early stages of sintering[93], [94].

Hardy and Green[88] showed that the fracture toughness, K_{1C} , of partially sintered alumina followed the same relationship as elastic modulus: increasing linearly after the initial steep increase at green density up to full density, equation 2.23.

$$\frac{K_{1C} - K'_{1C}}{K_{1C}^0 - K'_{1C}} = \left(\frac{\rho - \rho_0}{1 - \rho_0} \right) = \left(1 - \frac{\phi}{\phi_c} \right) \quad 2.23$$

Where:

K'_{1C} = Fracture toughness at the onset of densification

K_{1C}^0 = Fracture toughness of the fully dense material

Fracture in ceramics is dominated by the presence of flaws, with a critical crack length, a , linking the mode 1 fracture toughness to the stress at failure, σ_f , by a shape factor, Y , according to equation 2.24.

$$\sigma_f = \frac{K_{1C}}{Y\sqrt{a}} \quad 2.24$$

Equations 2.22 - 2.24 can be combined to calculate the critical flaw size for partially sintered ceramics, from the measured flexural strength and elastic modulus. Hardy and Green[88] used this relationship to show that flaw size increased with increasing processing temperature during the initial stages of densification in alumina as the critical crack length is a formation of interconnected pores. Studies have also shown that with increasing density the critical flaw size reduces, leading to an increase in strength according to equation 2.24[87], [95]. Models to link the reduction in critical flaw size to the relative density of the material was first derived by Lam *et al.*[87] and then Ostrowski and Rödel[95] with the addition of an exponent, n , shown in equation 2.25 and were fit to experimental data plotted in Figure 2.9.

$$\sigma_f = \frac{K_{1C}^0 \left(1 - \frac{\phi}{\phi_c} \right)^n}{\sqrt{Y^2 a \left(\frac{1 - \phi_0}{1 - \phi} \right)^{\frac{1}{3}}}} \quad 2.25$$

Figure 2.9 shows the disparity between the two approaches. The log-linear plot shows the rapid increase in strength with little increase in density[88], [96], followed by a linear increase in properties compared to the increasingly steep rise in strength with increasing density of the critical flaw models fitted to experimental data[87], [95].

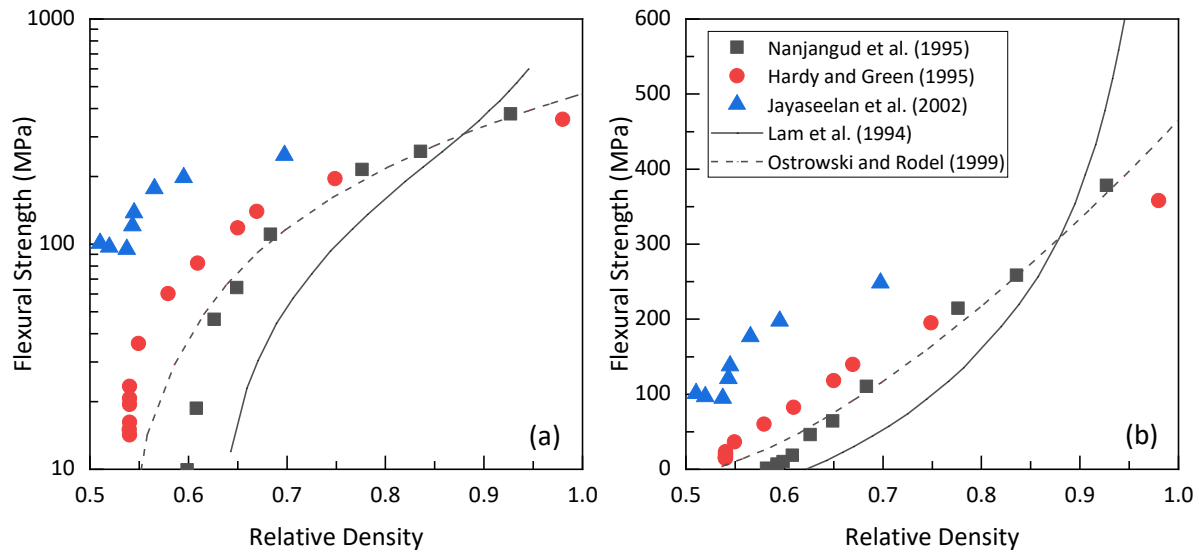


Figure 2.9 Strength data from various studies into the strength development of partially sintered alumina[88], [96], [97], and models for the relationship between strength and density[87], [95].(a) Log-linear plot showing the rapid increase in properties at green density, and (b) linear plot showing the difference in linear and exponential development.

As the steep rise in properties has been attributed to neck growth by surface diffusion, work has been done to exploit this mechanism to increase the strength of highly porous ceramic materials. Jayaseelan *et al.* used pulse electric current sintering (PECS) to promote neck growth and saw an increase in flexural strength at the green density increase considerably compared to pressureless sintering reported by other partially sintered alumina studies shown in Figure 2.9 [96].

2.3.3 Thermal Conductivity

One of the attractive properties of ZrB_2 for use in TPS is its high thermal conductivity to rapidly dissipate heat away from the leading edge. When dealing with a porous ceramic, the solid phase and pore phase must be considered. For the solid phase, the factors to note are the effective conductive path through the solid phase and the barriers within that, such as grain boundaries. For the pore phase, convective and radiative heat transfer can occur. Convective transfer is only significant in pores in the millimetre order of magnitude whereas at the application temperature of 2000 °C radiative transfer is significant[80]. Thermal conductivity not only depends on pore volume fraction but pore morphology. Large, open pores result in a greater dependence on radiative conduction[80]. Due to relatively small pores and low thermal conductivity of gas (air or coolant N_2) in the porous phase, the thermal conductivity through the solid phase dominates at ambient temperatures in partially sintered ceramics[98].

As with other physical properties, the particle necks dominate the thermal conductivity near the green density. The narrow contact points between particles create higher thermal resistance than expected for similarly porous ceramics[99]. Studies into various ceramics have performed heat treatments on

green bodies to promote neck formation without densification or grain growth, these have shown fourfold increase in thermal conductivity in tin oxide[100], sixfold increase in alumina[98], and eightfold increase in zinc oxide [99] without any reduction in porosity from a green relative density of 0.50 – 0.55.

After initial neck growth, as density increases, thermal conductivity will also increase. Models for the relationship between porosity and thermal conductivity include considering the pores as the second phase in a composite material with negligible thermal conductivity, and as such ignore any rise in thermal conductivity at the green density[80].

Yuan *et al.* measured the thermal conductivity for porous alumina made by both partial sintering and from fugitive inclusions, finding that the thermal conductivity closely matched the young's modulus when both were normalised by the values for fully dense [89]. The elastic modulus and thermal conductivity of the alumina made by fugitive inclusions followed a trend with the form $\left(1 - \frac{\phi}{\phi_c}\right)^n$ comparable to equation 2.20 and 2.22 for relative densities between 0.50 – 1.0, whereas the partially sintered material had a linear relationship for both properties comparable to equation 2.22 between relative density 0.65 – 1.0.

The porous ZrB₂ made by SPS-RS by Yuan *et al.* had relative density from 0.62 to 0.79 and room temperature thermal conductivity from 28.9 W m⁻¹ K⁻¹ to 56.5 W m⁻¹ K⁻¹ [42]. The porosity is cited as the dominant factor in thermal conductivity compared with the grain size.

2.4 Fluid Flow in Porous Materials

The permeability of porous ceramics has been the focus of study mostly due to applications in filtration of gas and liquids, with much focus has been on ceramic foams with porosity > 60 vol%[101]. ZrB₂ with 40 vol% porosity have been tested by Ifti *et al.* to assess their permeability and flow characteristics with the intended application of transpiration cooling[6]. The materials exhibited throughflow behaviour as expected from Darcy-Forchheimer type permeability. The distribution of flow leaving the material was also assessed, finding the flow to be generally well distributed due to the fine porous network, but with some spots of low and high permeability.

2.4.1 Darcy Permeability

Darcy's law describes the unidirectional flow of fluid through a porous medium, with initial experiments showing a directly proportional relationship between flow rate and applied pressure [102]. This relationship is defined by;

$$\frac{\Delta P}{x} = -\frac{\mu}{\kappa_D} q_f \quad 2.26$$

Where:

q_f = flux of fluid

μ = fluid viscosity

κ_D = permeability of the material

ΔP = pressure gradient across the material

x = thickness

It can be seen, therefore, that materials of low permeability result in higher required pressures for the same flux of coolant fluid. At high flow rates, the permeability becomes non-linear and can be modelled by adding the Forchheimer term to Darcy's Law to give the Darcy-Forchheimer Law [103];

$$\frac{\Delta P}{x} = -\frac{\mu}{\kappa_D} q_f - \frac{\rho}{\kappa_F} q_f^2 \quad 2.27$$

Where:

κ_F = the inertial permeability, or Forchheimer coefficient

ρ = the density of the fluid

ΔP is then given as a function of absolute pressure either side of the porous material. When using incompressible fluids, the following correction can be made[6];

$$\Delta P = P_i - P_0 \quad 2.28$$

where P_i is the pressure upstream of the material, and P_0 the pressure downstream. For ideal gasses, which are considered compressible fluids, ΔP can be calculated by;

$$\Delta P = \frac{P_i^2 - P_0^2}{2P_0} \quad 2.29$$

Flow through a porous material is dependent on the characteristics of the pore structure. Not all porosity gives rise to fluid flow, pores can be completely closed or dead-ends and therefore contribute nothing to the flow. Porosity that allows for fluid flow is termed the effective porosity, ϕ_E , and gives rise to the labyrinth factor ϕ_E/ϕ . This shows the amount of open porosity to closed for a given material[104].

The tortuosity of the pores also affects permeability. This is defined as the average path length required for fluid to flow through the porous body divided by the displacement, or most direct path. The more direct the path through the material, the easier it is for fluid to flow through as bends in the

path result in pressure drops[80]. Sani *et al.* promoted fluid flow through 50 – 60 % porous ZrB₂ by creating pores by ice templating[105]. With the intention that with direct and open pores, the fluid flow properties would be improved.

The pore size also has a significant effect on permeability, larger pores permit flow more readily, whereas smaller pores will lead to greater pressure. A few small pores restricting flow can mean that average pore size may not be representative of the pore size effects [80]. Innocentini *et al.* reviewed Darcy permeability of ceramic foams with porosity fractions > 60 %, the permeability was not dependent on porosity but pore size, confirming that larger pores resulted in greater the permeability [106].

2.4.2 Flow through channels

Darcy-Forcheimer coefficients describe the flow of fluid through a permeable material such as partially sintered ceramic, but reinforced substructures for a partially sintered layer would be channelled. Like Darcy permeability through porous networks, the flow through cylindrical channels is dictated by the channel radius, r , and length, l , according to the Hagen-Poiseuille equation [107];

$$\Delta P = \frac{8}{\pi} \mu Q_f \frac{l}{r^4} \quad 2.30$$

Where:

ΔP = pressure gradient across the channel length

μ = viscosity of the fluid

Q_f = volumetric flow rate

Flow characterisation of porous ZrB₂ has highlighted the need for a uniform distribution of surface flux[6]. When introducing flow via channels as in Figure 1.1 an even distribution will intuitively be promoted by narrow channels spaced closely together, however the Hagen-Poiseuille model predicts that reducing channel diameter will limit fluid flow.

2.5 Conclusions

Temperatures greater than 1800 °C are required for full densification of ZrB₂ by any method. Porous UHTCs can be made by halting standard sintering programmes below temperatures required for full densification. Large powders and increased oxygen content result in higher porosity as the driving force for densification is reduced due to low starting curvature and the promotion of rapid surface transport respectively.

Porous ZrB_2 has been demonstrated as an effective material for transpiration cooling. However, the physical properties are low compared to dense ZrB_2 , motivating the work to improve properties while maintaining permeability.

The strength, elastic modulus, and thermal conductivity of partially sintered ceramics is strongly dependent on the interparticle neck geometry, and all can be increased by promoting the growth of necks between powder particles in the initial stage of sintering. This occurs by surface transport mechanisms which are accelerated by the presences of oxide contamination in the form of B_2O_3 and ZrO_2 as a surface layer on ZrB_2 powders.

Increasing the permeability of porous structures can be done by increasing the porosity, or by increasing the pore size. The low strength and permeability of partially sintered ZrB_2 gives rise to the need for channelled substructures for reinforcement and greater flow, while the partially sintered layer provides good flow distribution due to the fine nature of the porous network. The competing effects of flow distribution and channel size in such a substructure require analysis to assess the trade-off between channel size and flow restriction.

3 Experimental Methods

This methods chapter will outline the measurement principles of the characterisation methods used for analysis of ZrB_2 powders and sintered products. This includes the development of a permeability measurement rig, and the continuous monitoring of density during hot-pressing. The details of powder preparation and hot-pressing methods are presented for each ZrB_2 fabrication method.

3.1 ZrB_2 Powder

Two grades of ZrB_2 powders were used, a larger-sized grade A powder and a finer grade B (H.C. Starck). The manufacturer's supplied particle size distribution and chemical composition is shown in Table 3.1, showing the grade A to be nominally twice the size of the grade B, while the grade B has a higher oxygen content tolerance.

Table 3.1 Manufacturer's information for ZrB_2 powders (H.C. Starck). Chemical compositions and mass fraction (g/g).

Particle Size Distribution	Grade A	Grade B
<i>D</i> 10 %	1.0 – 2.0 μm	0.5 – 1.0 μm
<i>D</i> 50 %	3.0 – 5.0 μm	1.5 – 3.0 μm
<i>D</i> 90 %	8.0 – 12.0 μm	4.0 – 6.0 μm
Chemical Characteristics		
<i>B</i>	min. 18.5 %	min. 18.5 %
<i>C</i>	max. 0.2 %	max. 0.2 %
<i>O</i>	max. 1.0 %	max. 1.5 %
<i>N</i>	max. 0.25 %	max. 0.25 %
<i>Fe</i>	max. 0.1 %	max. 0.1 %
<i>Hf</i>	min. 0.2 %	min. 0.2 %

3.1.1 Particle Size Analysis

For the work presented in the following results chapters, the size distribution of ZrB_2 powders was measured with a Mastersizer 2000 (Malvern Panalytical, UK) by dynamic light scattering (DLS). The diffraction pattern of a laser shone through a fluid containing the dispersed powder is measured and the particle size is calculated from the refractive index of the powder and solvent. This technique assumes the powder particles to be perfect spheres and the basic principle of the measurement is the smaller the particle size, the larger the angle of diffraction. The data provides incremental particle size with corresponding volume fraction. A particle refractive index of 1.77 was used and ethanol was used as the dispersing medium.

3.1.2 Thermal Analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed by simultaneous thermal analysis (STA) with a STA 449 F1 Jupiter (Netzsch, Germany). TG involves the heating of a sample in a crucible and monitoring the mass. The crucibles are heated in an inert environment under flowing Ar gas. After heating, key temperatures can be identified for reactions that produce gas, and therefore mass loss, or oxidation causing mass gain. For DTA, the temperature of a reference crucible is monitored during the heating schedule. The difference between the sample and the reference then gives exothermic/ endothermic reaction information and shows any changes in the thermal behaviour on heating. Crucibles were selected based on the maximum temperature of analysis, for temperatures up to 1600 °C alumina was used, otherwise carbon crucibles were used to heat up to 2000 °C.

3.1.3 Oxidation of Powders

Some samples were hot-pressed with as-received (AR) ZrB_2 powders, while others were hot-pressed from oxidised powder. TG analysis data for both grades of ZrB_2 powder, heated at 10 °C/ min in air, are shown in Figure 3.1. The mass of both powders drops from room temperature to 200 °C, before increasing in mass from 400 °C. The rate of mass gain increases with increased temperature for the finer grade B powder, but the grade A keeps a comparatively low rate of mass gain.

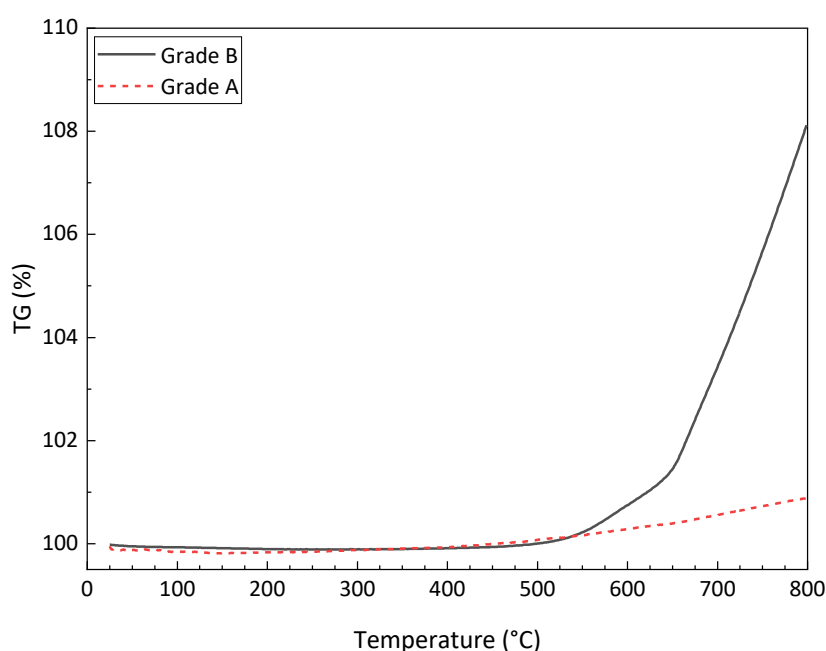


Figure 3.1 Thermogravimetric (TG) analysis for grade A and B ZrB_2 powders in air.

Thus, oxidation of powders for hot-pressing was achieved by heating powder in varying quantities from 100 – 400 g in alumina crucibles to 450 – 540 °C in a box furnace (CWF1200, Carbolite, UK). The oxygen content was measured by combustion analysis with EMGA-830 (Horiba, Japan). 10-100 mg of powder was sealed in nickel capsules and heated by passing a current through the graphite crucible.

With additional nickel pellets as flux, any oxygen in the sample would react with the graphite to form carbon monoxide. The oxygen content of the sample is then measured by a non-dispersive infrared (NDIR) detector measuring the amount of CO produced. The mass of oxygen produced was calculated from the integration of the signal over time and compared to a calibration with a Y_2O_3 standard reference material. The mass of the sample used was matched relative to the standard to ensure the mass of oxygen was within calibration. Where sintered samples were measured for oxygen content, they were first crushed by pestle and mortar.

The achieved oxygen content of various heat treatments of grade A and B ZrB_2 powder is recorded in Table 3.2. The heating rate was uncontrolled, as was cooling, which may contribute to the variability in oxygen content achieved. To target a specific oxygen content of close to 2 wt%O in the grade A powder, the temperature of the furnace was increased by 10 °C from 470 °C every 20 minutes until 2 wt%O was achieved. The final oxygen content was then measured after fully cooling.

Table 3.2 Thermal treatment definition and achieved oxygen content for grade A and B ZrB_2 in stagnant air.

Heat Treatment	Grade B						Grade A
	475 °C 1 hour	450 °C 1 hour	475 °C 1 hour	500 °C 1 hour	500 °C 1 hour	475 °C 5 hours	480 - 540 °C
Oxygen content (wt%O)	1.65 ± 0.06	1.91 ± 0.08	1.99 ± 0.10	2.17 ± 0.03	2.65 ± 0.06	2.81 ± 0.10	2.09 ± 0.08

For comparison to typical ZrB_2 hot-pressing which would employ sintering aids, grade B powder was planetary milled (PM100, Retsch, Germany) in a WC crucible with WC milling media for 3 hours at 300 rpm with 2 wt% B_4C , 2 wt% carbon black, and 2 wt% stearic acid to prevent clumping.

3.2 ZrB_2 Hot-Pressing

ZrB_2 powders were packed into an 80 mm graphite die lined with one sheet of graphite paper around the circumference and 2 discs each side of the powder in the loading direction. The die assembly was then compressed with a hydraulic pump to 2 tonnes before loading into the hot press (FCT, Germany).

3.2.1 As-Received Powders

Table 3.3 details hot-pressing steps for as-received ZrB_2 powders, during which a pinch load of 5 kN was applied while running an initial evacuation over 5 minutes, this equated to a load of 1.0 MPa which was then held throughout heating. The vacuum of 0.3 kPa absolute pressure was held while heating to 1450 °C at 10 °C/ min, the chamber was then backfilled with argon and held at a pressure of 30 mbar/ 3 kPa while heating to the final processing temperature (1500 – 2000 °C) at 5 °C/ min. A load of 60 kN/ 12 MPa was then applied in the final 10 minutes of heating. The 12 MPa load was then

held during a 15-minute hold at the maximum temperature. The load was then reduced over 10 minutes, either during uncontrolled cooling or an extended hold at the maximum hold temperature. The 1 MPa pinch load was then maintained for the duration of this extended hold and cooling.

Table 3.3 Details of hot-pressing steps for as-received ZrB_2 powders.

	Time (minutes)	Heating Rate ($^{\circ}\text{C}/\text{min}$)	Temperature ($^{\circ}\text{C}$)	Atmosphere	Force (kN)	Pressure (MPa)
Initial Evacuation	5			Vacuum	5	1
Heating 1	20-30	15 kW	500			
Heating 2	95	10	1450			
Heating 3	0-100	5	50 below final	Argon – 3 kPa		
Load Application	10	5	1500 – 2000		60	12
Hold	15		1500 – 2000			
Load Removal	10		0/ 1500 – 2000		5	1
Additional Holds	0/ 35 /565		1500 – 2000			
Cooling	180	uncontrolled	0			

Experimental trials were also conducted to assess the effect of long hold times, atmosphere, and heating rate during hot-pressing. These were otherwise hot-pressed identically to the standard programme in Table 3.3, and specific details of variations are given alongside results.

3.2.2 Oxidised Powder

Where oxidised powders are used in this work, the vacuum is only held during initial loading and heating to 500 $^{\circ}\text{C}$ as detailed in the hot-pressing steps in Table 3.4. After reaching 500 $^{\circ}\text{C}$, an argon atmosphere of 30 mbar/ 3 kPa is held through the entire heating and cooling cycle.

Table 3.4 Details of hot-pressing steps for oxidised ZrB_2 powders.

	Time (minutes)	Heating Rate ($^{\circ}\text{C}/\text{min}$)	Temperature ($^{\circ}\text{C}$)	Atmosphere	Force (kN)	Pressure (MPa)
Initial Evacuation	5	n/a		Vacuum	5	1
Heating 1	20-30	15 kW	500			
Heating 2	95	10	1450	Argon - 3 kPa		
Heating 3	0/40/80	5	1450/ 1650/1850			
Load Application	10	5	1500/ 1700/ 1900		60	12
Hold	15		1500/ 1700/1 900			
Load Removal	10	uncontrolled	0		5	1
Cooling	180		0			

3.2.3 Constant Pressure

Where a constant pressure was applied throughout hot-pressing. As shown in Table 3.5, a load of 30 kN was then applied during the initial 5-minute evacuation, equating to pressures of 24 MPa for

40 mm diameter dies. This load was held throughout heating, and held for 15 minutes at 1700 °C. The load was then reduced in the first 10 minutes of cooling as before.

Table 3.5 Details of hot-pressing steps for constant pressure hot-pressing samples.

	Time (minutes)	Heating Rate (°C/ min)	Temperature (°C)	Atmosphere	Force (kN)	Pressure (MPa)
Initial Evacuation	5			Vacuum	30	24
Heating 1	20-30	15 kW	500			
Heating 2	95	10	1450	Argon – 3 kPa		
Heating 3	50	5	1700			
Hold	15		1700			
Load Removal	10	uncontrolled	0		5	4
Cooling	180		0			

3.3 Hot-Press Data

To measure the densification during hot-pressing, each run had to be under identical conditions to ensure that no additional densification occurred during cooling. 37 mm diameter dies were used, with 30 - 40 g ZrB₂ powder each time. The ZrB₂ powder was loaded into the die with three discs of graphite paper each side in the direction of pressing, and one sheet of carbon paper wrapped around the circumference. When running a blank correction, the set-up is identical, including carbon paper, only without powder.

The die assembly was then compressed manually with a hydraulic press to 1 tonne force before placing between the rams of the hot-press. The load required for each run was then applied during a 5-minute initial evacuation. This load was 24 MPa in all instances other than one run at 4.7 MPa, the minimum load possible with 37 mm die and 5 kN load. Following evacuation, the chamber was backfilled with argon and the hot-press was heated to 500 °C with a set 10kW power, before switching to a controlled heating rate to 2000 °C. This heating rate was varied between 2, 5, and 10 °C/ min. The temperature was then held at 2000 °C until the ram movement had ceased, indicating a lack of further densification.

Cooling was then allowed to happen uncontrolled, with the applied load still active to measure the total ram displacement before and after the heating run. After cooling, the ZrB₂ sample was then surface ground to remove the graphite paper layers before measuring density by the Archimedes method.

Data from the hot-press was exported as a .csv file, with temperature, force, and ram position. From this data, the blank correction was subtracted to account for the thermal expansion of the graphite rams and the machine around it. The difference between the initial and final ram positions is used to calculate the green density of the powder compact in the hot press by comparing thickness change

with density, assuming a constant mass. This was required as the absolute thickness of the samples was not known either before or after pressing. First, the final thickness, t_f , was calculated as;

$$t_f = \frac{M}{\pi r^2 \rho} \quad 3.1$$

Where:

M = Mass of powder

r = Die radius

ρ = ZrB₂ density

The sample thickness during hot-pressing was calculated through the run by;

$$t = t_f - (S_f - S) \quad 3.2$$

Where:

t = Instantaneous sample thickness

S = Ram displacement

S_f = Final ram displacement after cooling

A coefficient of thermal expansion of $7.0 \times 10^{-6} \text{ K}^{-1}$ was used to correct the thickness value as the temperature is increased to 2000 °C with the formula;

$$\alpha = \frac{t - t_0}{t_0 \Delta T} \quad 3.3$$

Where:

α = Coefficient of thermal expansion

t_0 = Corrected thickness of the sample

ΔT = Temperature difference

This thickness was then used to calculate density with equation 3.4, relative density calculated by dividing by the nominal density of ZrB₂, 6.15 g/ cm³.

$$\rho = \frac{M}{\pi r^2 t_0} \quad 3.4$$

The sintering rate is then calculated by differentiating the density data against time. To make this possible, density data was first smoothed with a Savitzky-Golay filter (30-point window, 2nd order polynomial). To calculate sintering rate as a function of temperature, sintering rate was divided by the heating rate.

3.4 ZrB₂ Sample Characterisation

After hot-pressing, ZrB₂ samples require removal of the graphite paper from the surface. This was done manually with a Model 540 Surface Grinder (Jones & Shipman, UK). The ZrB₂ disc was wax mounted on a flat steel plate, each side was then ground until a uniform, dark, porous surface could be seen, typically requiring 0.5-1 mm grinding depth each side

3.4.1 Archimedes Density

Density of fabricated samples was measured as per the definition of density, ρ , given by the mass, M , and volume, V ;

$$\rho = \frac{M}{V} \quad 3.5$$

The volume of samples was measured by the Archimedes method. This calculates solid volume from the mass of water displaced by submersion, since the mass of a submerged object (M_{sub}) is given by the mass of the object (M), the volume (V_s) and density of the water displaced (ρ_w);

$$M_{sub} = M - V_s \rho_w \quad 3.6$$

This calculated volume was then used for density calculation with equation 3.5. For objects with open porosity, water ingress during submersion means the entire volume of the object is not measured as the open pores do not displace water. The volume of the open pores, V_p , therefore can be calculated by the mass of the saturated sample, M_{sat} , where;

$$M_{sat} = M + V_p \rho_w \quad 3.7$$

The total volume of the sample therefore is $V = V_s + V_p$;

$$V = \frac{M - M_{sub}}{\rho_w} + \frac{M_{sat} - M}{\rho_w} = \frac{M_{sat} - M_{sub}}{\rho_w} \quad 3.8$$

Combining equations 3.5 to 3.8 gives the bulk density of the object;

$$\rho = \frac{M}{M_{sat} - M_{sub}} \rho_w \quad 3.9$$

The greatest source of error in the measurement arises from the measurement of M_{sub} which relies on infiltration of open pores and M_{sat} which relies on accurate transferal of saturated pores to be weighed. Handling of samples can reduce the saturation of pores, leaking the infiltrated water. This error is exacerbated by small samples with high surface area to volume ratio so large monolithic

samples were used where possible, always > 1.5 g. This variation in M_{sat} was measured to be < 0.01 g, which results in a maximum error in Archimedes density of 5 %, or 2 vol% at 40 vol% porosity.

3.4.2 Mercury Intrusion Porosimetry

Mercury intrusion porosimetry (MIP) was used for characterisation of the pore morphology. MIP was performed with an Auto Pore IV (Micromeritics, USA). The sample was placed into the chamber of a penetrometer, which was then evacuated. The penetrometer was then filled with mercury. As mercury is a non-wetting liquid, it requires pressure to intrude into the pores of the sample, which can be applied incrementally to measure the volume intruded into the pores at each step by a capacitance measurement between the mercury and outside surface of the penetrometer.

The sample bulk volume (V_b) is measured by the displacement of mercury at the initial pressure of 0.53 psia, with bulk density calculated from the pre-measured sample mass (M). The total intrusion volume (V_{tot}) can be measured at the maximum pressure of 33 000 psia, and used to calculate open porosity (ϕ_{open}) by;

$$\phi_{open}(\%) = 100 \times \frac{V_{tot}}{V_b} \quad 3.10$$

The skeletal volume (V_s) and density (Y_s) can also be calculated by;

$$V_s = V_b - V_{tot} \quad 3.11$$

$$Y_s = \frac{M}{V_s} \quad 3.12$$

The average pore diameter is calculated from the assumption that pores are open and cylindrical, with the geometry of a cylinder of diameter (D) and height (h) having a volume (V);

$$V = \frac{\pi D^2}{4} \times h \quad 3.13$$

The area of the sides of the cylinder are then;

$$A = \pi D h \quad 3.14$$

Combining equations 3.13 and 3.14 gives the expression for the pore area equation 3.16;

$$h = \frac{4V}{\pi D^2} = \frac{A}{\pi D} \quad 3.15$$

$$A = \frac{4V}{D} \quad 3.16$$

This allows for calculation of the average pore diameter (D_{av}) from the total specific intrusion volume (I_{tot}) and total specific pore area (A_{tot});

$$I_{tot} = \frac{V_{tot}}{M} \quad 3.17$$

$$D_{av} = \frac{4I_{tot}}{A_{tot}} \quad 3.18$$

A_{tot} is then measured based on Washburn's equation[108];

$$D = \frac{-4\gamma \cos \theta}{P} \quad 3.19$$

Where:

D = Pore diameter (m)

γ = Surface tension of mercury; 485 dynes cm⁻¹

θ = Contact angle of mercury; 130°

P = Applied pressure (Pa)

Again, cylindrical pores are assumed[109] such that area is;

$$A = \frac{PV}{\gamma \cos \theta} \quad 3.20$$

With the average pore area summed over the incremental application of pressure from 0.53 to 33 000 psia.

$$\Sigma A = - \frac{\Sigma PV}{\gamma \cos \theta} \quad 3.21$$

Tortuosity is the measure of how direct a path a pore takes through the material, defined in equation 3.22 as the actual distance travelled through a pore divided by the total displacement, or shortest path. Like pore size, this pore characteristic affects permeability, as direct pores have lower resistance to flow compared to highly tortuous pores.

$$tortuosity = \xi = \frac{\text{actual distance travelled}}{\text{shortest distance}} \quad 3.22$$

This is calculated from MIP data with equation 3.23, the principle of which is to define a pore length from the measurement of Katz-Thompson Permeability[110] (K), along with calculations for pore diameter (D_{avg}), skeletal density (Y_s), and total specific intrusion volume (I_{tot}).

$$\xi = \sqrt{\frac{D_{avg}^2}{4 \cdot 24K(1 - Y_s I_{tot})}} \quad 3.23$$

3.4.3 Physical Properties

The flexural strength of samples was measure by 4-point-bend in accordance with ASTM standard C1161-18[111]. Bars nominally 2.0 x 1.5 x 25 mm were cut from porous ZrB₂ with a diamond saw, then polished up to 4000 grit SiC paper.

The rams were loaded with pins of span 18 mm and 9 mm at a loading rate of 0.2 mm/ min by with a 2.5 kN load frame (Zwick/Roell, Germany). Depending on material availability, 3-10 bars were tested per sample, so standard deviation cannot be calculated accurately, and absolute error is used as the half measurement range.

The flexural strength (σ_f) is then calculated from the maximum load applied (F) with 3.24;

$$\sigma_f = \frac{3 FL}{4 bt^2} \quad 3.24$$

Where:

L = Length of the bar

b = Width of the bar

t = Thickness of the bar

Elastic modulus of samples was measured by impulse excitation. This was done with a resonance frequency and damping analyser (RFDA) (IMCE, Belgium) in accordance with ASTM standard C1259-15[112]. Bars were placed for excitation to be as free as possible, being supported at node locations across the width of the bar. During excitation, the vibration is measured with a transducer and frequency of vibration calculated within the software by Finite Fourier Transform (FFT). The elastic modulus, E , is then calculated by the following formula;

$$E = 0.9465 \left(\frac{mf_f^2}{b} \right) \left(\frac{L^3}{t^3} \right) T_1 \quad 3.25$$

Where:

m = Mass of the bar

f_f = Frequency

T_1 is a correction factor for Poisson's ratio, the full details of which can be found in the general standard test method ASTM C1259 – 15 [112]. The error in measurement is calculated from the

cumulation of measurement error for mass and dimension lengths along with variability in measurement repeats.

The thermal diffusivity of samples was measured by the LFA 427 Laserflash (Netzsch, Germany). The top side of a flat sample was heated by a laser pulse, the temperature increase on the back side of the sample is then measured with an infrared detector. This signal is used to calculate thermal diffusivity, α , within the software. The thermal conductivity, λ , can be calculated as the product of the diffusivity, density, ρ , and specific heat capacity, c_p , as;

$$\lambda = \alpha \cdot c_p \cdot \rho \quad 3.26$$

3.4.4 Thermal Analysis

The thermal expansion behaviour of samples was measured by a Dilatometer DIL 402 C (Netzsch, Germany). Samples were loaded into a tubular graphite furnace, held against the end of the tube by a graphite push rod connected outside the furnace to a displacement transducer (LVDT). As the sample is heated, changes in the length are measured by movement of the LVDT. A blank correction file was subtracted from the experimental data. This correction used a 25 mm graphite standard in place of the 25 mm ZrB₂ samples, so thermal expansion of the graphite standard was subtracted from the measured machine expansion. The resulting correction file is then subtracted from sample test runs to accommodate for the expansion of the machine and push-rod.

This technique can be used to show thermal expansion during heating and densification reactions that cause a reduction in the length measured. Heating rates of 10 °C/ min and a He atmosphere were used for all dilatometry.

For all thermal analysis, the onset and end temperature for reactions were found graphically. This is defined as the intercept of the tangent to the curve at the maximum rate of change in length with the tangent for the preceding or proceeding baseline period of heating.

3.4.5 Scanning Electron Microscopy

Sample imaging was done by scanning electron microscopy (SEM) (JSM-6010LA, Jeol, Japan). For topographical contrast, secondary electron imaging (SEI) was used. SEI detects the emission of low energy electrons that are ejected from the sample after being scattered by the electron beam as it rasters across the sample surface. Compositional contrast is achievable by back-scattered electron imaging (BEI). BEI detects high-energy electrons from the original beam, scattered by elastic interactions with the nuclei of sample atoms, the higher the atomic mass, the greater the scattering and the brighter a phase will appear.

Finally, X-rays emitted when the beam electrons scatter secondary electrons can be used to characterise specific elements within a sample, a technique called energy dispersive X-ray spectroscopy (EDS). EDS maps are generated by rastering the electron beam across a sample surface and highlighting the count for detection of specific elements.

Prior to SEM imaging, samples were prepared by various combinations of resin impregnation, slicing, grinding, and polishing. Details for each of these processes are given for each sample in the relevant chapter results. Impregnated samples were gold coated and Imaging was then performed with accelerating voltage of 20 keV, with a working distance of 10 – 20 mm by SEI unless otherwise stated.

3.4.6 Permeability

Permeability measurements were made either by Hassan Ifti (Oxford Thermofluids, Oxford University) by published methods[6] or by the method outlined here. Two permeability measuring rigs were used, for 40 mm and 80 mm diameter ZrB_2 discs.

Compressed air was used as a fluid, using the building main gas supply of 7.5 bar. This was controlled by a valve at the inlet tap and connected through a mass flow meter (FMA-1609A, Omega, USA) before feeding into the chamber of the jig, as shown in Figure 3.2. The sides of the partially sintered ZrB_2 were sealed with a nitrocellulose lacquer (Polish 010, Boots, UK) to prevent fluid flow out the sides of the sample, and the ZrB_2 disc was held between two O-rings of diameter 78 mm, with a cross sectional radius of 2 mm. Six M6 wing-nuts held applied pressure through the O-rings, each was tightened sequentially by hand until firm. When flowing gas through the set-up, foaming water spray was used around the edges to ensure there were no leaks from the pressure transducer (PXM409, Omega, USA) and gas tube connections, or from the sides of the sample.

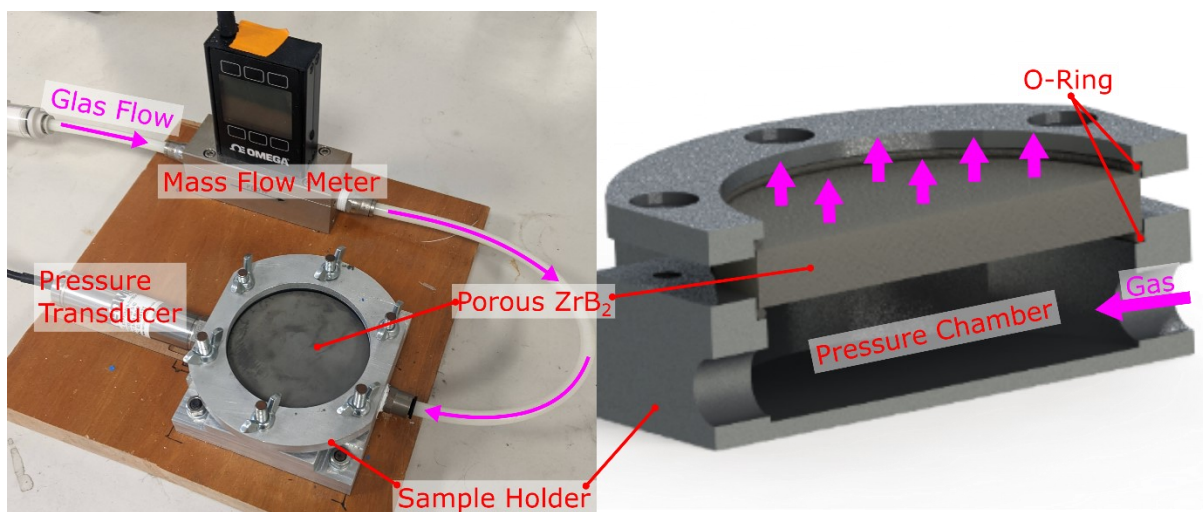


Figure 3.2 Photo of experimental set-up for permeability measurements of 80 mm discs along with the cross-section of the 3D model of testing jig.

To test the pressure and mass flow for a sample, the pressure valve was fully opened, and the pressure monitored in real time. Once the pressure had stabilised the pressure was recorded, and a reading was taken for mass flow rate. Flow rate was then incrementally decreased by partial closure of the valve, with measurements taken after the pressure had equalised after each adjustment.

To calculate permeability, the mass flow rate (SLPM) must be converted to a velocity. This is done by applying equation 3.27 to calculate the volume litres per minuets (LPM) by adjusting the standard litres with the temperature and pressure of the gas. This volume flow rate can then be converted to speed by 3.28, dividing by the cross-sectional area of the disc and correcting the units from minutes and litres to seconds and metres. A correction is then applied to the pressure, first the pressure on the top side of the porous ZrB₂, P_1 , is assumed to be solely atmospheric, 1.014 bar. This makes the back pressure, P_2 , the measured pressure + atmospheric, as shown in equation 3.30. A compressibility correction is then applied for ΔP , 3.29.

$$1LPM = 1SLPM \frac{T_{gas}}{273.15} \frac{1bar}{P_{gas}} \quad 3.27$$

$$\frac{v}{m_s^{-1}} = \frac{1LPM}{\pi r^2} \frac{1}{60 \times 10^3} \quad 3.28$$

$$\Delta P = \frac{P_2^2 - P_1^2}{2P_2} \quad 3.29$$

$$P_2 = P_{gas} + 1.01352 \text{ bar} \quad 3.30$$

This data is then fitted to a 2nd order polynomial, and compared to the Darcy-Forscheimer equation for fluid flow;

$$\frac{dP}{dx} = \frac{\mu}{\kappa_D} v + \frac{\rho}{\kappa_F} v^2 \quad 3.31$$

Where:

dP = Pressure difference (Pa) across the thickness dx (m)

μ = Viscosity of air; $1.81 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$

κ_D = Darcy coefficient of permeability (m²)

v = Fluid velocity/ volumetric fluid flux (m s⁻¹)

ρ = Density of air; $1.29 \times 10^{-5} \text{ kg m}^{-3}$

κ_F = Forchheimer coefficient of permeability (m)

4 Porous ZrB₂ By Hot-Pressing

4.1 Introduction

Transpiration cooling of hypersonic vehicles requires porous ultra-high-temperature ceramics (UHTCs). Reaching temperatures of 2000 °C, these will allow an inert coolant fluid to flow through, cooling the leading-edge material from within and creating a protective film at the surface.

ZrB₂ with 40 vol% porosity has been previously demonstrated as an effective material for transpiration cooling in plasma tunnel testing[4], [5]. Larrimbe *et al.* showed that making this porous ZrB₂ by hot-pressing was stronger and more permeable than by pressureless sintering or hot-pressed with fugitive inclusions[10]. However, the flexural strength was 50 MPa with a room temperature thermal conductivity of 35 W m⁻¹ K⁻¹[10], low compared to expected values for dense ZrB₂ of 300 – 600 MPa and 130 W m⁻¹ K⁻¹[12].

This study follows the work by Larrimbe *et al.* by aiming to increase the strength and thermal conductivity of the porous ZrB₂ while maintaining permeability. A high permeability is evident of high open pore volumes and large pore sizes. However, a large pore size and high volume fraction of porosity is typically associated with a reduction in both strength and thermal conductivity in UHTCs[42]. This would present a trade-off in properties, but studies into other partially sintered ceramics have shown that strength can be improved without densification by promoting strong neck growth between powder particles[96].

The growth of necks between particles can be encouraged by promoting surface transport mechanisms, typically considered an issue to minimise during sintering of UHTCs[31]. The greatest influence on the surface transport in ZrB₂ sintering is the oxide contamination, which exists as a surface layer and provides fast surface diffusion and increased vapour-phase transport[58]. Many methods exist to suppress the role of oxides during sintering of ZrB₂ and promote densification, these include control of the atmosphere to remove volatile B₂O₃, fast heating rates to prevent time for coarsening, reduction of particle size, and reactive sintering aids to reduce residual ZrO₂[32], [69], [72], [76].

This chapter will therefore aim to promote surface transport mechanisms during the hot-pressing of ZrB₂. This is first attempted by altering the hot-pressing conditions, such as atmosphere and heating rate, using a commercially available ZrB₂ (Grade B, H.C. Starck) commonly used for ZrB₂ fabrication. Larger grades of ZrB₂ powder (Grade A, H.C. Starck) are then used to assess the effects of powder particle size, while oxygen content is also increased to promote surface transport.

4.2 Initial Characterisation

4.2.1 Powder Characterisation

Two grades of ZrB_2 powder were used to make hot-pressed samples, grade A and B (H.C. Starck). Grade B is commonly used in literature for its small particle size compared to the coarser grade A. The shape and size of these two powders can be seen by secondary electron scanning electron microscopy (SEM) in Figure 4.1. The powders are granular, both being angular with high sphericity, and there is a difference in size between the two grades.

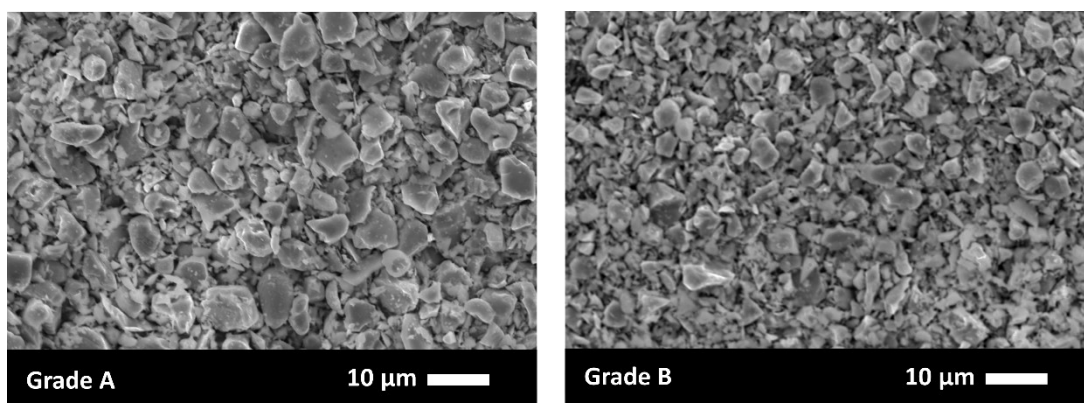


Figure 4.1 SEM images of the two grades of ZrB_2 powder. Powder particles are highlighted to demonstrate the low aspect ratio, granular nature of the powder, rather than needles or plates.

Figure 4.2 shows the result of particle size analysis (Mastersizer, Malvern Panalytical, UK) by dynamic light scattering (DLS) of the two grades of powder. As discussed in the methods, DLS assumes a spherical particle shape which is a reasonable match for the granular powder, rather than needles or plates. The size distribution for both powders is bimodal. There is a peak around $0.1\ \mu\text{m}$ and a peak for the larger particle sizes: $3.3\ \mu\text{m}$ for grade B, and $5.8\ \mu\text{m}$ for grade A. $D(0.5)$ for the grade A powder is $4.12\ \mu\text{m}$ and $2.61\ \mu\text{m}$ for grade B. A summary of powder size distribution statistics along with oxygen content, measured by combustion analysis (EMGA-830, Horiba, Japan), is given in Table 4.1.

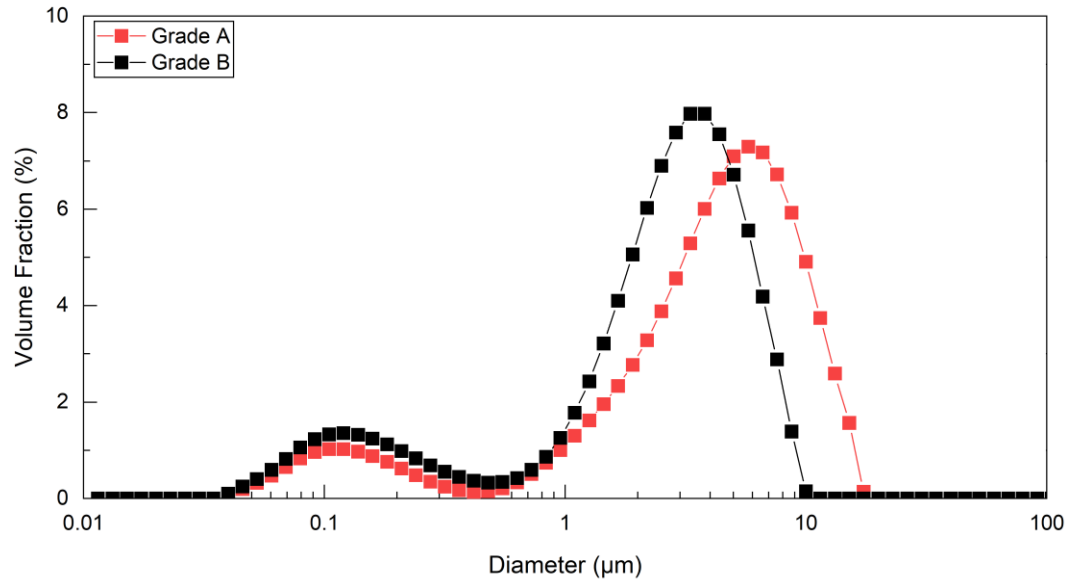


Figure 4.2 Particle size distribution for the two grades of ZrB_2 powders. Compared to grade B, grade A contains a greater fraction of powders $> 5 \mu\text{m}$, with measurable particle up to $20 \mu\text{m}$ compared to $10 \mu\text{m}$ in grade B. Both grades have a similar content of fine submicron powder.

The oxygen content of the finer grade B powders is greater than the grade A. The majority of oxide contamination will be a layer of ZrO_2 and B_2O_3 on the surface of the powder, rather than mixed in as secondary particles. The larger surface area of the finer powder therefore leads to a greater quantity of oxide[69].

Table 4.1 Powder characterisation of ZrB_2 powder types.

Powder	$D(0.1)$ (μm)	$D(0.5)$ (μm)	$D(0.9)$ (μm)	Mean Particle Size (μm)	Oxygen Content (wt%O)
A	0.338	4.12	9.43	4.66	0.50 ± 0.02
B	0.164	2.61	5.54	2.82	1.04 ± 0.10

4.2.2 Initial Permeability Assessment

The initial production of partially sintered ZrB_2 by hot-pressing for this study was done with as-received grade B ZrB_2 powder, to establish a baseline for further development. Hot-pressing aimed to replicate porous ZrB_2 made by Larrimbe[10] which were hot-pressed at 1700°C and 12 MPa to produce ZrB_2 with 40 – 42 vol% porosity with a Darcy permeability of $3 - 4 \times 10^{-14} \text{ m}^2$, as measured and reported by Ifti *et al.*[6]. The hot-pressing method is outlined in ‘Chapter 3.2: ZrB_2 Hot-Pressing’, with specific hot-pressing schedule details shown in Figure 4.3 for the $10^\circ\text{C}/\text{min}$ and $5^\circ\text{C}/\text{min}$ heating rates, showing the variation in pressure hold time at 1700°C are shown in Figure 4.3a.

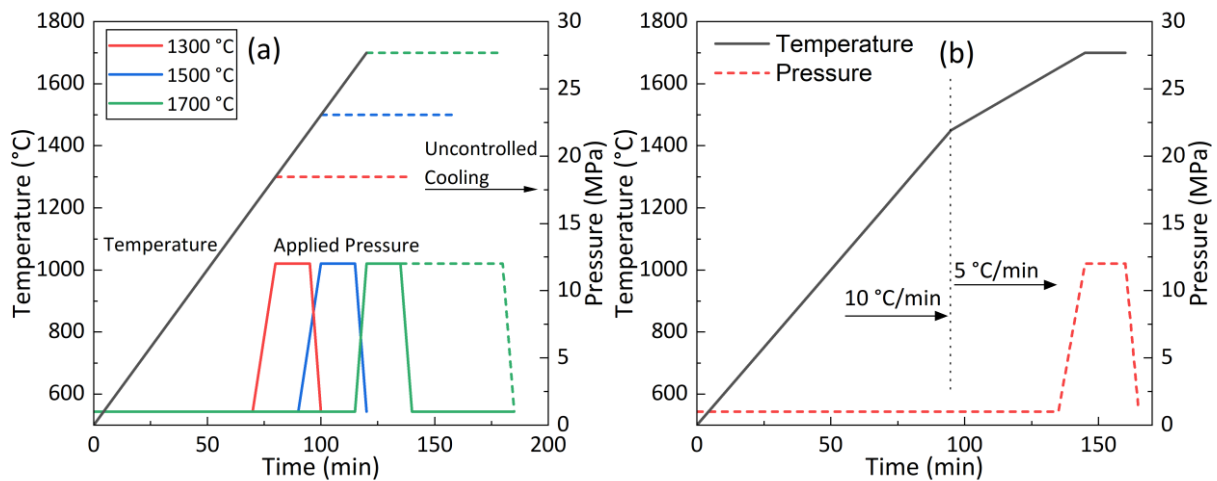


Figure 4.3 Heating and pressure schedules for hot-pressing conditions outlined in Table 4.2 for (a) 10 °C/min heating rate and (b) 5 °C/min heating rate.

The achieved density and permeability of hot-pressed ZrB_2 from these conditions are recorded in Table 4.2, also measured by Ifiti. The density of hot-pressed samples ranges from 3.05 g cm^{-3} while hot-pressing at 1300 °C to 4.21 at 1700 °C under vacuum, the equivalent of 31.6 – 50.5 vol% porosity. This results in a range of permeability from $0.28 - 1.05 \times 10^{-14} \text{ m}^2$ in the finer grade B powder, with grade A significantly higher at $2.59 \times 10^{-14} \text{ m}^2$. Such a high permeability is comparable to 42 % porous B-AR from Larrimbe *et al.* [10]. This increase in permeability will be due to an increase in pore size as a result of using larger powders.

Table 4.2 Hot-pressing details and permeability of initial ZrB_2 trials.

Powder Grade	Initial Press (MPa)	Time at 1700 °C (Minutes)	Time at 12 MPa (Minutes)	Atmosphere	Heating Rate (°C/min)	Density (g cm^{-3})	Porosity (vol%)	Permeability[6] (10^{-14} m^2)
B	4	60	60	Argon	10	4.15 ± 0.10	32.5 ± 0.8	0.340 ± 0.027
B	4	60	60	Vacuum	10	4.21 ± 0.11	31.6 ± 0.8	0.280 ± 0.024
B	4	60	15	Argon	10	4.15 ± 0.10	32.6 ± 0.8	0.392 ± 0.027
B	4	60 1300 °C	15	Argon	10	3.05 ± 0.08	50.5 ± 1.3	n/a
B	4	60 1500 °C	15	Argon	10	3.72 ± 0.09	39.5 ± 1.0	1.045 ± 0.037
B	4	15	15	Argon	5	4.02 ± 0.10	34.6 ± 0.9	0.75 ± 0.026
B	1	15	15	Argon	5	3.69 ± 0.09	40.0 ± 1.0	0.793 ± 0.027
A	4	15	15	Argon	5	4.15 ± 0.10	32.6 ± 0.8	2.59 ± 0.044

Changes to the hot-pressing programme were responsible for changes to porosity and permeability. The use of vacuum during hot-pressing resulted in an increase in density as boron vapour will facilitate coarsening between 1200 °C – 1400 °C by vapour phase mass transport[58]. By evacuating the chamber during hot-pressing the partial pressure of boron will be reduced, reducing the effect of

microstructural coarsening which will benefit further densification when pressure is applied at 1700 °C.

Reducing the pressure from 12 to 1 MPa during the hold at 1700 °C had little effect, changing from only 32.5 to 32.6 vol% porosity, meaning that the majority of densification occurs during the application of pressure and is relatively slow while holding. The permeability increased slightly from 0.34 to $0.39 \times 10^{-14} \text{ m}^2$, suggesting an increase in pore size from coarsening during the low pressure hold at 1700 °C. However, reducing the heating rate from 1450 °C has a more substantial effect. By slowing the heating rate, more time is spent between 1450 – 1700 °C, too low for the onset of rapid densification above 1750 °C[29], so allowing time for coarsening and pore enlargement.

The highest permeability for grade B ZrB₂ was achieved by hot-pressing at 1500 °C, a temperature too low for any considerable densification (hence 39.5% porosity). ZrB₂ with similar density (40 %) to this 1500 °C sample was hot-pressed at 1700 °C by reducing the pre-hot-pressing die compression from 4 MPa with a hydraulic press prior to hot-pressing to just the 1MPa hot-press pinch load, therefore starting with a lower green density. Despite a large increase in porosity in both these 1500 °C and 1700 °C samples, the permeability is still well below the $2\text{-}3 \times 10^{-14} \text{ m}^2$ target, being both in the range $0.8\text{-}1 \times 10^{-14} \text{ m}^2$. This result implies that the pore size is still the limiting factor and is unchanged as there was no other change to hot-pressing schedule was made to promote alternative mechanisms. The green density of hot-pressed compacts was a difficult variable to assess and control, as the hydraulic control of the hot-press would apply a variable load up to 30 kN when first engaging which would compress the die. As the change in green density has not had a dramatic effect on permeability, future samples were still pre-compressed to maintain consistency. The maximum porosity achieved by hot-pressing was 50.5 %, hot-pressed at 1300 °C. This material had little more strength than a green body, with negligible mechanical properties and was easily damaged during routine handling so permeability could not be measured.

Methods to encourage coarsening to increase the size and volume fraction of pores in permeability had expected results but failed to achieve the high permeability of samples by Larrimbe[10]. Such a dramatic increase in permeability with little increase in porosity between the samples of this study and the Larrimbe study suggest pore size is being increased by a phenomenon not captured in these experiments, as the same hot-pressing programmes were initially used. This increase is indicative of surface diffusion have also been shown to increase pore size in the early stage of sintering[113]. Such an effect shows the potential for microstructural manipulation of ZrB₂ to improve the permeability.

Two methods for improving the permeability of the ZrB₂ made for this study where therefore pursued: the use of larger powders, and the promotion of surface diffusion during sintering by manipulating

the oxygen content in the pre-sintered powder. These will be explored in the following sections, both with the aim of increasing pore size, allowing for higher density products with retained permeability.

4.3 Porosity and Microstructure

4.3.1 Effect of Powder Size, Oxygen Content, and Hot-Pressing Temperature

Porous ZrB_2 was hot-pressed from both as-received (AR) and oxidised grade A and B powders. Powders were oxidised by heating in a crucible in stagnant air at 500 – 540 °C as detailed in ‘Chapter 3.1.3: Oxidation of Powders’. Figure 4.4 shows the typical microstructure of a partially sintered ZrB_2 sample, hot-pressed at 1700 °C/ 12 MPa from AR powders. The sample made with grade A powder has features at a larger scale than that of the grade B, but otherwise is similar in structure, with an open network of pores comprised on the space between powder particles that have joined at contact points. This morphology of microstructure is similar to porous ZrB_2 fabricated in literature[114] and other partially sintered UHTCs[58]. The larger feature size of the grade A is an expected result of the larger powder size.

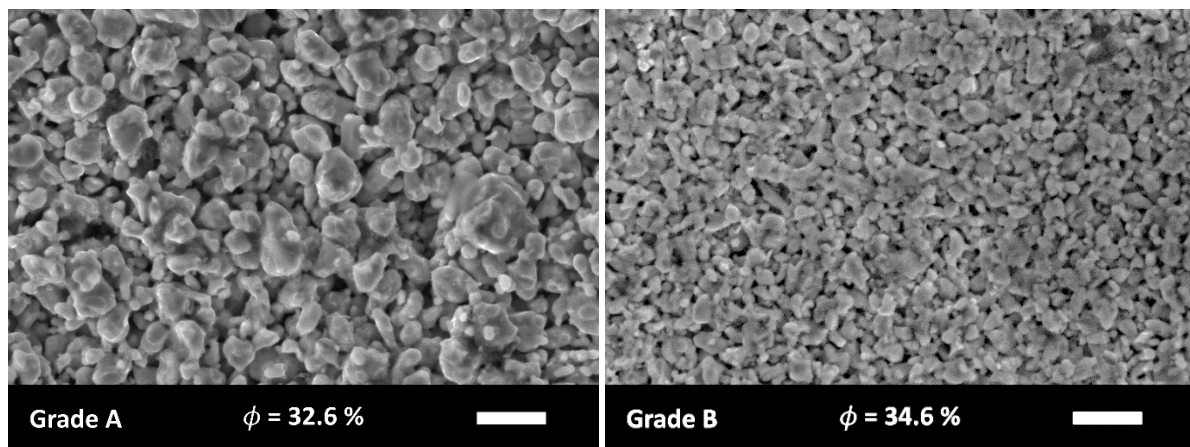


Figure 4.4 Microstructure for porous ZrB_2 hot-pressed at 1700 °C/ 12 MPa from grade A and B powders. Scale bars are 10 μm .

Powders were also oxidised to a range of oxygen contents (1.6-2.8 wt. %), as shown in Table 4.3 with the achieved density hot-pressed at 12 MPa at 1700 °C, as well as 1500 °C and 1900 °C for some powders. The small initial batch size of oxidised powders did not allow for a complete range of hot-pressing temperatures to be trialled. The achieved density, as measured by Archimedes method, is plotted against hot-pressing temperature in Figure 4.5, for both AR powders and the oxidised powders where samples were hot-pressed across multiple temperatures.

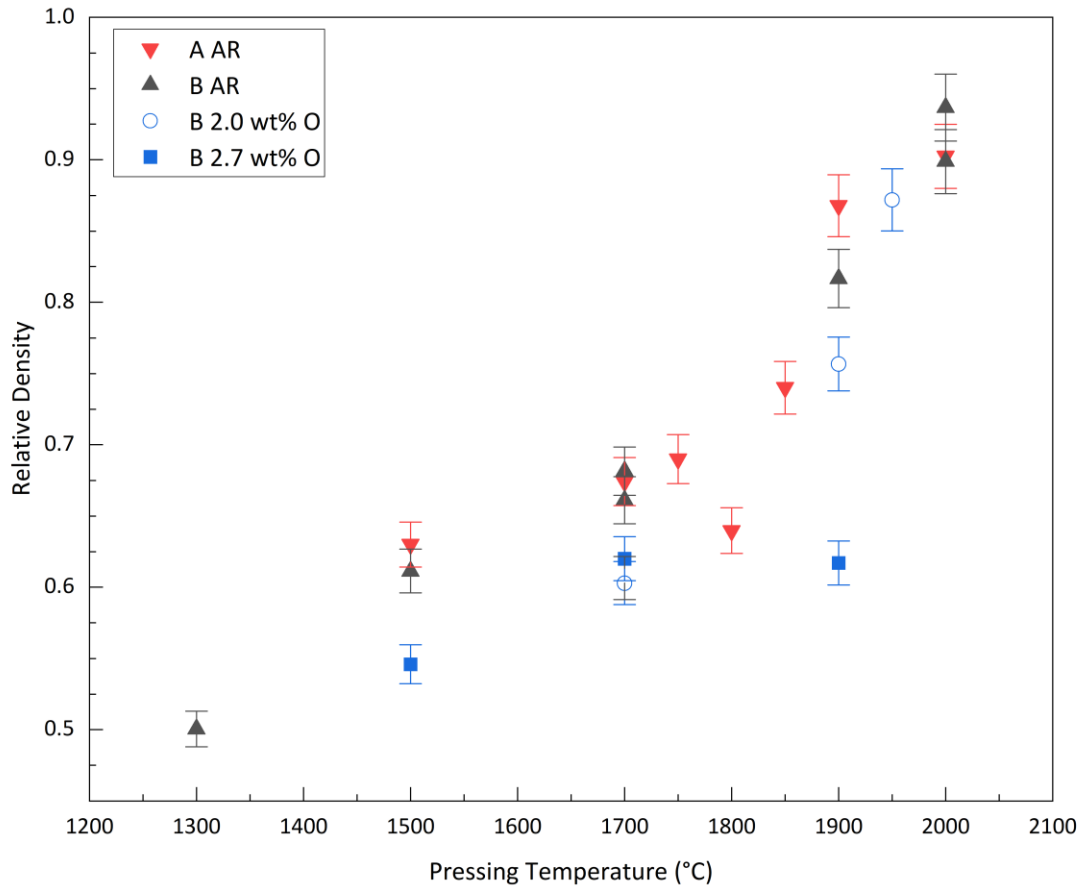


Figure 4.5 Relative density of hot pressed ZrB_2 against hot-pressing temperature for as-received (AR) powders of grade A and B, and oxidised grade B powders.

Figure 4.5 shows that the density of hot-pressed ZrB_2 increases steadily from 1300 °C then rapidly above 1800 °C for both AR powders and the grade B powder oxidised to 2.0 wt%O. This aligns with expected densification behaviour as studies have previously shown densification onset temperatures of 1750 °C for sintering of ZrB_2 [29]. The pressure of 12 MPa used for hot-pressing is lower than what is typically used to hot-press dense UHTCs so there is less increase in the density of samples hot-pressed below 1800 °C.

The achieved density of both the larger grade A-AR powder and the higher oxygen content grade B-AR powder are similar across the entire range of hot-pressing temperatures studied. As densification is motivated by a reduction in surface area and driven by local curvature, the larger powder size of the grade A should result in less densification[69]. However, the surface area can also be reduced by surface diffusion, aided by oxide contamination which is present in greater quantity in the grade B powders, allowing for coarsening to reduce the surface area and remove driving force for further densification. Where the oxygen content is increased to 2.7 wt%O the density of ZrB_2 is not increased when hot-pressing at 1900 °C compared to 1700 °C, despite the density increasing significantly for AR

powders and the lesser oxidised 2.0 wt%O powder. The relative density for the full range of oxidised grade B ZrB₂ hot-pressed at 1700 °C, 12 MPa are shown in Table 4.3.

Table 4.3 shows a general increase in porosity with oxygen content, e.g., for samples hot-pressed at 1700 °C from powders with ≥ 1.9 wt%O, the achieved porosity is between 37 – 40 vol%, with no further correlation with oxygen content in this range. The 1.6 wt%O sample has 29 vol% porosity, closer matching the study in ‘Chapter 4.2.2: Initial Permeability Assessment’, which consistently produced porosity of 31 – 35 vol%.

Table 4.3 Powder oxygen content from heating batches in air to 500 °C, hot-pressing temperatures and achieved density details, as measured by Archimedes method, for oxidised grade B ZrB₂ hot-pressed for 15 minutes at 12 MPa. The average pore diameter was measured by mercury intrusion porosimetry.

Oxygen Content (wt%O)	Hot-Pressing Temperature (°C)	Density (g/cm ³)	Relative Density	Porosity (vol%)	Average Pore Diameter (μm)
1.6	1700	4.37 ± 0.11	0.71 ± 0.018	28.9 ± 0.72	0.97
1.9	1700	3.85 ± 0.10	0.63 ± 0.016	37.4 ± 0.94	1.06
2.0	1700	3.71 ± 0.09	0.60 ± 0.015	39.7 ± 0.99	1.13
	1900	4.65 ± 0.12	0.76 ± 0.019	24.3 ± 0.61	0.74
2.2	1700	3.69 ± 0.09	0.60 ± 0.015	40.0 ± 1.00	1.41
2.7	1500	3.36 ± 0.08	0.55 ± 0.014	45.4 ± 1.14	0.78
	1700	3.81 ± 0.10	0.62 ± 0.016	38.0 ± 0.95	1.20
	1900	3.79 ± 0.09	0.62 ± 0.016	38.3 ± 0.96	1.97
2.8	1700	3.84 ± 0.10	0.62 ± 0.016	37.6 ± 0.94	1.21

Surface transport assisted by contaminant oxides is a common issue in densifying UHTCs and is a widely reported issue when attempting to sinter to full density[58], [69], [115]. The increased porosity with increased oxygen content shows that even at 1700 °C the additional coarsening from fast surface transport facilitated by surface oxides prevents densification. This is a positive result for transpiration cooling as the resulting material has up to 30 % greater pore volume available for fluid flow.

The present method for estimated porosity by measuring density by Archimedes and dividing by a nominal density of 6.15 g cm⁻³ is effective, but also measures closed porosity that will not contribute to fluid flow. Open porosity can be measured by mercury intrusion porosimetry (MIP) and is used for comparison to pore size in Figure 4.6a. The general trends of the data in Figure 4.6a show that for AR and < 2 wt%O powders the pore size reduces with reducing porosity, with larger pores found in the oxidised and grade A powder. The > 2 wt%O powders show no clear correlation, and due to the range of temperatures used during hot-pressing a clearer picture of what is happening is required from Figure 4.6b where pore size is plotted against oxygen content for the different grades of powder hot-pressed at 1500, 1700, and 1900 °C. In part (b) a more monotonic relationship is found, suggesting oxygen content was the dominant factor, compared to (c) which shows little change to porosity in

samples hot-pressed at 1500 °C and 1700 °C, with higher porosity achieved only with the highest oxygen content at 1900 °C.

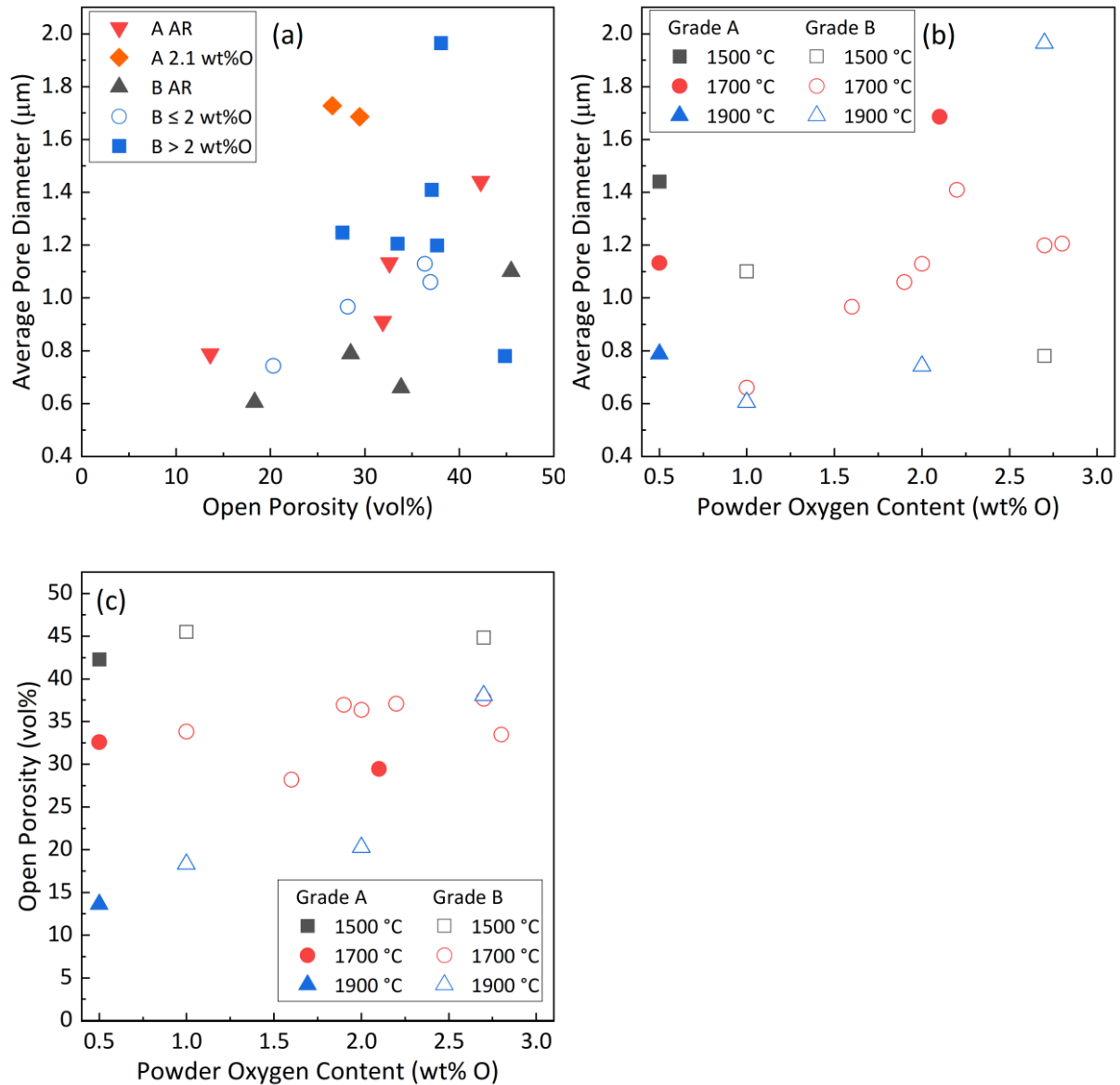


Figure 4.6 Average pore diameter as measured by mercury intrusion porosimetry (MIP) for the as-received (AR) and oxidised grade A and B powders. (a) Plotted against open porosity measured by MIP and (b) against powder oxygen content achieved by heating in air to 500 – 540 °C. (c) open porosity plotted against powder oxygen content, showing no strong trend.

As a ceramic densifies the pores reduce in size, but as coarsening progresses pores enlarge[88], [116]. These competing mechanisms result in the breakdown of correlation between density and pore size for samples hot-pressed from oxidised powders in Figure 4.6a, which are made with a across a range of temperatures and powder oxygen content. Figure 4.6b then groups samples hot-pressed at 1500, 1700, and 1900 °C, showing a consistent pattern of increasing pores size with increasing oxygen content in both grades of powder when hot-pressing at 1700 and 1900 °C as coarsening is further promoted by fast diffusion pathways at the surface of the powders.

Figure 4.7 shows the fracture surface of three of these oxidised powder samples hot-pressed at 1700 °C. Despite MIP measuring a larger pore size of 1.41 μm in the 2.2 wt%O sample compared to 1.21 μm in the 2.8 wt%O, the 2.8 wt%O has larger grains and a more angular morphology indicating a lower surface curvature from increased coarsening even though the measured pore size is reduced.

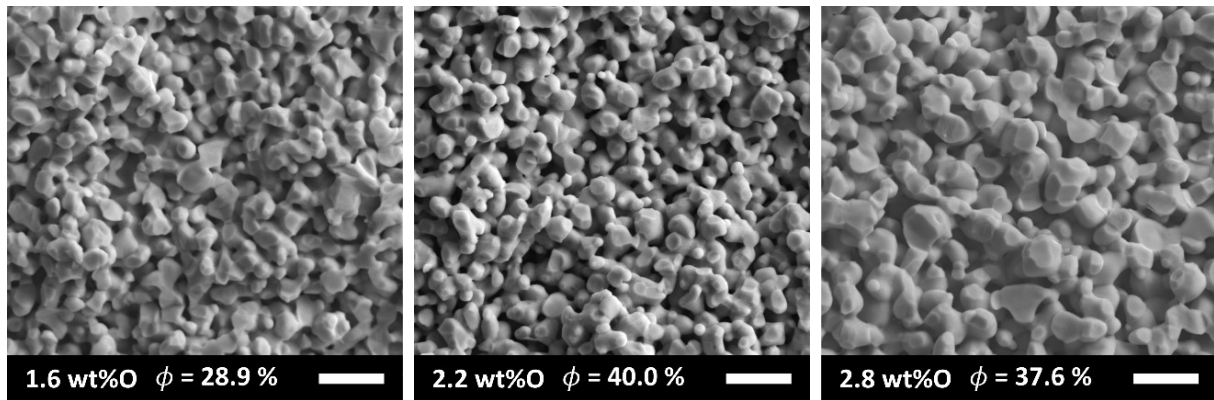


Figure 4.7 Fracture surface of varying oxygen content grade B powder hot-pressed at 1700 °C, 12 MPa. ϕ = Archimedes porosity, scale bar is 10 μm .

The change in microstructure with hot-pressing temperature for the 2.7 wt%O and 2.0 wt%O grade B ZrB_2 are shown in Figure 4.8 and Figure 4.9 respectively. The 2.7 wt% sample hot-pressed at 1500 °C has the appearance of the original powders, with no visible necks between particles. At 1700 °C the porosity has reduced but pore size increased, necks are visible and the grains have enlarged through coarsening by surface diffusion. Hot-pressing at 1900 °C then shows a similar change in microstructure as when increasing the oxygen content in Figure 4.7; grains are larger and more angular in shape. Coupled with the lack of densification despite the higher temperature of pressing, this shows that increasing the temperature has only resulted in faster coarsening by surface diffusion, also resulting in a larger pore size.

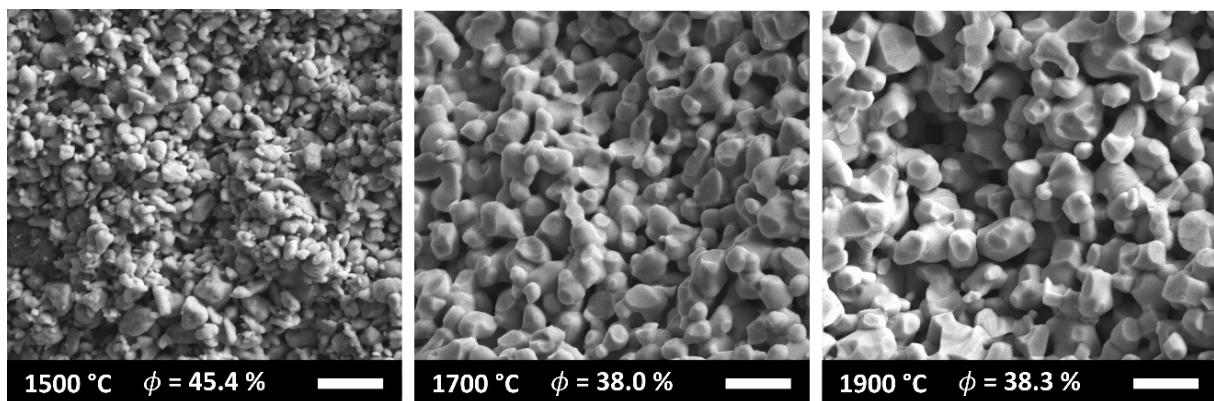


Figure 4.8 Fracture surface of 2.7 wt%O grade B powder hot-pressed at varying temperatures and 12 MPa. ϕ = Archimedes porosity, scale bar is 10 μm .

Despite a powder oxygen content double the original 1.0 wt%O in grade B, the 2.0 wt%O in Figure 4.9 shows densification and pore size reduction when increasing the hot-pressing temperature above 1700 °C. This was first noticed by the increase in density in Figure 4.5 while the reduction in pore size is shown in Figure 4.6 and Table 4.3.

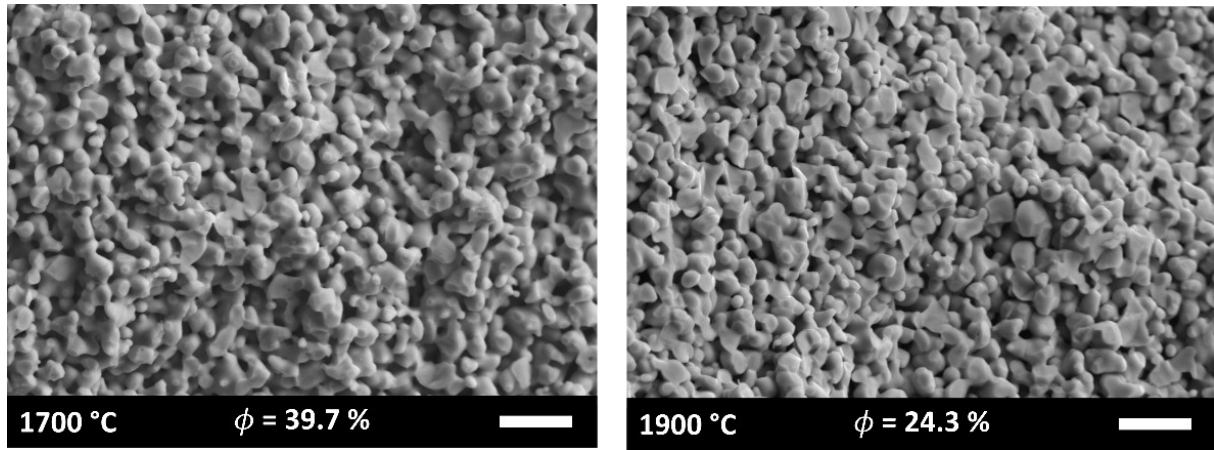


Figure 4.9 Fracture surface of 2.0 wt%O grade B powder hot-pressed at varying temperatures and 12 MPa. ϕ = Archimedes porosity, scale bar is 10 μm .

These changes in microstructure with increasing hot-pressing temperature can be shown clearly across all powders by plotting pore size against hot-pressing temperature, as in Figure 4.10a. A-AR, B-AR, and B-2.0 wt%O all show reducing pore size with increased hot-pressing temperature as the ceramic densifies by bulk diffusion pathways. Although the 2.7 wt%O shows the opposite trend in pore size, the sintering mechanisms are still all driven by surface energy reduction. Surface diffusion to reduce curvature is faster for these high oxygen content powders than bulk diffusion to reduce pore volume. Figure 4.10b shows the specific pore surface area of the AR and oxidised powders as hot-pressing temperature is increased, showing a consistent trend across all powders for reducing the surface area with increasing hot-pressing temperature.

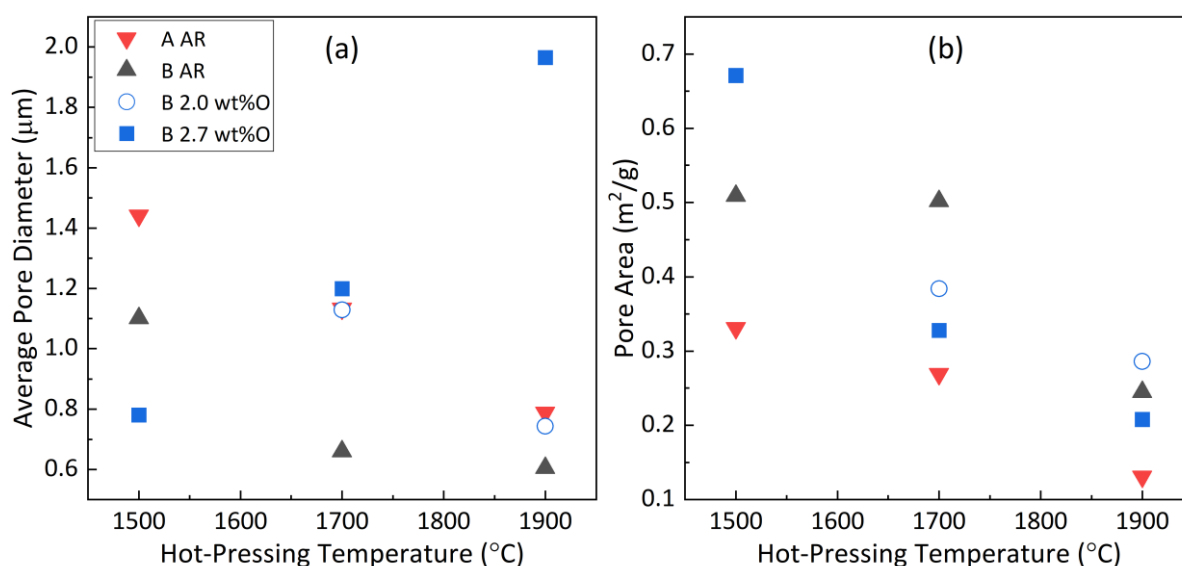


Figure 4.10 Average pore diameter (a) and specific pore area (b) measured by mercury intrusion porosimetry for as-received (AR) and oxidised grade A and B ZrB₂ powders hot-pressed at 12 MPa, plotted against hot-pressing temperatures.

Due to sample availability the B-AR sample hot-pressed at 1500 °C used for MIP analysis was held at 1500 °C/ 1 MPa for 10 hours, for a separate study on microstructural stability, rather than 15 minutes as is the case for the sample reported in Figure 4.5. Despite this, trends for porosity and pore size still align well, however the apparent lack of surface area reduction in Figure 4.10b when increasing from 1500 to 1700 °C could be explained by this hold time discrepancy.

4.3.2 Effect of Pressure

The oxygen content of powders was difficult to control when baking powders. Therefore, to produce consistent results, larger batches of powders were made and the effect of changing the pressure applied during hot-pressing studied. The aim was to create consistent materials for analysis of underlying mechanisms, but primarily to produce consistent samples for application testing with collaborators.

Table 4.4 shows the porosity and pore size for samples hot-pressed under the original 12 MPa pressure programme and corresponding samples hot-pressed under a constant pressure of 24 MPa.

The density increases for all samples when hot-pressed at the higher pressure of 24 MPa. The largest reduction in porosity is for the 2.2 wt%O grade B powder, due to the high porosity of the original 12 MPa sample. There is no clear trend for reducing pore size with reducing porosity with the B-AR and A-2.1 wt%O showing a fractional increase in pore size. Increasing pressure does show a reduction in pore area in all powders apart from A-AR which sees an increase in pore area from 12 to 24 MPa.

Table 4.4 Pore characterisation details as measured by mercury intrusion porosimetry for as-received (AR) and oxidised grade A and B powder. Samples were hot-pressed at 1700 °C with the pressure recorded.

Grade	Oxygen Content (wt%O)	Pressure (MPa)	Open Porosity (vol%)	Pore Size (μm)	Specific Pore Area (m^2g^{-1})
A	0.5 (AR)	12	32.6	1.13	0.269
		24	31.9	0.91	0.341
	2.1	12	31.4	1.69	0.166
		24	26.6	1.72	0.142
B	1.0 (AR)	12	33.8	0.66	0.502
		24	28.5	0.79	0.336
	2.2	12	37.1	1.41	0.281
		24	27.6	1.24	0.213

This shows that despite the increased pressure, the temperature is too low to facilitate any large degree of densification, as changes are modest for the twofold increase in pressure. The lack of reduced surface area or change in density in the A-AR powders is indicative of the low oxygen content not providing fast surface diffusion pathways. The larger changes to pore size and pore area for the powders with greater oxygen content support this.

Figure 4.11 shows the polished cross-sections of samples hot-pressed under these changing pressure programmes. Both grade B-AR samples in (a) and (b) have a similar grain size but the 24 MPa in (b) has some spots of very high density. This inhomogeneous microstructure is likely the cause of the apparent increase in pore size with increased pressure; areas with small pores will be most prone to densification so by fully densifying these areas the density will increase but the average pore size will also increase as small pores are completely removed, so do not contribute to the average pore size.

The low-pressure B-AR in Figure 4.11(a) also shows fewer connecting necks between grains than the B-AR hot-pressed under 24 MPa, with the appearance of isolated circular grains instead of a connected network. The SEM images are a 2D slice of material, observing necks between particles requires the slice to align with these necks. Their lack of presence in the resulting SEM images implies these necks are narrower, and therefore less likely to coincide with the 2D plane of the slice.

This shows that densification caused by the increase in pressure is focused at necks between particles. The lack of connectivity in the 24 MPa grade A-AR sample in Figure 4.11(c) shows that surface diffusion is still required to form necks, as these are areas of high curvature, and the 0.5 wt%O present in grade A powders is not sufficient to allow neck growth even by increased pressure.

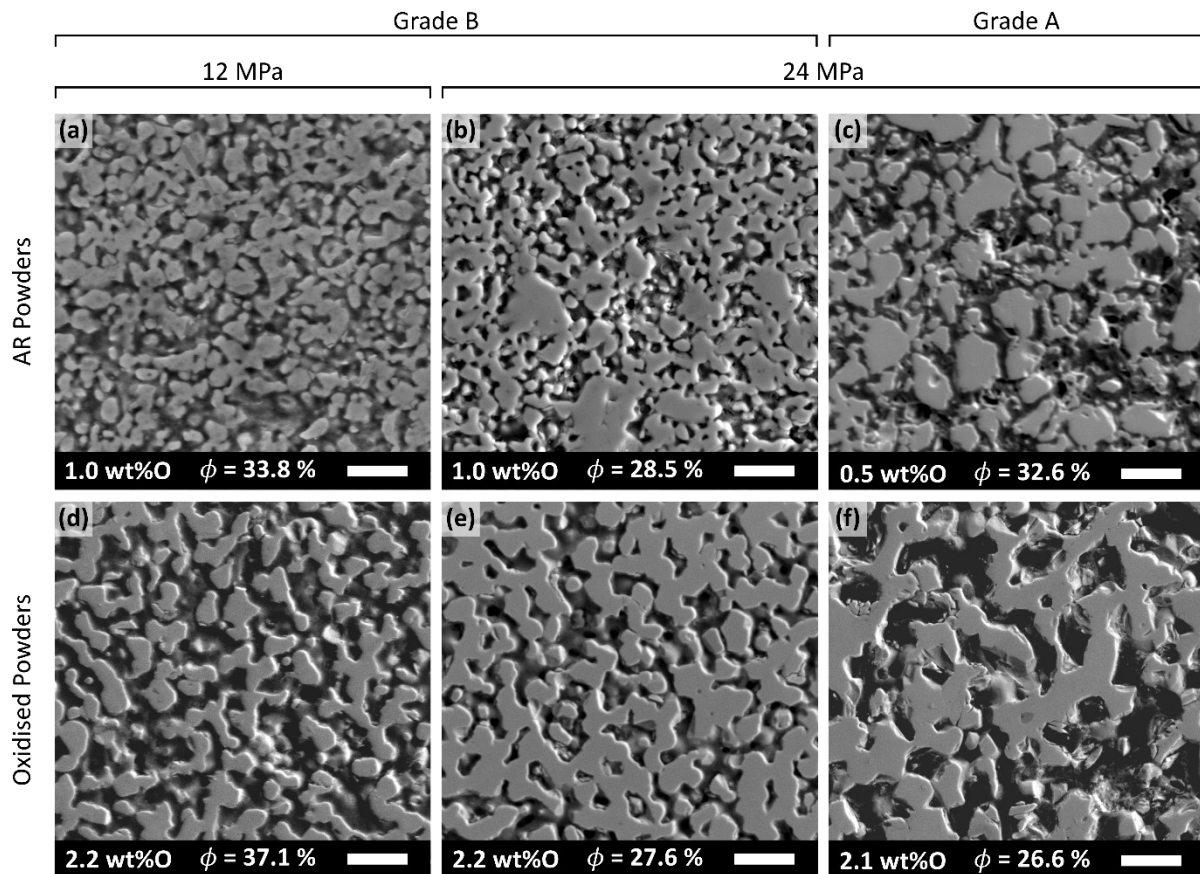


Figure 4.11 Polished microstructure of porous ZrB_2 hot-pressed at 1700 °C. Constant 24 MPa pressure applied throughout heating during is compared to 1 MPa pinch load followed by 12 MPa applied during the final 10 minutes of heating to 1700 °C. (a) As-received (AR) grade B powder hot-pressed with 12 MPa, (b) B-AR powders hot-pressed with 24 MPa (c) A-AR powder hot-pressed with 24 MPa, (d) grade B powder oxidised to 2.2 wt%O hot-pressed with 12 MPa, (e) grade B powder oxidised to 2.2 wt%O hot-pressed with 24 MPa, (f) grade A powder oxidised to 2.1 wt%O hot-pressed with 24 MPa. ϕ = Archimedes porosity, scale bar is 10 μm .

Comparing the AR powder samples in Figure 4.11(a) – (c) with the oxidised powder samples in (d) – (f), the increased surface diffusion from oxide contamination has enlarged pores, grains, and improved connectivity of the microstructure through the formation of necks. The increase in pressure has increased density in the grade B-2.2 wt%O, as is reported in Table 4.4, but to a comparable density with the AR powder.

4.3.3 Tortuosity

Finally, tortuosity of the porous network can be calculated from MIP data, as detailed by Washburn's equation in 'Chapter 3.4.2: Mercury Intrusion Porosimetry'. This gives an evaluation of the degree to which the pores twist and turn. Pores that take a short, direct path through the material have low tortuosity, resulting in high permeability as fluid can flow with little resistance. A complex porous network that does not allow for direct fluid flow through the thickness of a sample is defined by high tortuosity, with high resistance to fluid flow and low permeability.

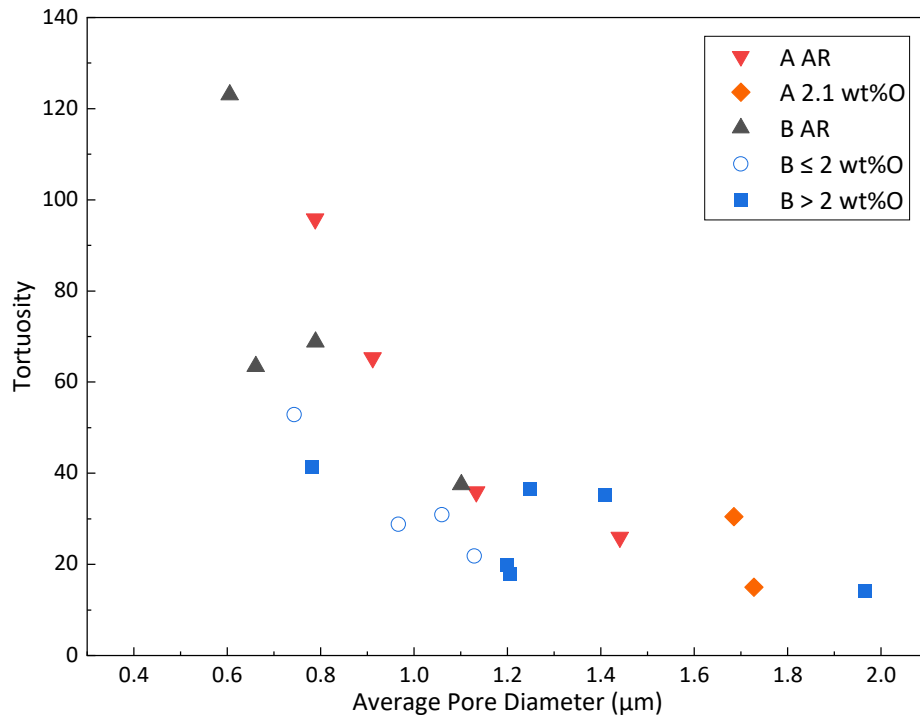


Figure 4.12 Tortuosity and average pore diameter of the porous network for ZrB_2 samples made from as-received (AR) and oxidised grade A and B powders measured by mercury intrusion porosimetry.

Figure 4.12 groups all hot-pressed samples regardless of hot-pressing temperature and pressure into the groups of AR, low oxygen content and high oxygen content, plotting the relationship between pore size and tortuosity. It is apparent that as pore size reduces, the tortuosity also increases. To examine this trend, Figure 4.13 then plots the tortuosity against the inverse of pore size, showing a linear relationship.

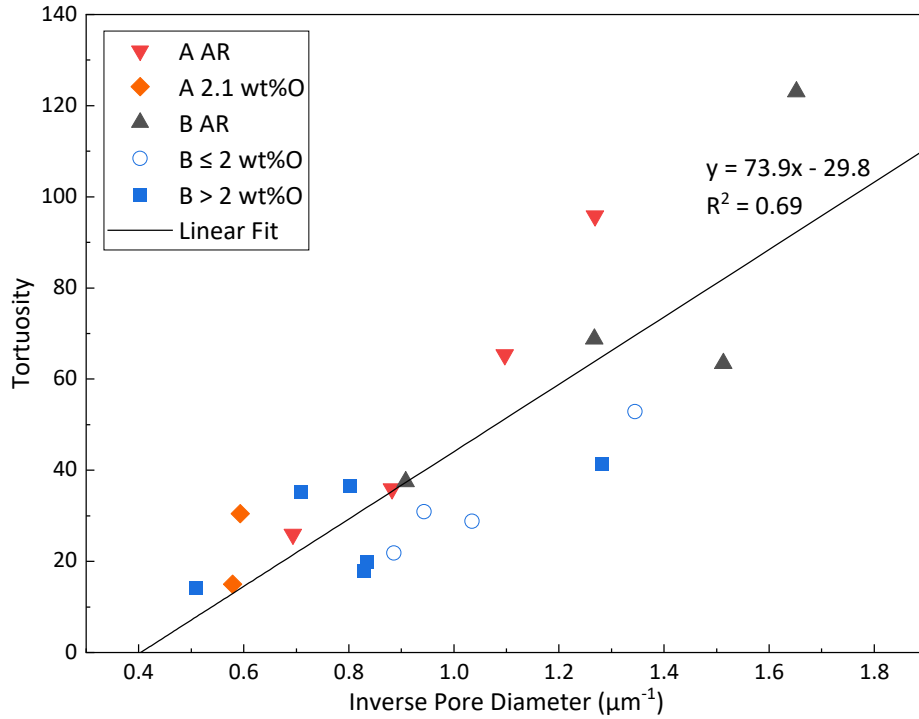


Figure 4.13 Tortuosity plotted against inverse of the average pore diameter of the porous network for ZrB_2 samples made from as-received (AR) and oxidised grade A and B powders measured by mercury intrusion porosimetry.

Both high tortuosity and low pore size will negatively affect permeability, this inverse relationship between pore size and tortuosity explains the orders of magnitude drop in permeability when increasing density in the B-AR samples from the initial permeability assessment in ‘Chapter 4.2.2: Initial Permeability Assessment’. Samples with higher density were also measured by Ifti *et al.*[6] but the permeability was too low to measure within the range of the equipment, due to the smaller pore size and increased tortuosity that come with increasing density in the AR powders.

4.4 Final Permeability Assessment

A key property for UHTCs for transpiration cooling is permeability, allowing for a coolant gas to flow through the porous layer. This was first assessed for B-AR samples in ‘Chapter 4.2.2: Initial Permeability Assessment’, and the changes to pore structure from oxidation of powder prior to hot-pressing will have impacted permeability.

Figure 4.14 plots the permeability of samples tested by Ifti *et al.*[6] from both present work, Table 4.2, and the Larrimbe[10] study alongside oxidised and increased hot-pressing pressure samples measured as detailed in ‘Chapter 3.4.6: Permeability’. All samples from the present work were hot-pressed at 1700 °C and variation in density arises from change in applied pressure during hot-pressing, as detailed in ‘Chapter 3.2: ZrB_2 Hot-Pressing’.

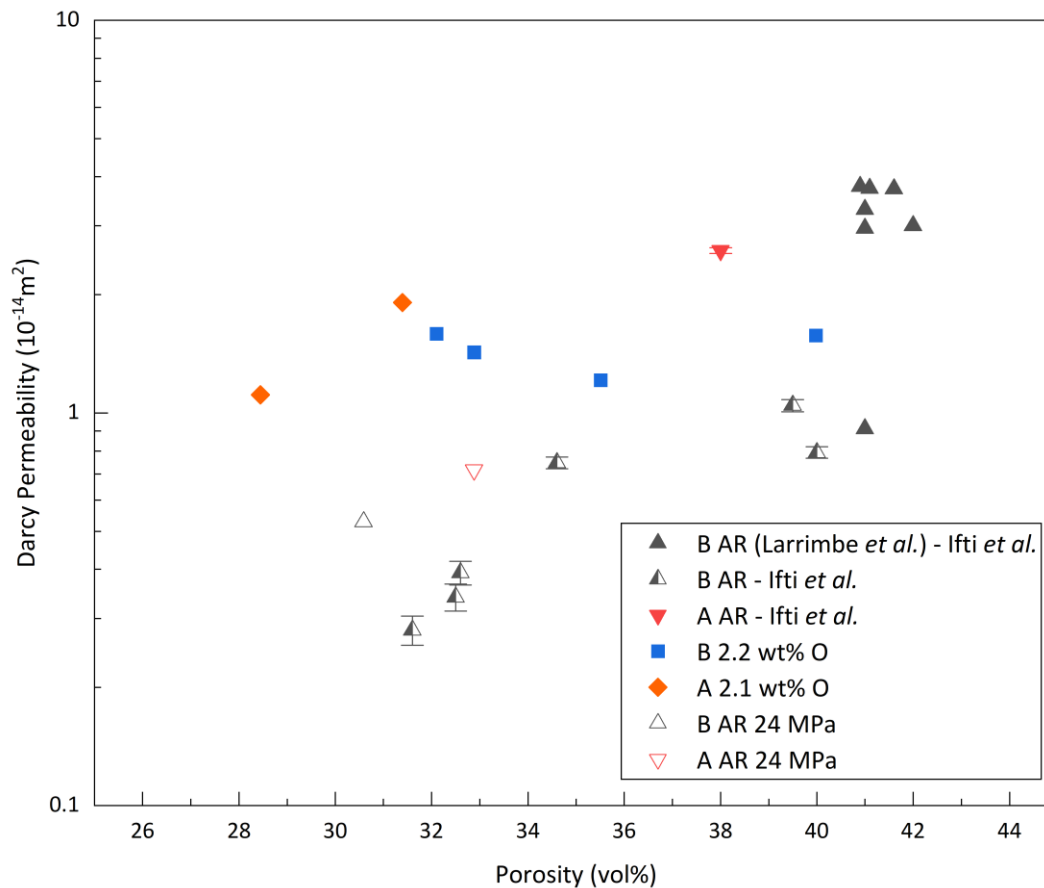


Figure 4.14 Permeability of hot-pressed ZrB_2 measured according to 'Chapter 3.4.6: Permeability' and by Ifti et al.[6] compared to samples made by Larimbe et al.[10].

The oxidised grade B material (blue squares) shows little change to permeability, despite large changes in porosity. This runs in contrast to the B-AR samples (black & white triangles) that reduce in permeability with reduced porosity. While the permeability of the AR and oxidised is similar at 40 vol% porosity, this leads to an order of magnitude increase in permeability for the grade B material at 32 vol% porosity. Even though pore volume is reduced, so there is less pore volume available for fluid flow, the measured pore size does not reduce significantly when the pressure is increased (Table 4.4). This result shows the pore size is the dominant factor in permeability rather than the combined pore volume/ porosity.

The grade B-AR sample made with 24 MPa (open black triangle) had a permeability of greater than expected for the achieved porosity. This links back to the discussion of 'Chapter 4.3.2: Effect of Pressure' where densification was heterogenous, being concentrated on points of small pore sizes which would not have contributed significantly to the overall permeability. As such, it is possible for the material to maintain permeability while increasing in density.

The higher density grade A-AR sample made with a higher pressure (open red triangle) shows a reduced porosity compared to the original A-AR sample of 38 vol% porosity (closed red triangle) tested by Ifti *et al.* [6]. With very little oxygen content to promote coarsening, it is assumed that the conditions that lead to a lower density also resulted in larger pores compared to the sample hot-pressed at 24 MPa, however, pore size measurements were not taken from this specific 12 MPa sample. The oxidised grade A samples are both higher in density and permeability compared to this 24 MPa A-AR material, showing a result of the increased pore size previously discussed.

4.5 Microstructural Stability

The desired application of transpiration cooling of the leading edges of hypersonic vehicles requires the permeability assessed in the previous sections to be maintained after repeated heating to 2000 °C. The previous sections have shown that hot-pressing at temperature above 1700 °C can lead to rapid densification, and the onset of pressureless densification in ZrB₂ is typically cited to be 1750 °C under pressureless conditions[29]. Any increase in density for the porous ZrB₂ will be detrimental to the pore size and permeability. This section aims to assess whether densification occurs in the partially hot-pressed materials by running dilatometry on samples up to 2000 °C.

Figure 4.15 shows dilatometry results for as-received (AR) grade B ZrB₂ hot pressed at 1500 °C and 1700 °C under a 12 MPa load. Samples were held for extended durations at the sintering temperature at a reduced stress of 1 MPa immediately following the 12 MPa dwell to allow time for coarsening without densification.

Figure 4.15 shows the thermal expansion matches previous measurements by for dense ZrB₂ by Zimmermann *et al.* up to 1700 °C [24]. This is expected as porosity does not contribute to the thermal expansion of a material[80], but above 1700 °C there is rapid shrinkage in each of the samples measured as densification occurs. The densification onset temperature for each sample is recorded in Table 4.5.

The 1500 °C sample held for 10 hours has a greater porosity than the 1-hour sample despite having more time for densification. The lack of densification below 1700 °C previously observed suggests the difference in density is a result of inconsistent packing. This 10-hour 1500 °C sample is the sample used during the previously discussed MIP measurements, showing large pore size and low specific surface area compared to the sample hot-pressed at 1700 °C. Although there is no direct comparison with the 1-hour sample these values align with the goal of allowing coarsening to occur by holding at 1500 °C for 10-hours.

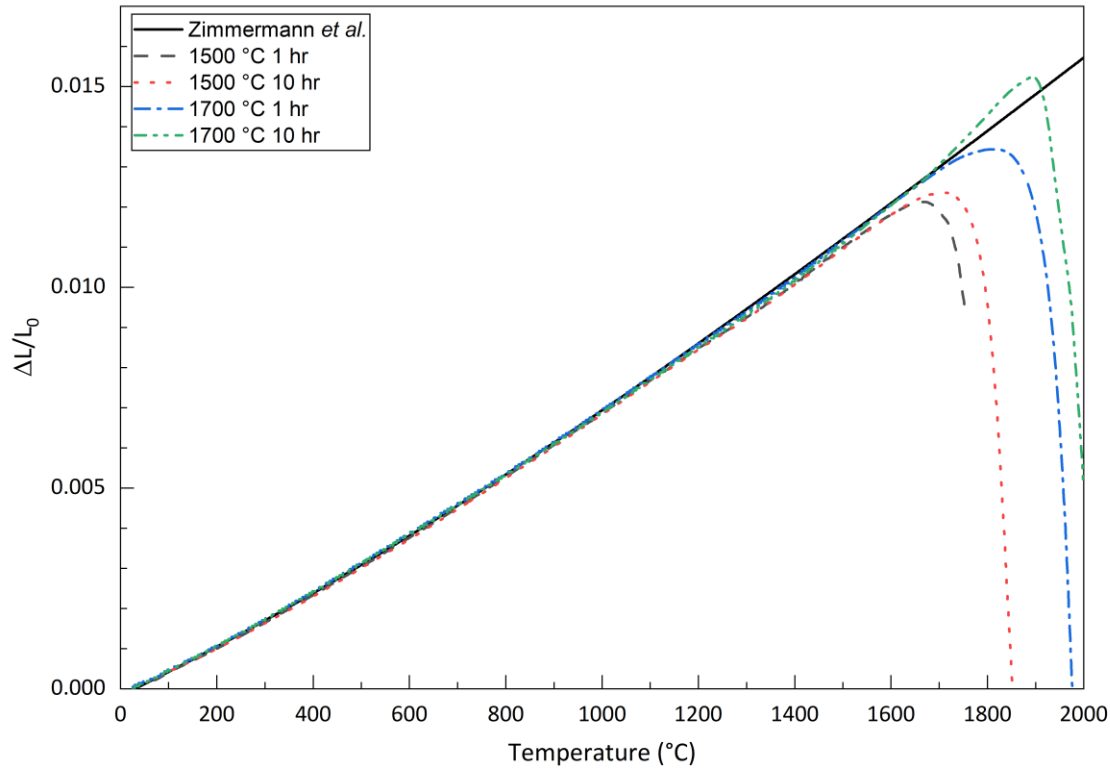


Figure 4.15 Dilatometry data for samples hot-pressed from as-received grade B ZrB_2 powders hot-pressed for 15 minutes at 12 MPa at the temperature specified with a hold time of 1 or 10 hours at 1 MPa. Thermal expansion data from for fully dense ZrB_2 Zimmermann *et al.*[24] is plotted, extrapolating their trend above 1400 °C.

The onset for densification in the 1500 °C/ 10-hour sample is 50 °C greater than for the 1-hour sample. The lowest observed onset temperature of 1760 °C aligns with Monteverde *et al.*[29] observation of densification onset in pressureless sintering from 1750 °C. This increase in densification onset, despite a higher porosity, is further evidence that coarsening has occurred at 1500 °C to reduce the internal surface area, and curvature, of the porous microstructure. However, the effect is minor in comparison to the increased density of the samples hot-pressed at 1700 °C, which have onset temperatures above 1900 °C.

Table 4.5 Summary of results from dilatometry with of ZrB_2 hot-pressed from as-received grade B powders hot-pressed for 15 minutes at 12 MPa at the temperature recorded.

Temperature (°C)	Time (hours)	Porosity (%)	Densification Onset (°C)
1500	1	39.5 ± 0.5	1760
1500	10	47.3 ± 0.9	1820
1700	1	32.5 ± 0.5	1940
1700	10	28.8 ± 1.3	1950

Holding for 10 hours at 1700 °C only reduced the porosity of the ZrB_2 by 3.7 vol%, agreeing with the previous results showing densification is slow at 1700 °C. Despite the increase in density and presumed coarsening that will occur from the extended hold at 1700 °C the densification onset temperature is only marginally increased from 1940 °C to 1950 °C.

These results show that rapid densification will occur in grade B ZrB_2 hot-pressed from AR powders at the intended application temperatures of 2000 °C. This is intolerable for transpiration cooling due to the permeability requirement and a need for geometric stability.

Oxidising powders has been shown to promote coarsening in ZrB_2 , which should also reduce the drive for further densification. The dilatometry results for the oxidised grade B ZrB_2 samples, hot-pressed at 12 MPa/ 15 minutes, are shown in Figure 4.16. None of these samples show an onset of rapid densification below 2000 °C. The 2.7 wt%O/ 1500 °C sample peaks in length at 1950 °C, showed more clearly in the zoomed view of Figure 4.18(b), shrinking rather than expanding while heating to 2000 °C, implying some densification does still occur below 2000 °C.

There is, however, greater deviation between the curves that showed solely thermal expansion in the as-received grade B sample. Changes to the porous microstructure and relative density of ZrB_2 will not change thermal expansion, as is shown for the range of densities in Figure 4.15. The reason for variability in dilatometry measurements is unclear, as deviation occurs at temperatures too low for either coarsening or densification of ZrB_2 . The reason is suspected to be experimental error arising from the presences of oxides in the porous ZrB_2 .

Oxides at the sample surface will create an additional interface between the sample and the carbon push rod which could cause movement to introduce error when these oxides melt or soften. The melting point of boria is 450 °C, while zirconia will soften from sintering temperatures of 1400 °C[117]. The binary phase diagram of ZrO_2 and B_2O_3 in Figure 4.17 also shows that the fraction of ZrO_2 in the oxide liquid will increase rapidly around 1400 °C. Reduction reactions using carbon as a sintering aid in the sintering of ZrB_2 are energetically favourable above 1044 °C when the partial pressure of CO is 25 Pa[71]. Residual oxides in the samples could react with the graphite of the pushrod or dilatometry chamber to give the effect of sample shrinkage. The coefficient of thermal expansion (CTE) of zirconia is also greater than that of ZrB_2 [118], but as the oxide is a surface layer rather than a second phase, the difference in CTE is not expected to restrict expansion. The key result, however, is that there is no onset of rapid densification for any grade B sample made from oxidised powder, even when hot-pressing at 1500 °C.

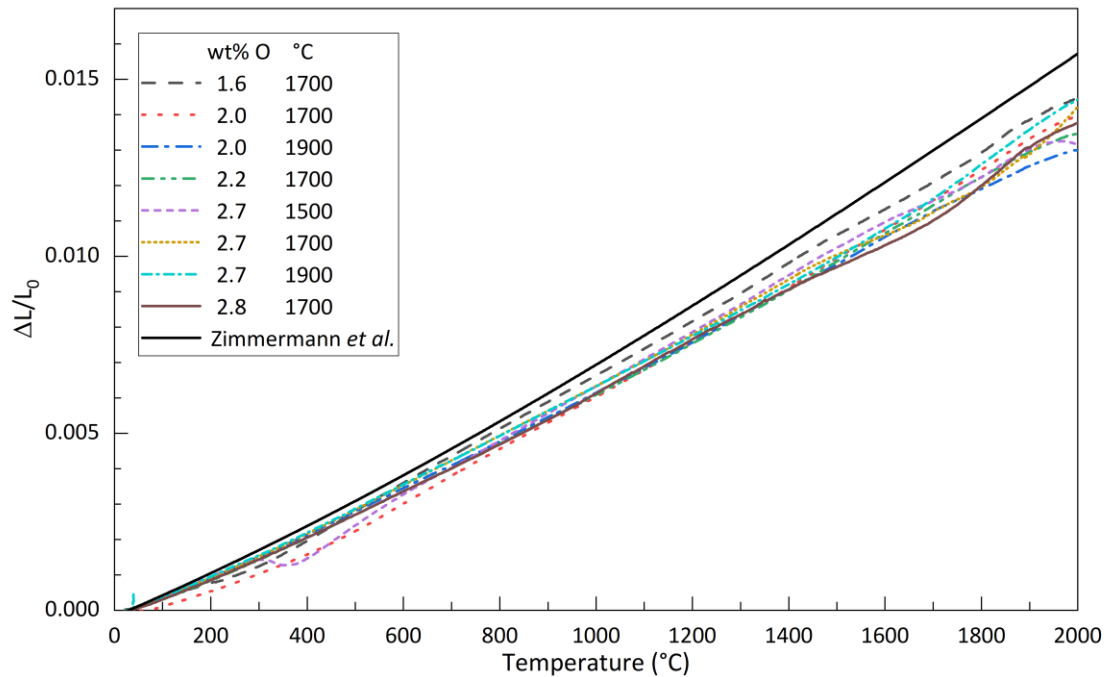


Figure 4.16 Dilatometry data for samples hot-pressed from oxidised grade B ZrB_2 alongside thermal expansion data from Zimmermann *et al.*[24]. Samples are hot-pressed at 12 MPa for 15 minutes at the temperature recorded.

The cause of deviation in thermal expansion is complicated by the fact that, at temperatures above the observed densification onsets from 1760 °C, further deviation from expected thermal expansion could be slow densification. This slow densification can be observed during the final hold at 2000 °C for samples shown in Figure 4.18 and Figure 4.19.

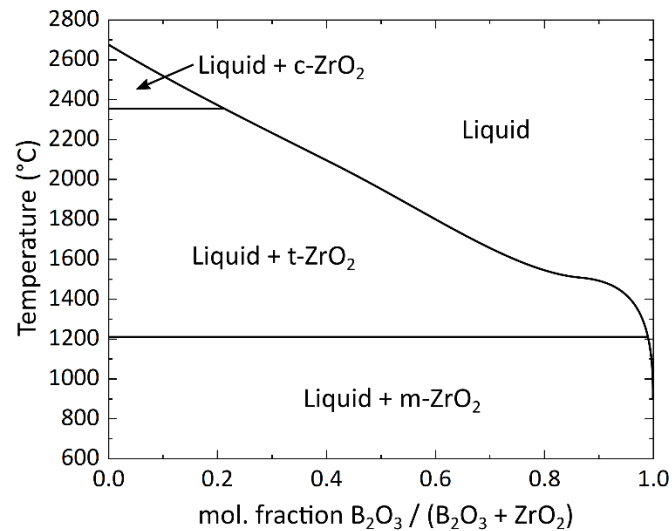


Figure 4.17 Calculated phase diagram of B_2O_3 and ZrO_2 adapted from Karlsdottir *et al.*[119].

Figure 4.18(a) and (b) show that the samples made from oxidised grade B ZrB_2 powder do not densify significantly before 2000 °C when hot pressed at 1500 °C, 1700 °C, or 1900 °C. This is a vast improvement on the behaviour of the B-AR material despite a consistently higher porosity.

The lack of a rapid reduction in length means an onset temperature for densification is not as clear as for the previous AR samples in Figure 4.15, but this shrinkage is clearly observable during the holds at 2000 °C. The rate of shrinkage for the 1500 °C sample at 2000 °C is greater than for the 2.7wt%O grade B samples hot-pressed at 1700 °C and 1900 °C. The faster densification will be due to the higher porosity and smaller pore size of the 1500 °C sample, meaning a higher internal surface area to drive densification. The 1900 °C has coarser a microstructure than the 1700 °C, as shown in Figure 4.8, but appears to densify faster at 2000 °C.

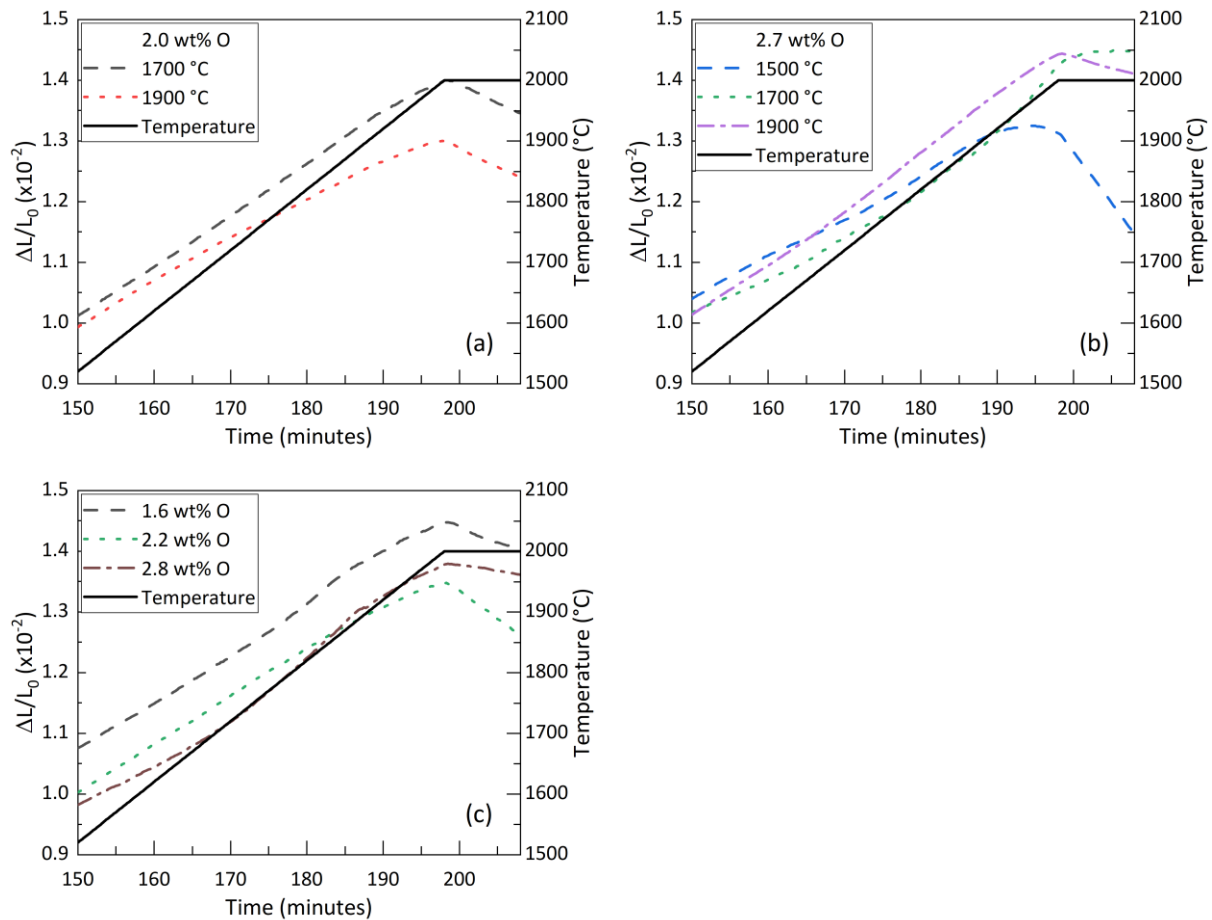


Figure 4.18 Dilatometry data for the oxidised grade B hot-pressed ZrB_2 samples (a) with 2.0 wt%O (b) 2.7 wt%O and (c) remaining samples hot-pressed at 1700 °C.

Figure 4.18(c) shows that the 2.8 wt%O sample densifies slowly at 2000 °C compared to the higher density 1.6 wt%O and larger pore size of 2.2 wt%O. This mirrors the observed coarser microstructure in Figure 4.7, the lower curvature of which will have less driving force for densification.

The driving force for densification depends on a number of complex factors including porosity, pore size, surface area and surface curvature. All these will be constantly changing by coarsening without further detectable densification during dilatometry while heating. As such, inferences into the changes to the microstructure based on densification alone are not accurate.

This coarsening has been shown to occur from 1500 °C with the AR powders and will be aided by faster diffusion pathways in the oxidised powders. Coarsening has also been shown previously to affect pore size in the oxidised powders. The precise microstructural changes occurring that will affect the final densification rates are not clear, but there is strong evidence to show that the coarser microstructures created by oxidised grade B powders resist further densification at 2000 °C despite a higher volume of porosity compared to as-received powder hot-pressed at 1700 °C.

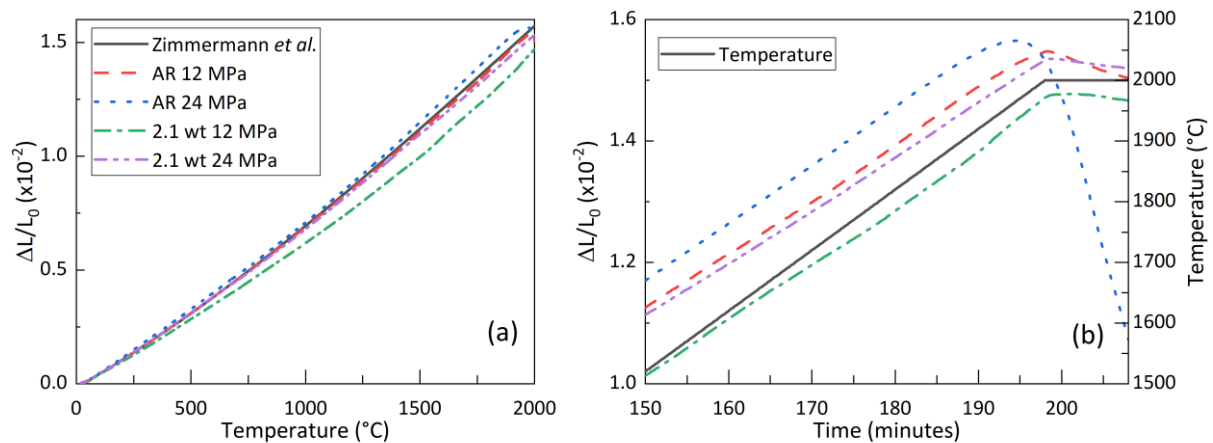


Figure 4.19 Dilatometry data for hot-pressed ZrB₂ made from as-received (AR) and oxidised grade A powders (a) against temperature and (b) against time in the final stage of heating to, and holding at, 2000 °C. Samples were hot-pressed for 15 minutes at 1700 °C with a pressure of 12 MPa or 24 MPa.

The dilatometry results for 1700 °C hot-pressed grade A ZrB₂ (coarser powders), AR and oxidised to 2.1 wt%O, are shown in Figure 4.19. The larger powder size and resulting microstructures have suppressed rapid densification below 2000 °C in all samples. However, the AR powder sample hot-pressed at 24 MPa densifies rapidly during the 2000 °C hold whereas the oxidised powder samples and the AR/ 12 MPa have a much slower shrinkage, similar to the previous oxidised grade B samples.

These results show that the material made with A-AR powder is potentially unsuitable for use at 2000 °C, despite a pore size similar to that of oxidised grade B samples. Table 4.3 shows that the AR/ 24 MPa sample has a much higher surface area than the 12 MPa which both have higher surface area than the oxidised powder samples. This greater surface area explains why the AR/ 24 MPa sample densifies more than the others, but it is unclear why the higher pressure resulted in greater surface area.

The dilatometry performed is akin to a secondary sintering step at 2000 °C, and slow densification is likely limited, with pore sizes expanding as coarsening also occurs. It is possible that to fully develop microstructures in materials for the application of transpiration cooling, a high temperature second sintering step will be required; to stabilise the microstructure and prevent permeability reduction by densification or increases by coarsening.

4.6 Conclusions

The heating rates, atmosphere, and holding times had little effect on the permeability of porous ZrB_2 , with hot-pressing temperature having the greatest impact of final density. The density was shown to increase rapidly when hot-pressing at 1800 °C and above. Holding at 1500 °C and 1700 °C was found to allow for coarsening with little further densification, but not enough to prevent densification when heating to 2000 °C.

Porous ZrB_2 made with larger powders were more permeable when hot-pressed from as-received powders with low oxygen content, due to larger pores. The resultant lower surface area from large pores and lower curvature also resulted in a more stable microstructure that did not densify when heating to 2000 °C.

Coarsening was promoted by increasing the oxygen content of powders, consistent with literature for surface transport in UHTCs. The result increased neck growth between particles while increasing pore and grain size. This improved permeability and microstructural stability at 2000 °C.

Increasing the hot-pressing temperature promotes both coarsening and densification. It was shown that for low oxygen content powders (≤ 2.0 wt%O), hot-pressing at 1900 °C would produce a higher density product. For 2.7 wt%O powder, the increase in hot-pressing temperature coarsened fast enough to prevent densification, by reducing the surface area and thus consuming the available energy reduction.

The volume of porosity itself was not the most important factor for permeability, with pore size and tortuosity bearing a stronger link to the permeability of the samples. Generally, for porous ceramics the pore size reduces with increasing density, but this was only the case for increased density resulting from an increase in hot-pressing temperature in this study. Minor density increases resulting from increased hot-pressing pressure did not significantly affect pore size or permeability.

Higher pressure during hot-pressing was shown to promote neck growth between particles without coarsening, although the 0.5 wt%O powders did not show this effect due to the lack of additional surface diffusion. The further densification from higher pressure focused on hot spots rather than increasing homogeneously across the microstructure. A measured average pore size increase suggests small pores are removed, resulting in an increase in density and average pore size. The effects of these microstructural changes on other physical properties of ZrB_2 will be discussed in the following chapter.

Future work to assess specifics of coarsening mechanisms and rate of neck and pore growth is required for full understanding of fabrication methods. Inferences can be made towards the development of

pore and neck geometries from physical property changes, which are compared in Chapter 5. Further assessment of mechanisms is then undertaken in Chapter 6.

5 Properties of Porous ZrB₂

5.1 Introduction

The previous chapter has shown how porous ZrB₂ can be made by hot-pressing, and how particle size and oxygen content change the density, pore size, and microstructure. The aim of this chapter is then to link these microstructural changes to physical properties relevant for use in transpiration cooling. The development of physical properties has been studied for a range of partially sintered ceramics, but UHTC studies typically focus on achieving high density for high strength.

Strength in high-density UHTCs can be improved by reducing grain size, as grains act as critical flaws for brittle fracture[75]. Both the oxide contamination and the slow heating rates used to make the porous ZrB₂ have been shown to increase grain size and reduce strength in dense ZrB₂[58], [75]. However, in highly porous ceramics the critical flaw can be pores rather than grains. Increasing porosity in ceramics will reduce strength by introducing potential critical flaws and reduce elastic modulus as there is less load bearing solid phase[80]. However, for partially sintered ceramics the strength and elastic modulus have been shown to be strongly dependant on not just the porosity, but also the geometry of the necks between particles during the early stages of sintering[88], [96].

Grain size and porosity also have a strong influence on the thermal conductivity of ZrB₂. Increasing average grain size has been shown to improve thermal conductivity in ZrB₂[24] while porosity has been demonstrated to reduce it[42]. This behaviour is typical of polycrystalline ceramics[120], but for partially sintered materials with high porosity, the inter-particle necks are again pivotal to the development of thermal conductivity[98].

The coarsening mechanisms demonstrated in ‘Chapter 4: Porous ZrB₂ By Hot-Pressing’ both increases pore size and neck growth; the first section of this chapter will assess the affect these two mechanisms have on the elastic modulus, thermal conductivity, and flexural strength of porous ZrB₂.

In addition to the physical properties measured, thermal shock behaviour is a concern for transpiration cooled systems as the intended applications will experience high heat fluxes. The second section of this chapter will then calculate predicted thermal shock behaviour based on Hasselman’s equation for thermal stresses[121].

Assessment of material properties for the partially hot-pressed ZrB₂ will provide further insight into the microstructural changes observed in previous sections. Understanding the effect processing parameters have on the microstructure and then properties of the porous ZrB₂ will allow for informed

decisions on optimising processing, while providing a clearer picture of the challenges and compromises required for the material selection process for transpiration cooling.

5.2 Physical Properties

5.2.1 Elastic Modulus

The elastic modulus of each sample tested by RFDA as described in ‘Chapter 3.4.3: Physical Properties’ is plotted against relative density in Figure 5.1. All as-received (AR) grade B and oxidised powder samples fit the same trend from the development of physical properties around 0.6 relative density and 100 GPa with a linear increase towards the literature data and full density. Extending the linear trendline of these groups to full density results in a stiffness of 507 GPa, in agreement with literature values for ZrB_2 stiffness at near full density[32].

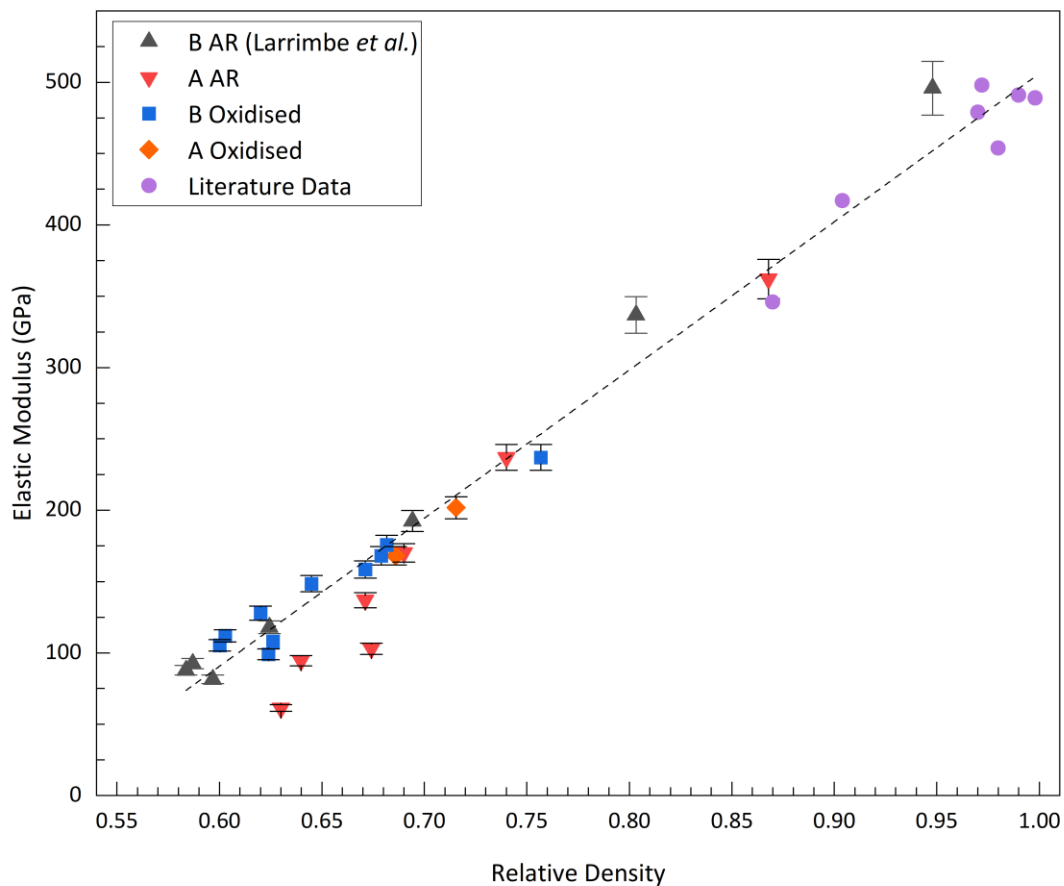


Figure 5.1 Elastic modulus of ZrB_2 samples hot-pressed from both as-received (AR) and oxidised grade A and B ZrB_2 . B AR data was supplied by Larrimbe[10] and literature data is from a range of sources where elastic modulus and density are reported for ZrB_2 [18], [28], [29], [31]–[35], [41].

Samples hot-pressed from the larger grade A-AR powder have a lower elastic modulus than the trend in grade B-AR and oxidised powders below relative density of 0.70. The delayed development of elastic

modulus for the grade A powder can be attributed to a difference in neck formation between particles. As discussed in section ‘Chapter 4: Porous ZrB₂ By Hot-Pressing’, these necks are formed via surface diffusion and vapour transport, assisted by the presence of oxides[58]. The greater oxygen contamination of the grade B-AR powder and oxidised powders has resulted in faster neck formation and development of elastic modulus. Modelling by Wang[122] showed that the geometry of necks only contributed significantly to the elastic modulus of materials in the very early stages of sintering. Therefore, despite the late development of elastic modulus for the grade A powder, the final trend is not dependant on the neck geometry above 0.70 relative density and all samples then follow the same linear trend to full density.

The linear trend for elastic modulus matches the data and resulting empirical model for the development of elastic modulus in partially sintered ceramics by Hardy and Green[88]. The model describes the initial development of elastic modulus up to an initial value, E' , at a critical density, ρ_0 , as necks develop between powder particles without significant densification. The elastic modulus then linearly increases with increasing density to the theoretical elastic modulus at full density, equation 2.22, observed also for ZrB₂.

5.2.2 Thermal Conductivity

Figure 5.2 shows the room temperature thermal conductivity of the porous ZrB₂ samples, calculated from diffusivity measured by laser flash as described in ‘Chapter 3.4.4: Thermal Analysis’. The thermal conductivity of samples made with AR ZrB₂ powders show a similar trend to the elastic modulus in Figure 5.1: There is a linear increase in thermal conductivity with increasing density from the initial development of physical properties around 0.6 relative density. The trend is independent of powder grade and aligns with the porous ZrB₂ made by SPS-RS from Yuan *et al.*[42].

The trendline intersects full density at 87 Wm⁻¹K⁻¹. This predicted thermal conductivity at full density is low compared to estimates of the intrinsic thermal conductivity of ZrB₂, with the highest literature values being 113 – 127 Wm⁻¹K⁻¹ but is consistent with a wide range of reported thermal conductivity values in literature for near full density ZrB₂ from as low as 56 Wm⁻¹K⁻¹ [12], [19]. Low values for thermal conductivity at full density as typically attributed to the result of grain size or ZrB₂ purity[12], [80].

No chemical analysis other than initial oxygen content has been performed on these powders or products, but purity has been identified in the literature as the dominating factor in the dense thermal conductivity of ZrB₂[12]. As no sintering aids or milling media were used in the preparation of powders from their AR state, contaminants could be the surface oxides discussed, carbon from the hot-press

chamber, the common impurity of hafnium in ZrB_2 [9], or other elements found in commercial ZrB_2 such as iron, silicon, and niobium[123].

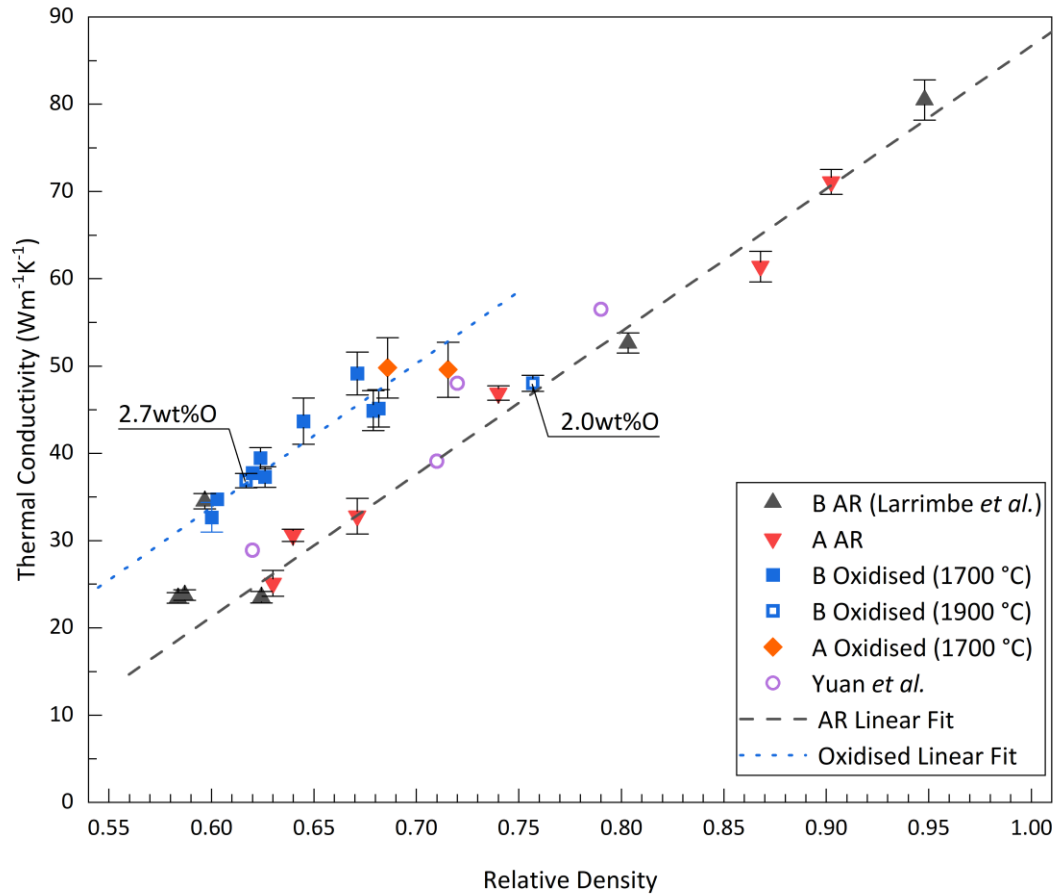


Figure 5.2 Room temperature thermal conductivity of hot-pressed ZrB_2 samples. The hot-pressing temperature of the oxidised powder samples was 1700 °C or 1900 °C as indicated with the oxygen content of the powder marked for samples hot-pressed at 1900 °C. Trendlines are calculated for two groups of samples that fit the lower trend of thermal conductivity of as-received (AR) samples and those that show increased thermal conductivity (oxidised samples). Room temperature conductivity for porous ZrB_2 from Yuan *et al.*[42] are included for comparison.

In literature, grade B ZrB_2 is used more commonly than grade A to achieve a smaller grain size from the smaller particle size. The matching trends in thermal conductivity with porosity for both grade A and B powder samples suggests grain size is not a strong distinguishing factor for thermal conductivity in porous ZrB_2 , with porosity being the key variable.

A second trend of thermal conductivity is shown in Figure 5.2 for the group of oxidised powder samples, the trend is also linear with the same gradient, offset by $13 \text{ Wm}^{-1}\text{K}^{-1}$ above the AR powder samples. The oxidation of powders before hot-pressing has caused rapid surface diffusion, resulting in an increased contact area between particles and increased grain size before any significant densification. This increased contact area results in increase thermal conductivity, consistent with models for partially sintered ceramics where the thermal conductivity is a factor of porosity, grain size,

and contact area between particles[98]. The samples made from the oxidised larger grade A ZrB₂ do not show a higher-than-expected thermal conductivity than the trend for oxidised powders, further indicating grain size is not as strong a factor as density and particle contact area.

Increasing the oxide content of ZrB₂ powders risks residual ZrO₂ in microstructure of ZrB₂. The comparatively low thermal conductivity of ZrO₂ (7 W m⁻¹ K⁻¹[124]) can result in a reduced overall thermal conductivity in dense ZrB₂ where ZrO₂ becomes trapped in closed pores and formed a second phase in the dense product[19]. The microstructure for all oxidised samples shows an open porosity with large pores, such that ZrO₂ will remain at the solid surface and any trapped ZrO₂ in closed pores would be insignificant compared to the far greater influence of the open porosity.

The oxygen content of hot-pressed ZrB₂ after heating to 2000 °C is shown in Table 5.1. Most of the oxide is removed during hot-pressing, with B₂O₃ evaporating and both B₂O₃ and ZrO₂ reducing in the carbon environment of the hot-press. Most of what remains can be removed by heating to 2000 °C in a carbon environment which will react to reduce remaining ZrO₂.

Table 5.1 Oxygen content of ZrB₂ powders, and samples after hot-pressing at 1700 °C and heating to 2000 °C in the hot-press furnace.

Powder Grade	Powder	Oxygen Content (wt%O)	
		Hot-Pressed at 1700 °C	1hr at 2000 °C
A	2.0	0.52	0.13
B	2.4	0.71	0.30

Some samples do measure thermal conductivity outside the expected trend for their powder type and relative density. Notable outliers are the 2.0 wt%O grade B powder hot-pressed at 1900 °C, and a grade B AR powder hot-pressed at 1700 °C from the Larrimbe[10] study.

‘Chapter 4: Porous ZrB₂ By Hot-Pressing’ showed that hot-pressing at 1900 °C had two different results for different oxygen content of ZrB₂ powder. The 2.7 wt%O powder showed a higher pore size, coarser microstructure, and no increase in density compared to the same powder hot-pressed at 1700 °C, whereas the 2.0 wt% ZrB₂ showed a reduction in pore size and increased density. This was evidence that the lower oxygen content was not retained or sufficient to promote coarsening by surface diffusion over densification at 1900 °C, a result that is reflected here in the thermal conductivity. The 2.0 wt%O powder sample hot-pressed at 1900 °C sits within the trend of AR powder samples, meaning there is not significant increase in contact area between particles. The 2.7 wt%O powder samples hot-pressed at 1900 °C sits within the expected trend for all oxidised powder samples, despite the previous demonstration of additional coarsening and larger grains the thermal conductivity is not further increased compared to the sample powder hot-pressed at 1700 °C.

This oxidised powder sample trend also includes one grade B sample from work done by Larrimbe[10]. Figure 4.14 showed that this study produced some samples with unusually high permeability when hot-pressed at 1700 °C, indicating that some samples made with the B-AR powder had increased coarsening resulting in larger pore size. This is evidenced in the permeability but would also lead to higher contact area between particles resulting in the increase to thermal conductivity for one sample shown in Figure 5.2.

5.2.3 Flexural Strength

Figure 5.3 shows flexural strength for the porous ZrB₂ hot-pressed from AR powders. As with the other physical properties, there is a linear relationship between strength and relative density. Density is increased in both A and B AR powder samples by hot-pressing at higher temperatures. Should this trend continue to fully dense ZrB₂, it would intercept relative density of 1.0 at 220 MPa, significantly below the flexural strength of near full density ZrB₂ in literature, also shown in Figure 5.3.

The highest density ZrB₂ samples from this study and material from Larimbe *et al.* [10] was hot-pressed at 2000 °C for 1 hour at 12 MPa, while pressures > 32 MPa allow for shorter hold times at temperature < 1900 °C to achieve similar and greater density in literature studies. While not quantified, as it is not the focus of study, a large grain size is likely the cause of the loss in strength compared to literature due to excessive coarsening from higher temperature processing.

A linear relationship between flexural strength and density matches studies of partially sintered alumina[88], [89], [97] shown in literature review Figure 2.9. However, these results do not fit models for fracture strength resulting from the porosity, with pore size reducing as density is increased, such as equation 2.25. These models for strength consider brittle failure resulting from a critical flaw in the microstructure, based on Griffith's fracture, equation 2.24.

However, the critical flaw in the partially sintered ZrB₂ results from a combination of interconnect pores, with strength also dependent on the thickness and geometry of inter-particle contact necks. This, therefore, leads to a more complex relationship between strength and density that cannot assume a reducing critical flaw size as the porosity is reduced.

The fracture toughness has also been shown to closely match the relationship between elastic modulus and relative density in partially sintered ceramics[88], which would further complicate the relationship between density and flexural strength of the porous material based on Griffiths fracture mechanics, which assumes constant fracture toughness.

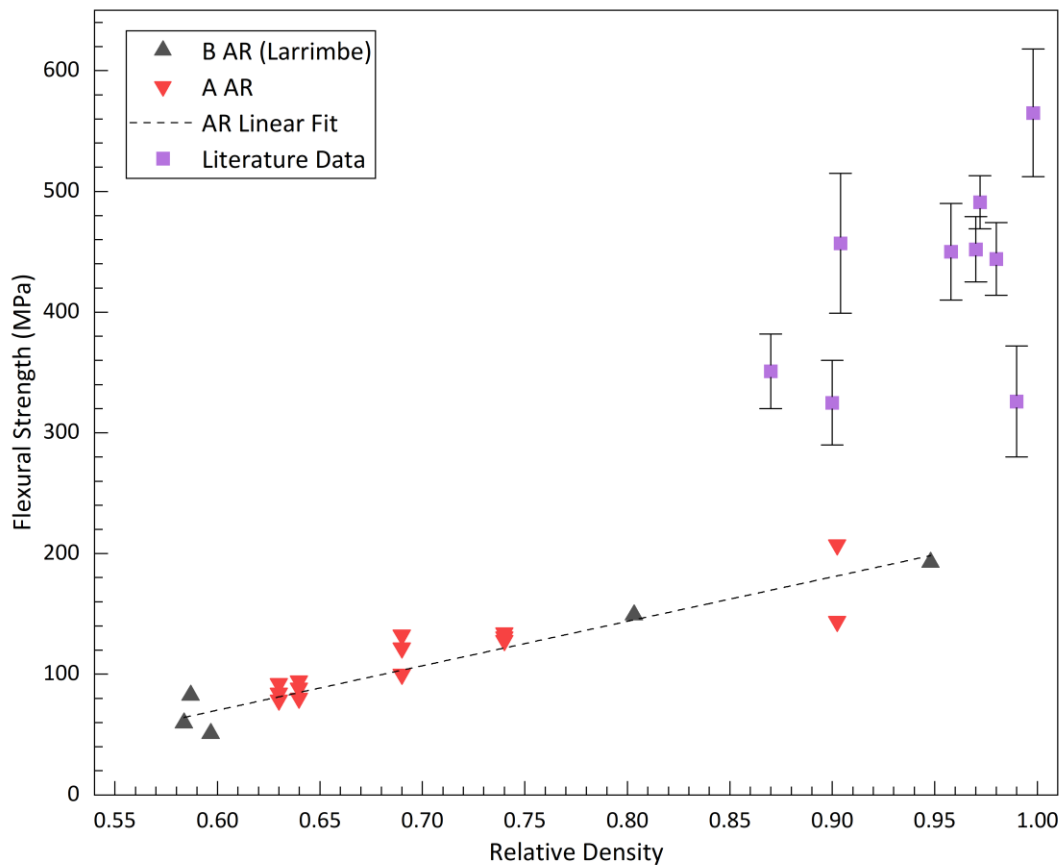


Figure 5.3 Four-point flexural strength of porous ZrB_2 made by hot-pressing at 12 MPa at temperatures ranging from 1500 °C to 2000 °C. Grade A and B [10] powders were used as received (AR) from supplier and literature data is selected where samples are also hot-pressed from ZrB_2 without sintering aids[12], [29]–[35], [37], [41].

[88], [89], [97][88]The flexural strength of the ZrB_2 hot-pressed to > 85 % density will have a closed porosity more consistent with Griffith's fracture. A maximum strength of 200 MPa at 0.90 relative density predicts a critical flaw size of 90 μm , assuming a shape factor $Y = 1.99$ [125] and $K_{1C} = 3.5 \text{ MPa m}^{0.5}$ [18].The focus of this work was on the highly porous material, so grain and pore size analysis was not performed on the dense materials, but the processing method of low pressure of 12 MPa and slow heating rates of 5 °C/ min to achieve dense ZrB_2 will have resulted in larger grains than expected in a strong, dense, ZrB_2 hot-pressed by conventional methods[9]. The strength of such materials has been shown to be closely connected to the grain size[126] so could account for the low strength of the > 90 % dense ZrB_2 in this study compared to the literature data.

Figure 5.4 shows the development of flexural strength with increasing hot-pressing temperature in the grade B-AR ZrB_2 and grade B ZrB_2 oxidised to 2.7 and 2.0 wt%O. 'Chapter 4: Porous ZrB_2 By Hot-Pressing' showed development of particle necking in the 2.7 wt%O powders which can be seen here to dramatically improve strength despite the pore size increasing (Figure 4.6). The B-AR powders also increase in strength between 1700 – 1800 °C with no increase in density. These results support the

explanation of the neck formation being critical to strength development in the early stages of sintering, which has been enhanced here by increasing oxide contamination resulting in improved strength in the 2.0 and 2.7 wt%O powders.

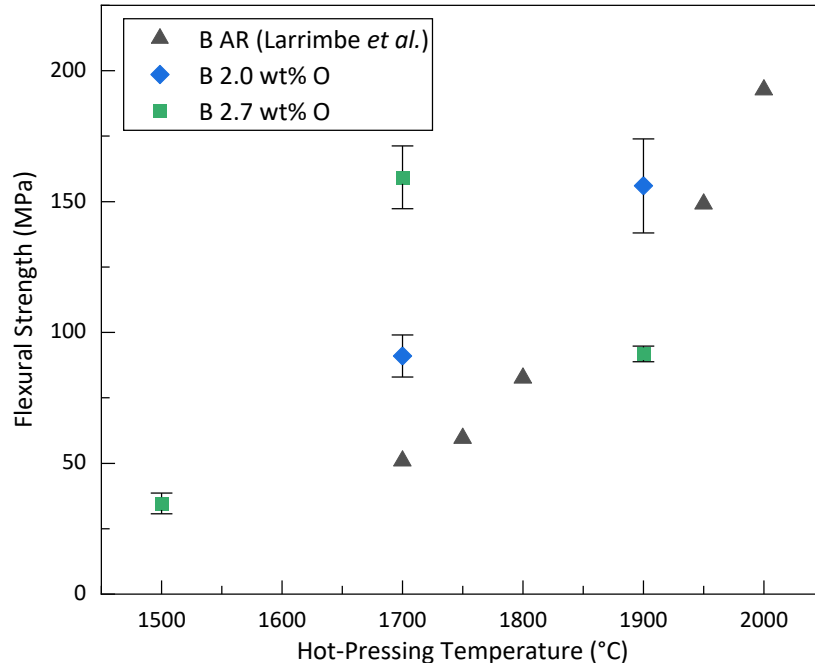


Figure 5.4 Mean four-point flexural strength of porous ZrB_2 vs. the temperature at which it was hot-pressed. Powders used were for grade A and B[10] ZrB_2 . Error bars are the half range all measurements.

Hot-pressing at 1900 °C was shown to promote densification in the 2.0 wt%O powder by increasing density and reducing pore size, while in the 2.7 wt%O the pore size increased and density remained unchanged, due to coarsening from the greater oxygen contamination. This coarsening has reduced the strength of the 2.7 wt%O material while the densification has increased the strength, but to similar values expected for AR powders, no longer showing increased strength expected from neck growth due to surface transport. This mirrors the results for thermal conductivity where the same 2.0 wt%O powder samples hot-pressed at 1900 °C showed thermal conductivity expected for the AR powder samples while the 2.7 wt%O showed an increase.

Figure 5.5 shows the flexural strength for all oxidised powder samples hot-pressed at 1700 °C alongside the strength data from samples made with as-received powder from Figure 5.3. The strength data reflects the effect of coarsening by surface diffusion in the oxidised powders. Formation of wide necks is visible in Figure 4.11 for the oxidised grade A powder. This neck formation produced samples with strength significantly greater than the trend for A-AR samples, consistent with strengthening effects of neck growth in other partially sintered ceramics [88], [96].

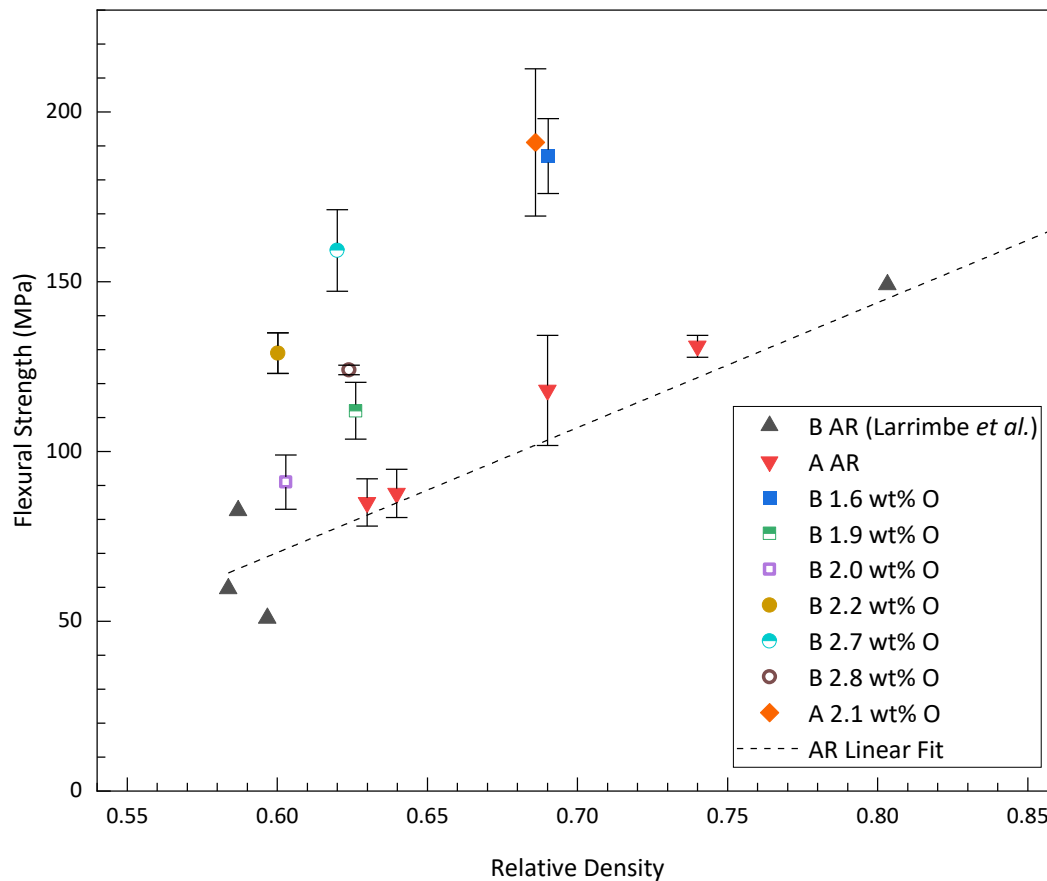


Figure 5.5 Flexural strength for hot-pressed ZrB_2 with varying oxide contamination. All oxidised powder samples were hot-pressed at 1700 °C, 12 MPa. Strength data and trendline for samples made with as-received (AR) powders are included from Figure 5.3. Error bars are the half range all measurements

The data for grade B powders covers a wider range of both density and strength due to the variation in oxygen content of the powder. Figure 5.5 shows the effect this oxygen content had on the grade B ZrB_2 powder during hot-pressing, first by increasing the strength for the 1.6 wt%O sample above the expected AR trend. As the oxygen content is increased to 1.9 – 2.0 wt%O the coarsening due to oxide contamination prevented densification, but has not promoted neck growth under these conditions, as the density and strength are both reduced.

As oxygen content is increased from 2.0 to 2.2 and 2.7 wt%O there is little change to the density, but the strength increases from 91 to 159 MPa. Increases in strength without an increase in the early stages of sintering is indicative of neck growth between particles in partially sintered ceramics[88], [96]. The previous chapter also showed that increasing oxygen content across this range promotes surface transport that which will promote neck growth, responsible for this increase in strength.

However, the 2.8 wt%O sample then shows a loss of strength compared to 2.7 wt%O. This sample does not show an increased pore size, Figure 4.6, expected from further coarsening. Figure 4.7 does show larger grain size from increased coarsening in the 2.8 wt%O sample. It is therefore likely that this

microstructural change, as a result of coarsening, has caused an increase in critical flaw size. This could be by grain growth or some effect to the combined interconnected pore network; creating large critical flaws that would account for the loss of strength compared to the 2.7 wt%O sample.

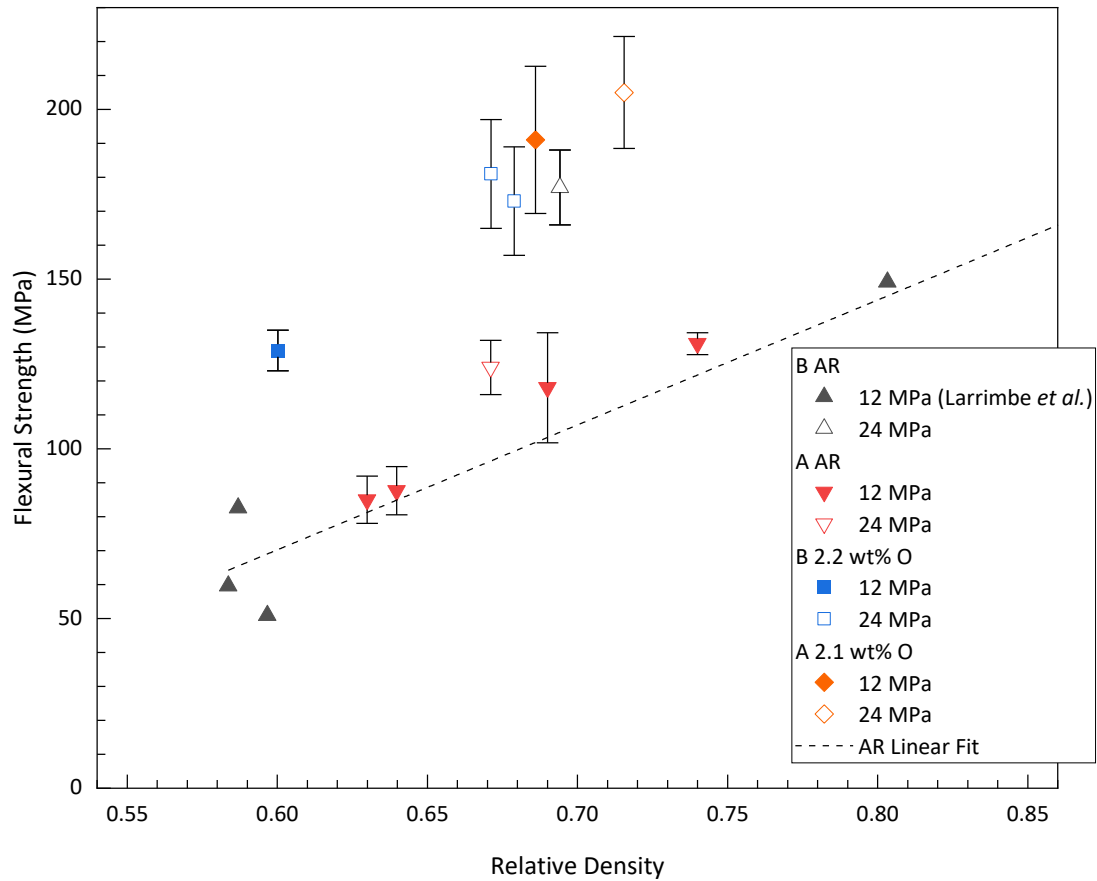


Figure 5.6 Flexural strength of porous ZrB_2 hot-pressed from grade A and B as-received (AR) and oxidised powders. Density variation in the AR powders is achieved by varied hot-pressing temperature, while oxidised and 24 MPa AR samples were hot-pressed at 1700 °C.

Figure 5.6 shows the effect of increasing pressure during hot-pressing in the as-received and oxidised powders. Figure 4.11 showed previously the increased connectivity of particles by neck growth in the B-AR powder when hot-pressing with high constant pressure. This increased neck growth is responsible for the as-received grade B powder hot-pressed at a constant 24 MPa having strength greater than expected for the previous trends in AR powder samples.

The larger grade A as-received powder hot-pressed under constant 24 MPa pressure shows only a slight increase in strength above the expected trend. This is consistent with the lack of connectivity observed in Figure 4.11 as the lower oxygen content means there is still less neck growth.

Increasing the pressure will not promote surface diffusion or coarsening as these are not densification processes[127]. Neck formation occurs by a combination of surface and bulk transport mechanisms[57], so increased pressure will promote the bulk transport at necks, leading to

densification and the strength from increased neck growth observed. Evidence for the lack of further coarsening by applying constant pressure in the as-received powders is shown in 'Chapter 4.3.2: Effect of Pressure' in the observed microstructure in Figure 4.11 and rapid densification during dilatometry in Figure 4.19.

Improved strength in porous UHTCs by increasing the pressure during partial hot-pressing is a result repeated in literature, with Hong *et al.* finding that increased pressure in hot-pressed 40 – 15 vol% porous TiB₂ improved strength[128], [129]. This was also attributed to neck growth between particles but also showed that a lower temperature was needed to achieve the same density. Achieving the same density in the porous material by hot-pressing at higher pressure and lower temperatures will lead to a smaller grain and pore size, which will also improve strength.

Mercury intrusion porosimetry in the previous chapter showed there was little difference in pore size when increasing hot-pressing pressure. The critical flaw for brittle fracture will also arise from a combination of several pores throughout the porous network. There is, therefore, little to suggest the increased pressure has reduced pore size to improve strength by reduction of critical flaw size. While there is evidence of enhanced neck formation from increased pressure in Figure 4.11.

5.3 Thermal Shock

The work with oxidised powders shows a further trade-off between properties for porous ZrB₂ when the application of transpiration cooling is considered. The original permeability and strength characterisation of porous grade B ZrB₂ by Itfi *et al.*[6] and Larrimbe[10] showed the need for high porosity to achieve high permeability at the cost of low strength. The current study has shown that oxidation of the ZrB₂ powder prior to hot-pressing improved neck-growth between particles, improving both permeability and strength. This also prevents further densification at application temperature of 2000 °C.

Coarsening of the porous microstructure can lead to a loss in mechanical properties. The use of higher pressures during hot-pressing alleviated this issue by promoting rapid neck formation without excess coarsening in 30 % porous ZrB₂. The materials made with constant pressure of 24 MPa and oxidised powders are permeable enough for use in transpiration cooling, and the density can be tailored through changes in pressure. Dilatometry shows that they will not densify rapidly during operation, but future work should conduct porosimetry of these materials after extended holds at 2000 °C to assess the coarsening effect of multiple exposures to ultra-high-temperature conditions.

The elastic modulus is shown to be independent of the morphology of the porous microstructure after the initial development of properties, so increases in strength without change in density suggest

improvement has also been made for thermal shock resistance. Hasselman's equation for thermal stresses[121] is given in equation 5.1, and determines a critical temperature difference for crack initiation, ΔT_c , which is commonly used as a parameter to compare resistance to thermal shock.

$$\Delta T_c = \frac{\sigma_f}{E} \cdot \frac{1 - \nu}{\alpha} \quad 5.1$$

Where:

σ_f = Flexural strength of the material

E = Elastic modulus

ν = Poisson's ratio

α = Coefficient of thermal expansion

Figure 5.7 shows that above 95 % density, the thermal shock resistance of ZrB₂ is predicted to improve as the increase in strength out-paces the increase in elastic modulus, as increases in strength are due to rapidly shrinking critical flaw size. With a reduction in elastic modulus and little change in strength, the literature data from 80 – 95 % density the literature values for ZrB₂ match the ZrB₂-SiC from Jin *et al.*[114], while the much weaker material from Larrimbe *et al.*[10] predicts lower thermal shock resistance.

Calculations from data in the present study predict a reduction in thermal shock resistance from 60 – 80 % density, like the experimental data from Jin *et al.*[114], as the increase in elastic modulus out-paces the increase in strength. Oxidising the powders to promote neck growth has allowed for an alternative method for increasing strength, instead of just increasing the density. As this does not cause an increase in elastic modulus, this results in an increase in predicted thermal shock resistance with increasing oxygen content of powders in Figure 5.7. Although, these oxidised powder samples still follow the downward trend in thermal shock resistance with increasing density.

The data makes a case for using as lower density ZrB₂ as possible. This is despite the promotion of surface transport increasing strength while maintaining permeability at higher density, as the trend shows a general decrease in thermal shock resistance as the density increases. Samples made from A-AR powders calculate better thermal shock resistance than B-AR samples due to the delayed development of elastic modulus, despite having the same strength/ density relationship.

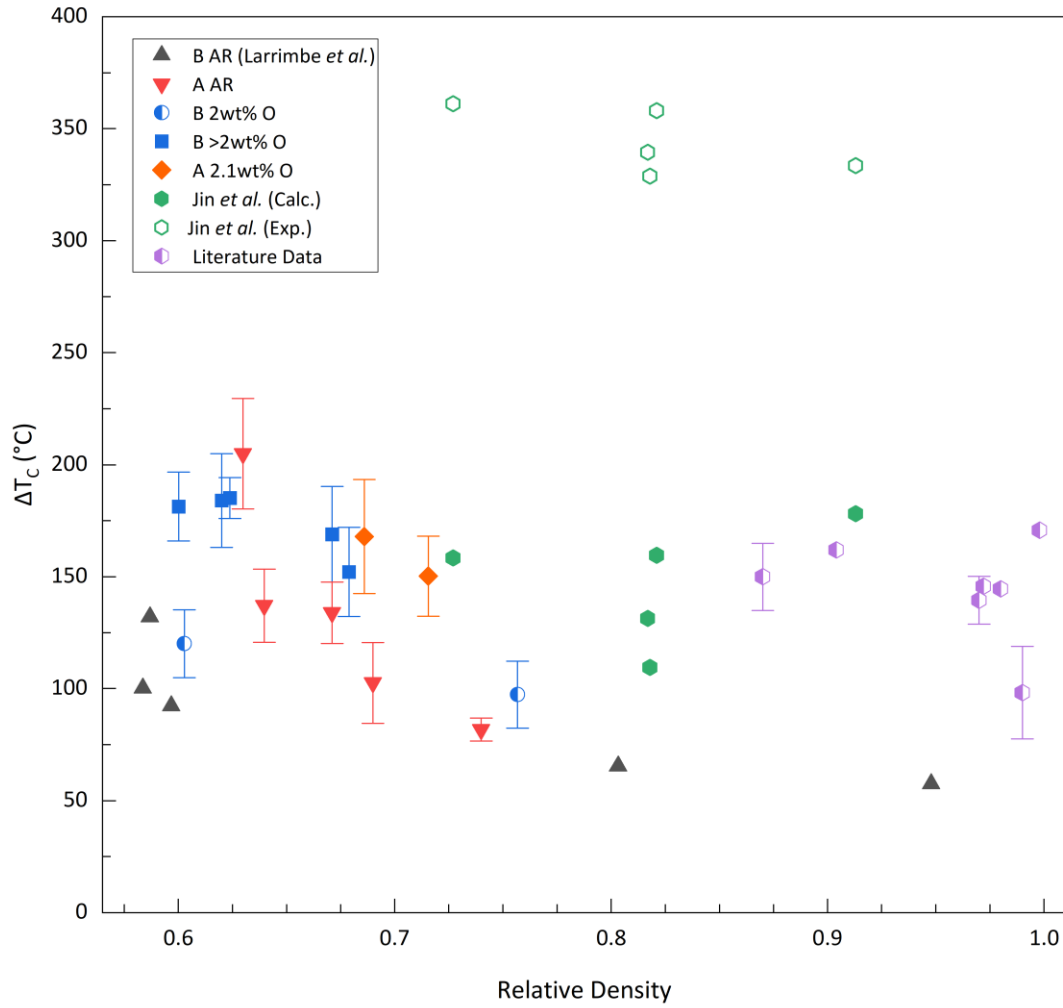


Figure 5.7 Thermal shock resistance calculation (equation 5.1) for partially sintered ZrB_2 samples alongside partially sintered ZrB_2 -SiC from Jin *et al.*[114], and calculated thermal shock resistance from literature data for strength and elastic modulus[18], [28], [29], [31]–[35], [41].

The trend of increasing thermal shock capability with increasing porosity is inconsistent with some studies of thermal shock in porous materials[130], [131]. These show a decrease in thermal shock resistance with increasing porosity, but also show porous materials with strength proportional to $\left(1 - \frac{\phi}{\phi_c}\right)^n$, typical of strength models based on critical flaws[87], [95], equation 2.25, rather than considering strength from neck growth without densification in partially sintered materials. The models predict rapid changes in strength with minimal change in density, and therefore elastic modulus, resulting in a loss of thermal shock resistance.

However, Jin *et al.* recently showed experimentally that increasing porosity from 8.7 vol% to 27.3 vol% porous ZrB_2 -SiC ceramics improved thermal shock resistance, despite the calculations predicting the opposite [114]. Both calculation and experimental data from Jin *et al.* is shown in Figure 5.7. The improvement was attributed to the effects of pore size and the author suggests further improvements could be made through manipulation of the pore size and morphology which appear to be realised for

the trends calculated for partially sintered ZrB_2 [114]. The calculated ΔT_c that predicted a negative trend were 30 – 50 % of the value determined experimentally, highlighting the need for further experimental validation of the behaviour seen in the porous hot-pressed ZrB_2 from this current study to confirm the calculated behaviour prediction.

5.4 Conclusions

The effects of the coarsening, neck growth, and densification on the physical properties of porous ZrB_2 are consistent with property development in partially sintered ceramics, with properties dominated the porosity and microstructure. Inferences can be drawn to neck growth consistent with literature studies in partially sintered ceramics, with correlation to microstructural changes observed in chapter 4, but quantification of neck growth is desired.

The larger powder size and lower oxygen content of grade A ZrB_2 has delayed the development of elastic modulus compared to the grade B powders. However, the strength of samples made by both as-received powders follows the same linear relationship with relative density. Hot-pressing with the relatively low pressures resulted in lower strength than demonstrated elsewhere in literature above 85 % relative density, due to slower densification allowing for growth of large pores and grains.

A higher oxide contamination of powders prior to hot-pressing led to increased neck growth between particles, which increases elastic modulus, thermal conductivity, and flexural strength with no increase in relative density. The results showed some variability in the success of increasing physical properties with neck growth, so increasing the hot-pressing pressure improved strength by consistently promoting neck growth between particles, but also increased densification.

Calculations for thermal shock resistance suggest the low elastic modulus and improved strength of 60 % dense ZrB_2 made with oxidised powders offers the best resistance. However, increasing the hot-pressing temperature of oxidised powders led to further coarsening of the porous microstructure which reduced the flexural strength due to the increased pore and grain size. This result raises concerns of coarsening at the intended application temperatures of 2000 °C reducing the strength of the partially sintered material. This potential loss of strength requires further investigation and highlights the need for further mechanical support by a dense, or composite, substructure.

6 Densification Mechanisms of ZrB₂

6.1 Introduction

The work in the previous two chapters has shown how porous ZrB₂ can be made by hot-pressing, and the way powder size, oxygen content, pressure, and temperature will affect the microstructure and properties of the material. The majority of samples were sintered at 1700 °C, based on previous work, and proved to be a temperature that consistently produced samples with enough strength to withstand testing, without densifying and reducing permeability. Despite the lack of partial sintering of ZrB₂ in literature, the use of 1700 °C is consistent with 1750 °C previously reported as the onset temperature of densification in ZrB₂[29], so hot-pressed slightly below this prevents excessive densification.

Despite the lack of rapid densification associated with a typical densification onset point, there is still densification from green bodies of around 50 vol% porosity and the 25 – 40 vol% porous partially sintered ZrB₂. As most samples were compared after sintering at 1500, 1700, or 1900 °C, a greater understanding of the sintering kinetics over the entire temperature range is required for greater control of the microstructure, and therefore tailoring of properties.

Therefore, this chapter aims to take a broader look at the densification of ZrB₂, with the aim of identifying onset temperatures for key mechanisms for neck growth and densification, to better understand the underlying sintering mechanics that make the observed porous microstructure. By doing so, a more complete toolkit will be available for those looking to optimise the microstructure and tailor properties to transpiration cooling requirements.

This chapter will first use thermogravimetric (TG) analysis to further characterise ZrB₂ powders used in the work, with the large (A) and fine (B) grades of ZrB₂ powders used as-received (AR), milled with sintering aids to reduce oxide contaminants, and oxidised to promote surface transport. The density and densification rates will then be calculated throughout hot-pressing, at a constant pressure of 24 MPa from 500 °C to 2000 °C, by the hot-press ram displacement as described in 'Chapter 3.2: ZrB₂ Hot-Pressing'.

6.2 Powder Thermal Analysis

The results of TG analysis for as-received (AR) and oxidised grade B ZrB₂ powders, as well as grade B powder milled with 2 wt%C and 2 wt% B₄C, are shown in Figure 6.1. Powder was oxidised by heating

in stagnant air to 500 °C as detailed in 'Chapter 3.1.3: Oxidation of Powders'. Samples were heated at 10 °C/ min under flowing Ar in an alumina crucible, as described in 'Chapter 3.1.2: Thermal Analysis'.

Each of the oxidised and AR powder show an initial mass loss between 75 – 200 °C, the scale of mass loss correlates with the starting oxygen content of the powder. They then each show a second mass loss above 1000 °C, the rate of loss accelerating with increasing temperature beyond the maximum temperature of 1600 °C.

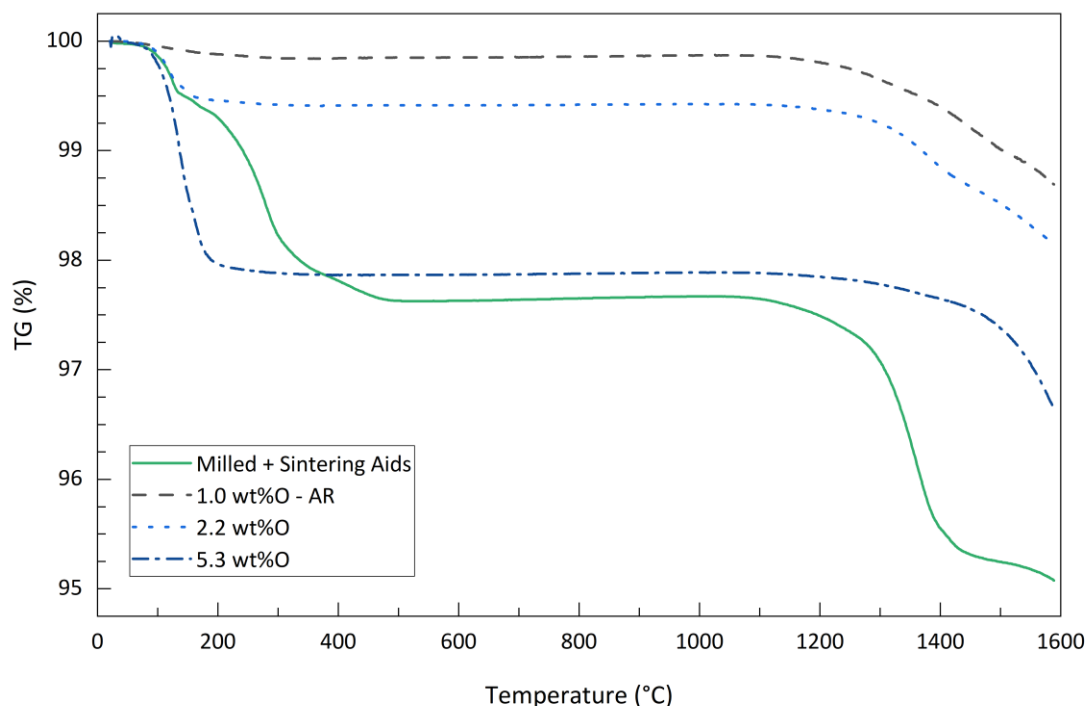


Figure 6.1 Thermogravimetric analysis for grade B ZrB_2 powders in argon.

The initial mass loss is decomposition of boric acid[132], which will have formed by boria in the powder being exposed to moisture. The second mass loss from 1000 °C will then be the vaporisation of this boria. The vapour pressure of boria is well documented as it can contribute to vapour phase sintering in of borides, and typically shows an increasing vapour pressure from 1000 °C in literature[133].

The powder milled with sintering aids shows a similar initial mass loss, followed by an arrest and further loss between 130 – 490 °C. This extended reduction in mass below 500 °C is from boiling of stearic acid, used to prevent agglomeration during milling, and matches the TG analysis for stearic acid in literature[134]. This powder then has a greater rate of mass loss above 1000 °C compared to the AR and oxidised powders, with the rate of mass loss slowing from 1400 °C. This suggests the mass loss is due to reduction reactions with the B_4C and C sintering aids, e.g. via the reactions 2.3 - 2.6, rather than from evaporation of oxides.

The STA results for the grade B powder with 5.3 wt%O when heated to 2000 °C in a graphite crucible and furnace are shown in Figure 6.2. As with the alumina set-up, the TG results show two mass loss events, the first between 80 – 150 °C and the second between 1200 – 1550 °C. The DTA data shows corresponding peaks for these mass reductions, an endothermic peak at 110 °C and an exothermic peak at 1450 °C. The endothermic peak at 110 °C further supports the decomposition of boric acid, which is endothermic[132].

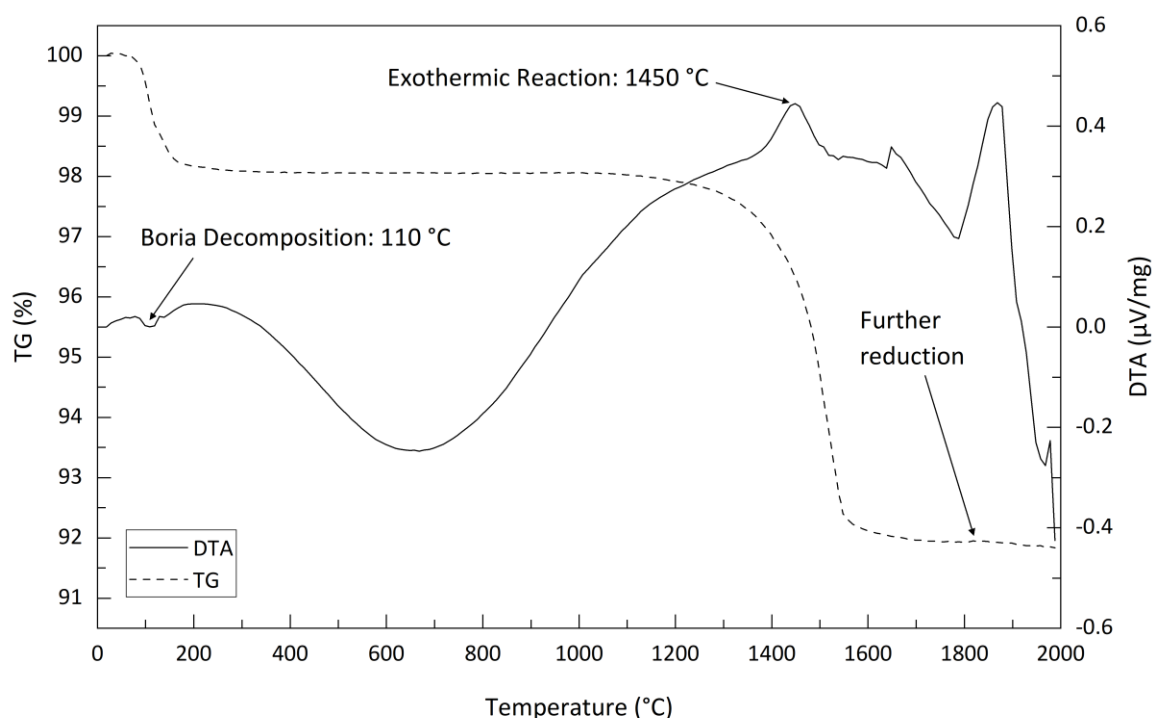


Figure 6.2 Simultaneous thermal analysis results for the grade B ZrB_2 powder with 5.3 wt%O, showing thermogravimetric (TG) and differential thermal analysis (DTA).

The second mass loss event is much faster than when using an alumina crucible in Figure 6.1, being completed by around 1550 °C, and the accompanying exothermic peak signifies a reaction rather than evaporation, which would be endothermic. This rapid mass loss is similar to the powder with sintering aids, but as no sintering aids were added to the powder the zirconia and boria oxides will be reacting with the graphite of the crucible, in addition to boria evaporation.

It is not clear whether the following DTA trace shows endothermic or exothermic behaviour due to the shifting global trend of the DTA trace from 1700 °C. However, further reduction in mass from 1800 °C implies carbothermal reduction of remaining oxides.

6.3 Densification During Hot-Pressing

6.3.1 Powder Size, Pressure, and Oxygen Content

The density of ZrB_2 powder was monitored as it was sintered by hot-pressing into a monolithic ceramic as detailed in 'Chapter 3.3: Hot-Press Data' for a range of conditions listed in Table 6.1. Different levels of oxygen contamination were used for both the larger grade A and finer grade B powders.

The calculations rely on final Archimedes density measurement and offset of LVDTs to calculate the thickness and therefore density during the run. The values of final density and powder mass used for each run are also recorded in Table 6.1.

Table 6.1 Conditions for densification monitoring during hot-pressing for the two grade of ZrB_2 powder along with the powder mass used and final density. Powder was heated at 5 °C/ min for each run, powders have been marked where used As-Received (AR) or with the oxygen content achieved by baking in air.

Powder Grade	Oxygen Content (wt%O)	Pressure (MPa)	Powder Mass (g)	Final Density (g cm^{-3})	Relative Density
B	(Sintering Aids)*	24	34.8	5.87	0.95
B	1.0 (AR)	24	30.5	6.05	0.98
B	2.2	24	21.4	6.02	0.98
B	2.2	4.7	31.4	5.76	0.94
B	5.3	24	21.5	4.79	0.78
A	0.5 (AR)	24	28.9	6.05	0.98
A	2.1	24	34.5	4.95	0.80

*Oxygen content is not reported where sintering aids are added due to the addition of stearic acid in addition to 2 wt%C + 2 wt%B₄C.

Figure 6.3 shows the density and densification rate of the as-received fine grade B powder and milled with sintering aids boron carbide and carbon black, heated at 5 °C/ min under 24 MPa load. There is no significant densification of the milled ZrB_2 powder below 1300 °C. From 1300 °C the densification rate increases steadily before increasing rapidly from 1525 °C, peaking at 1670 °C with relative density of 0.69.

A densification onset temperature of 1300 °C in the milled powder is consistent with early studies into ZrB_2 [135]. However, this onset is inconsistent with more recent studies into densification of ZrB_2 that show a densification onset of 1750 °C [29]. The discrepancy in onset temperature has been previously attributed to purity of powder during review [9]. The lack of an exponential increase in densification rate and of rapid densification in any ZrB_2 sample held at 1500 °C in the previous chapters implies this increase at 1300 °C is not the onset of rapid densification characteristic of intermediate stage sintering.

Oxide impurities in the AR powder will not be removed by reduction as readily as the powder with sintering aids, and therefore shows minor amounts of densification from 1000 °C, aligning with both

sintering temperatures for zirconia[137] and the reduction of oxides shown in Figure 6.2 which could allow space for further compaction of ZrB_2 powder.

Samples hot-pressed at 1500 °C in the previous chapters had sufficient physical properties to measure permeability and record strength and stiffness data, but they had the appearance of disconnected powder compared to the samples hot-pressed at 1700 °C. Holding at 1500 °C also showed evidence of coarsening, therefore this onset of densification at 1300 °C is not solely from rearrangement due to impurities but the initial stages of neck growth, that occurs by a combination of both densifying bulk transport and surface transport mechanisms.

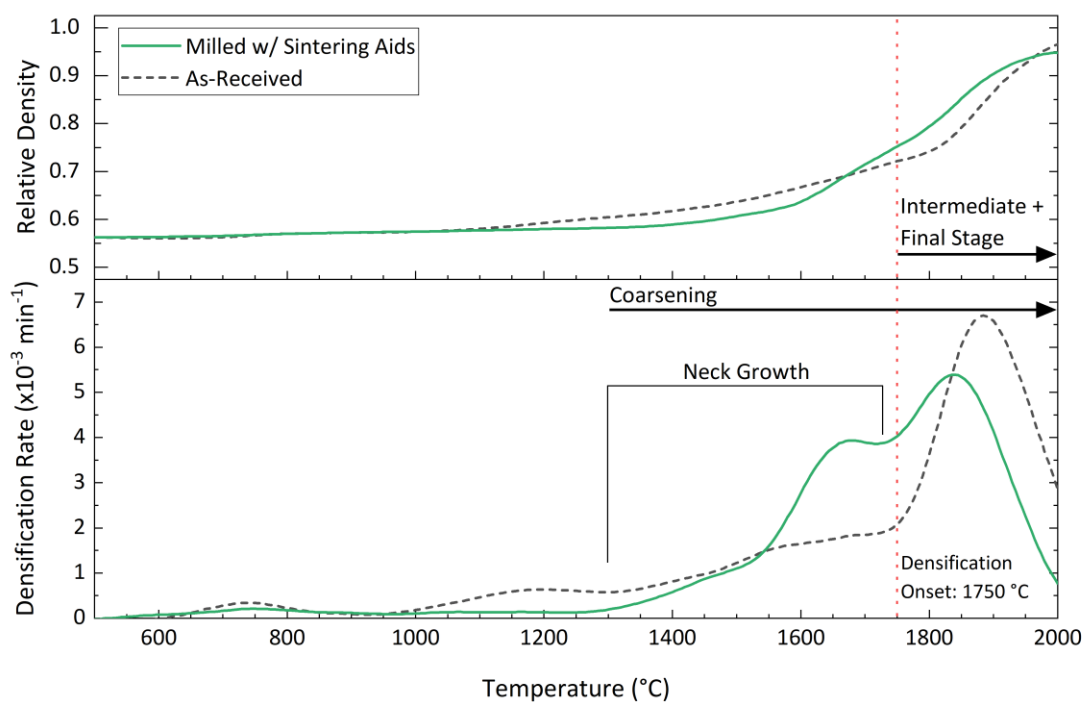


Figure 6.3 Relative density and densification rate for grade B ZrB_2 powders, used as-received or planetary milled with 2 wt%B₄C, 2 wt% carbon black and 2 wt% stearic acid. Hot-pressing was performed in argon at 5 °C/min under 24 MPa load.

The increase in densification rate from 1525 °C in the powder with sintering aids aligns with the development of strong necks between particles from 1500 – 1700 °C in the partially sintered ZrB_2 , discussed in the previous chapters. Neck growth between particles causes a limited amount of densification, with densification rates decreasing after reaching 0.69 relative density in the milled powder. Faster coarsening from oxide contaminants in the AR powder has resulted in less potential energy reduction from densification, and a lower densification rate from 1540 °C to 1830 °C, despite a lower density across this range.

[58]As TG analysis of the powder with sintering aids showed the mass loss from reduction of oxides was complete by 1400 °C, the AR powders will likely therefore have had greater activity from boria

vapour over this 1400 – 1700 °C range. It is well established in literature that vapour phase transport of boria leads to causing coarsening of UHTC borides [58]. This will prevent further densification, as observed by the delayed onset of rapid densification in the AR powder, which can therefore infer an increase in vapour phase transport due to the higher oxygen content.[58]

The reported densification onset temperature for hot-pressed ZrB_2 of 1750 °C[29] is marked on Figure 6.3, coinciding with a rapid increase in densification rate for both the AR and milled powder. Both powders then peak in densification rate at 0.84 relative density. The reduction in densification rates up to 2000 °C for both powders is indicative of final stage sintering as residual porosity is difficult to eliminate due to the reduced curvature gradients and surface area[57].

Figure 6.4 shows the how the density and densification rate with temperature changes as the oxygen content is increased from 1.0 wt%O in the AR powders to 2.2 and 5.3 wt%O.

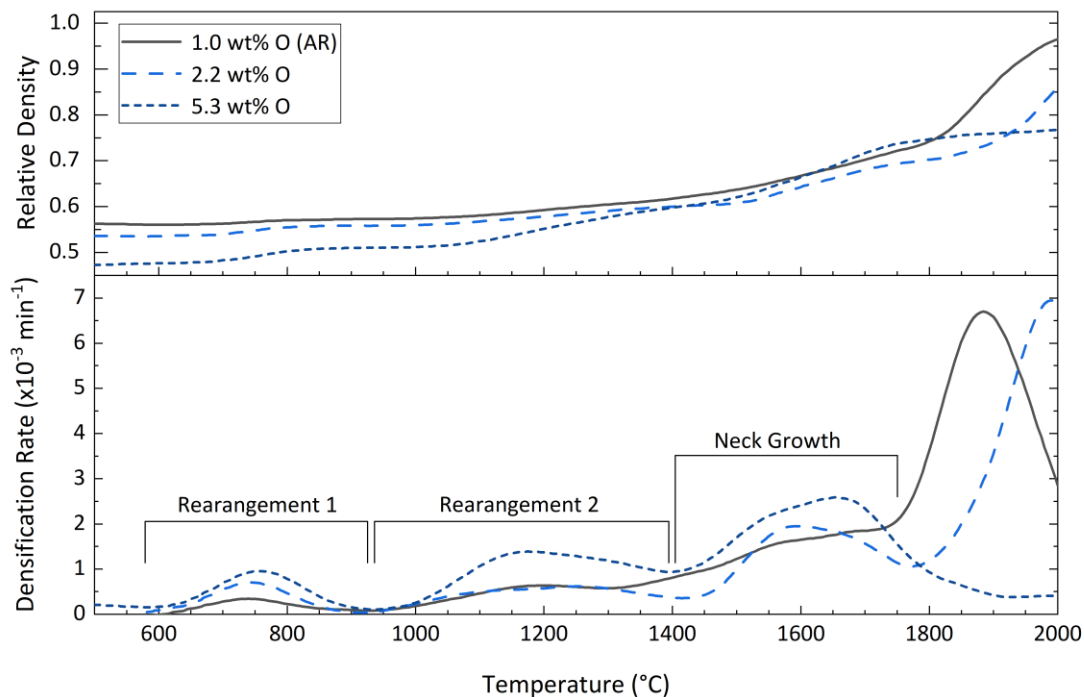


Figure 6.4 Relative density and densification rate for grade B ZrB_2 powders, used as-received (AR) or oxidised to the stated oxygen content. Hot-pressing was performed in argon at 5 °C/ min under 24 MPa load. Labels are assigned to densification regions aligned with the melting of boria (Rearrangement 1) [138], sintering temperatures of zirconia[137] and evaporation of bora (Rearrangement 2), and neck growth during the initial stages of sintering[55].

The first distinction noticeable for the oxidised powders is lower initial density at 500 °C followed by increased densification rates below 1400 °C compared to the AR powder. The densification is split into densification rate peaks at 600 – 900 °C, and 950 – 1400 °C.

The lower density at 500 °C will be due to less effective powder packing, as oxidising the powders will have fused large agglomerates which prevent dense arrangement, with a minor impact of a difference

in theoretical density due to the higher oxide content. By 1400 °C these differences in packing are all but equalised, as boria melting from 480 °C allows for the first re-arrangement peak, and the previously discussed sintering temperatures of zirconia, evaporation of boria, or reduction of both oxides causes densification of the powder compact up to 1400 °C.

The phase diagram Figure 4.17 shows increasing liquid fraction for ZrO_2 and B_2O_3 mixtures from 1000 °C, removing solid ZrO_2 would also allow for greater compaction of ZrB_2 powder. There is then also a large increase in liquid fraction from 1400 °C, where neck growth is inferred to occur with the assistance of rapid surface transport.

As with the AR powders, from 1400 – 1700 °C the densification rates are similarly subdued compared to the powder with sintering aids in Figure 6.3. The 2.2 wt%O powder again shows the expected onset for rapid densification from 1750 °C as bulk transport mechanisms become faster, but the rate of densification is lower than that of the 1.0 wt%O (AR) powder. The rate of densification of the 2.2 wt%O powder peaks at 1990 °C, exactly mirroring the AR powder and powder with sintering aids with a relative density of 0.84.

The higher densification rate in the 5.3 wt%O up to 1700 °C is only sufficient to equalise the relative density of samples, suggesting the higher oxygen content that prevented effective packing also then allows for rearrangement prior to intermediate stage densification. However, the densification rate of the 5.3 wt%O peaks at 1650 °C, with a relative density of just 0.69 this exactly matches the density of the peak in densification rate due to neck growth in the milled powder with sintering aids in Figure 6.3. The density of this sample then increases to just 0.77 while heating to 2000 °C. The high oxide content of the powders has led to such rapid coarsening that intermediate-final stage densification has been entirely prevented, even with 24 MPa pressure applied.

Figure 6.5 shows a photo and the fracture surface microstructure of the 5.3 wt%O sample after holding at 2000 °C to a final relative density of 0.78. The previous work has shown the large pore and grain size will lead to a high permeability and stable microstructure, while the excessive coarsening will be detrimental to physical properties. The photo in Figure 6.5b shows where this sample broke while removing from the hot-press, being the only sample not to withstand handling this is indicative of the low strength expected from such a large-grained material.

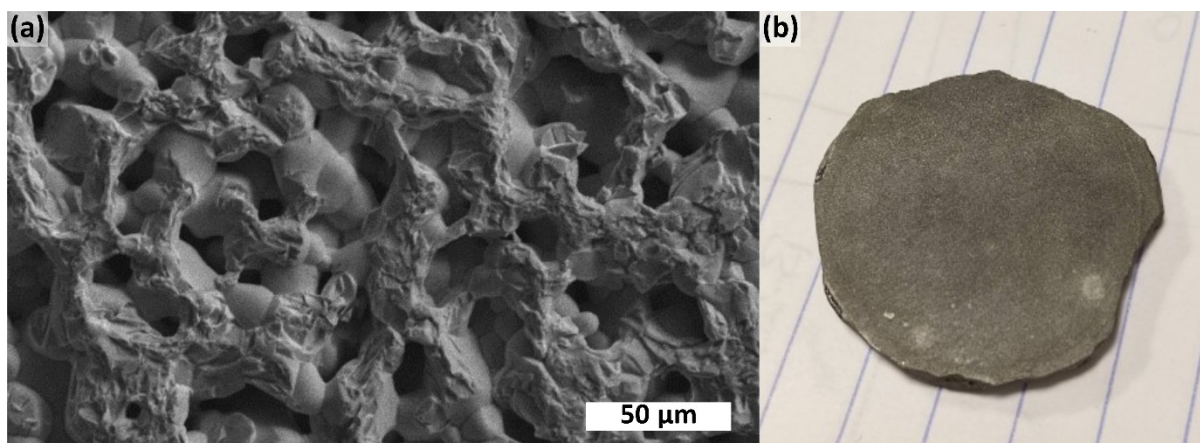


Figure 6.5 (a) SEM image of the fracture surface and (b) photo of the 37 mm diameter sample produced by the grade B ZrB_2 powder oxidised to 5.3 wt%O. Powder was heated at 5 °C/ min in argon under 24 MPa load to 2000 °C.

Figure 6.6 shows the effect of reducing the pressure has on the density and densification rate for the 2.2 wt%O grade B ZrB_2 powder. The lower pressure run has a consistently lower density from 500 °C, due to the lower pressure of initial compaction in the powder, with identical densification rates during the rearrangement due to oxide impurities up to 1400 °C. The lower densification rate from 1500 – 1700 °C supports previous strength data evidence that pressure contributes to neck formation over this temperature range, as applied pressure contributes to the sintering stress that drives plastic flow during neck formation[55]. The delay in onset of rapid densification with lower applied pressure could be due to insufficient driving force densify by grain boundary diffusion, with volume diffusion becoming active from 1850 °C in both cases. Volume diffusion then causes the onset of rapid densification in the 4.7 MPa case and becomes the rate determining step for the 24 MPa case. The final achieved relative density was 0.95, compared to 0.97 for the 24 MPa sample.

The density and densification rates of AR and oxidised powders for the larger particle size grade A ZrB_2 are then compared with grade B in Figure 6.7. Despite starting with a higher packing density due to a broader particle size distribution[139], the grade A-AR shows identical densification behaviour to the grade B-AR, other than between 1400 – 1700 °C where the grade B densifies more rapidly. This implies a lack of neck growth in the grade A powder, which was apparent from the SEM cross section shown previously in Figure 4.11. As discussed then, the reduced neck growth is due to the lower curvature and oxygen content of the grade A powder, leading to lower sintering stresses and slower surface transport mechanisms.

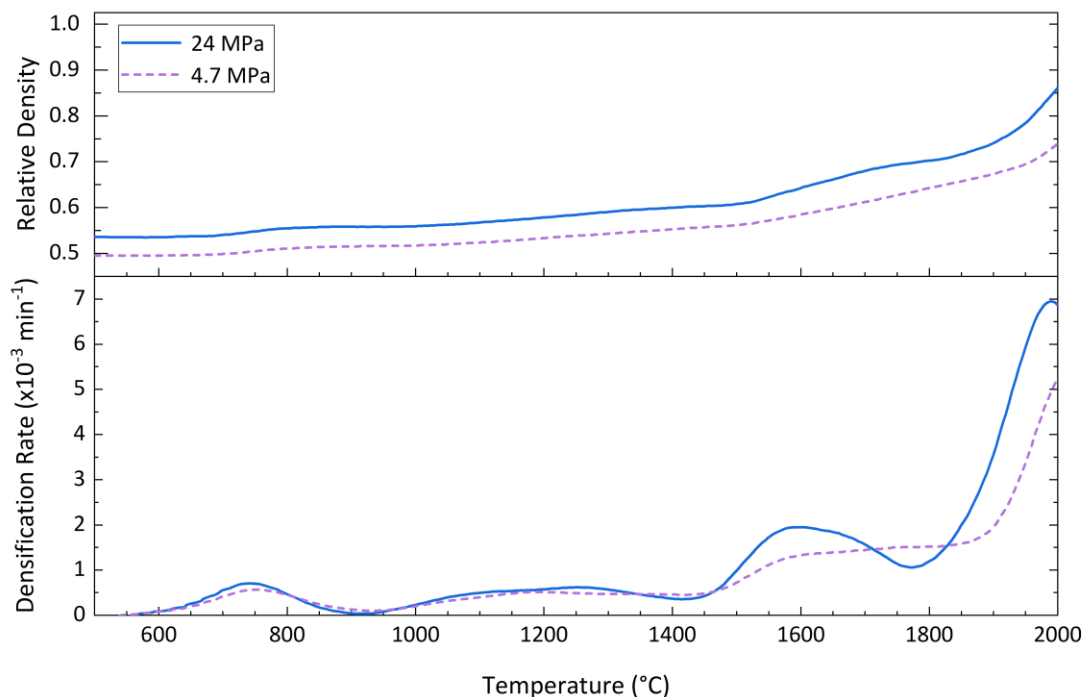


Figure 6.6 Relative density and densification rate for grade B ZrB_2 powders oxidised to 2.2 wt%O. Hot-pressing was performed in argon at 5 °C/ min under 24 MPa or 4.7 MPa load.

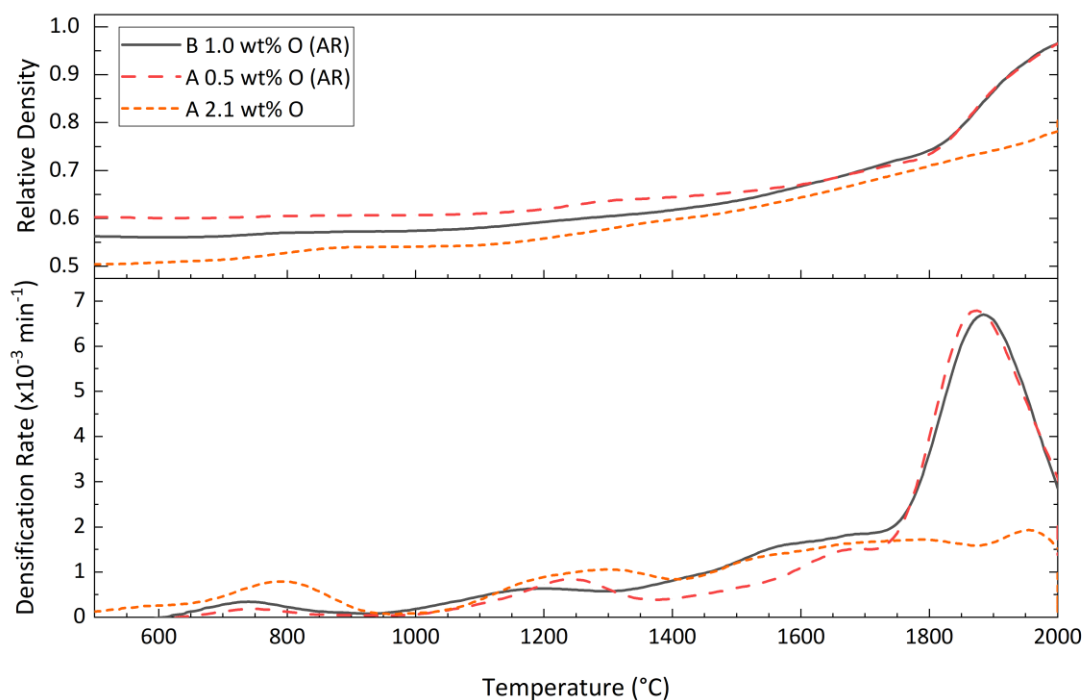


Figure 6.7 Relative density and densification rate for grade A and B ZrB_2 powders, used as-received (AR) or oxidised to the stated oxygen content. Hot-pressing was performed in argon at 5 °C/ min under 24 MPa load.

The oxidised grade A matches the patterns observed for grade B, with lower packing density, increased densification up to 1400 °C from rearrangement due to oxides, and densification from neck growth at similar rates to the grade B-AR between 1400 – 1700 °C. However, the larger powder size means there

will be a lower internal surface area, and the onset of rapid densification is fully suppressed, with a small increase in densification rate from 1880 °C that quickly peaks at just 0.76 relative density, reaching just 0.80 after holding at 2000 °C.

A potential issue with precise processing is exemplified in Figure 6.8a, where the edges of the sample appear close to full density while the centre remains porous. This density is reflected in the energy dispersive spectroscopy (EDS) of Figure 6.8b and e, with an increase in intensity of the overall image and of zirconium. EDS in Figure 6.8c and d shows oxygen and carbon depletion in the dense area, indicating that as carbon infiltrates throughout the ZrB₂ powder, it reacts to reduce surface oxides. This will result in less coarsening in this area of the powder compact, meaning densification will more readily occur at elevated temperatures. This effect has also been observed in reaction hot-pressing of ZrB₂, with a carbon rich layer near the surface of ZrB₂ billets[61].

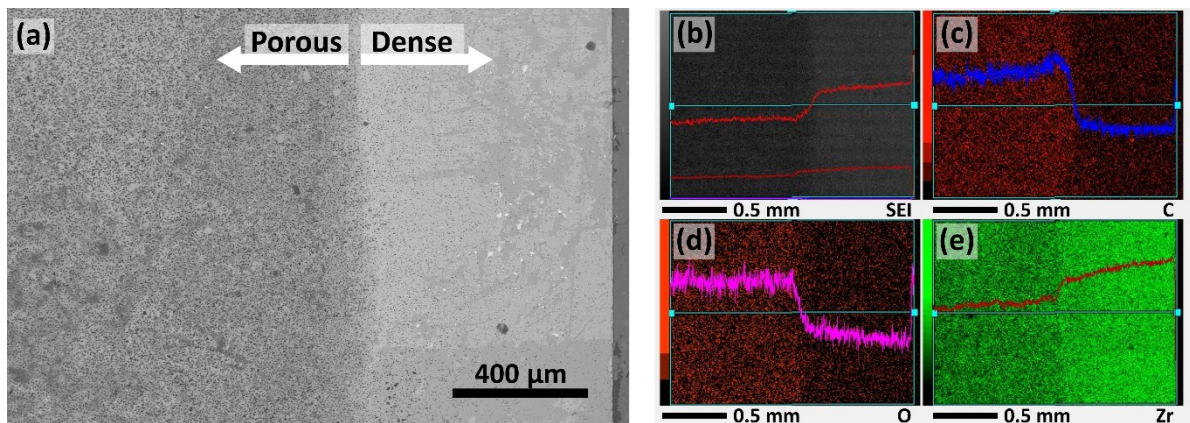


Figure 6.8 (a) Backscatter SEM image showing transition from dense to porous at the edge of the cross section of the 2.2 wt%O grade A powder sample, hot-pressed at 24 MPa/ 5 °C/ min to 2000 °C. Energy dispersive spectroscopy (EDS) maps of the SEM image showing (b) scanning electron image (SEI) intensity, (c) carbon intensity, (d) oxygen intensity, and (e) zirconium intensity.

6.3.2 Heating Rate Effects

The heating rate of the 24 MPa hot-pressing runs was varied for the AR and oxidised grade B powders to further examine the densification behaviour. Figure 6.9 shows the relative density of each of the AR and oxidised grade B powders while heating from 1000 °C to 2000 °C with a heating rate of 2, 5, and 10 °C/ min. For the 2 and 10 °C/ min rates, the density up to 1700 °C does not vary from the previously presented 5 °C/ min data. Density above 1800 °C shows higher density for the slower heating rates, due to the longer times available for densification.

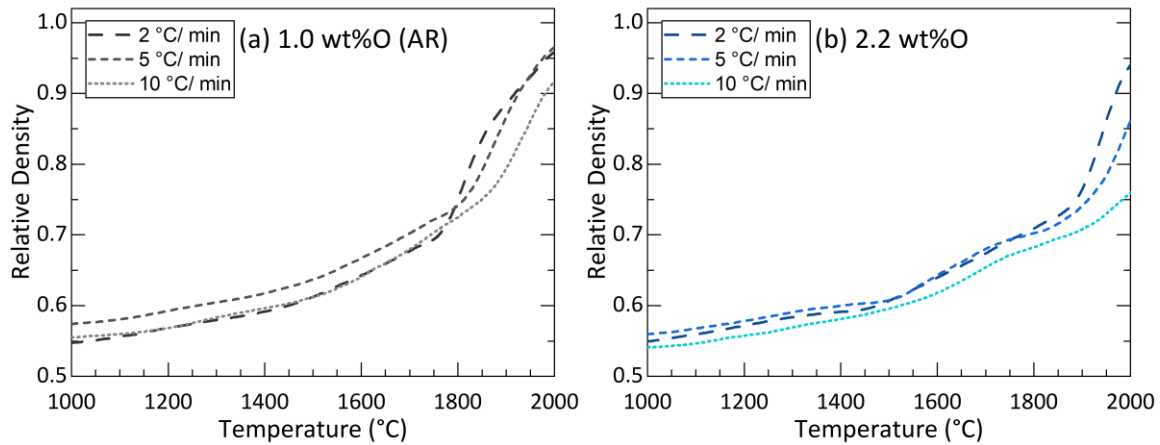


Figure 6.9 Relative density for grade B ZrB_2 powders hot-pressed under a constant pressure of 24 MPa in argon with varying heating rates. (a) As-received (AR) powder, (b) Oxidised to 2.2 wt%O.

Figure 6.10 shows the densification rates with varying heating rates. For both powders, the densification rates increase with increased heating rate across the entire temperature range from 1000 °C to 2000 °C. Figure 6.11 shows the dependence of densification rate to temperature by plotting the densification rate in K^{-1} rather than min^{-1} . This shows that the variation in densification with heating rate up to 1700 °C is tied completely to temperature and not suppressed by the additional coarsening expected from extended exposure of lower heating rates. This is typical of densification from plastic flow, which is expected during neck growth. Densification around particle necks rapidly reduces the dislocation density, preventing further densification by the same mechanism, so more time for densification by slower heating rates does not increase density until the temperature is increased[55].

At temperatures above 1700 °C, the faster heating rates allow less time for densification and coarsening, resulting in a potential energy reduction from sintering to be maintained at higher temperatures. This leads to the accelerated densification rates of the AR powder above 1700 °C. Coarsening will have had a greater effect of the surface area and curvature of the oxidised powders, so their densification rates are lower in comparison. Conversely, faster heating rates will allow less time for evaporation and reduction of oxides, which would benefit coarsening mechanisms. However, as a thermally activated process, evaporation rates are expected to increase exponentially with temperature rise, putting less weighting on heating rate/ time available.

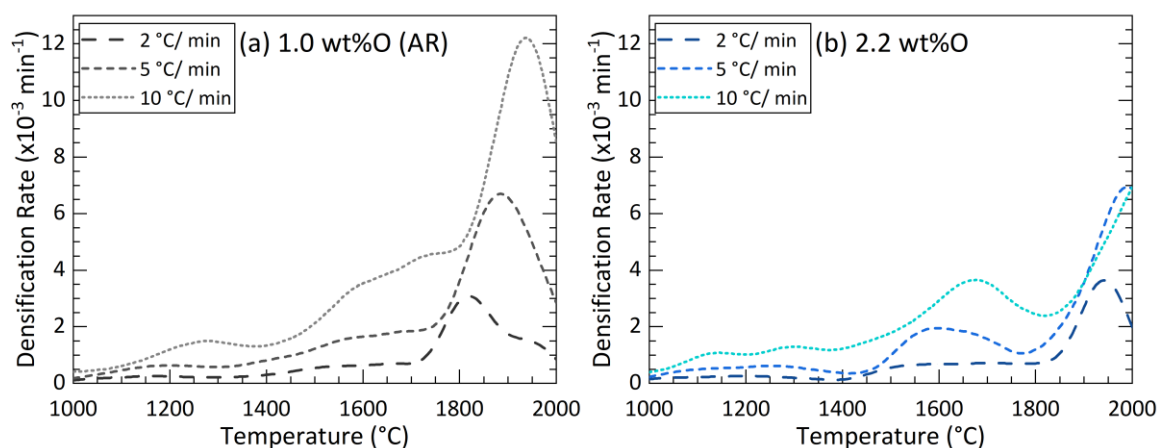


Figure 6.10 Densification rates for grade B ZrB_2 powders hot-pressed under a constant pressure of 24 MPa in argon with varying heating rates. (a) As-received (AR) powder, (b) Oxidised to 2.2 wt%O.

The peak densification rate, signalling a transition to final stage sintering, occurs at lower temperatures with slower heating rates and is strongly tied to density, as was observed in 'Chapter 6.3.1: Powder Size, Pressure, and Oxygen Content'. Table 6.2 records the locations of the peak densification rate, showing all cases in Figure 6.9 - Figure 6.11 peak in densification rate when relative density reaches 0.84, other than the B-AR heated at 2 °C/ min.

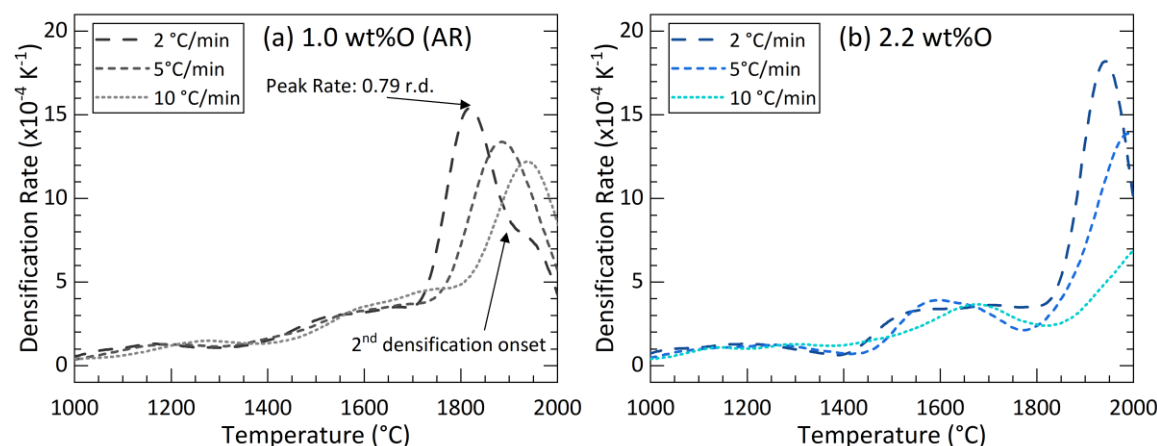


Figure 6.11 Densification rate with respect to temperature for grade B ZrB_2 powders hot-pressed under a constant pressure of 24 MPa in argon with varying heating rates. (a) As-received (AR) powder, (b) Oxidised to 2.2 wt%O. The relative density (r. d.) of the densification rate peak and the 2nd densification onset are indicated for the 2 °C/ min AR sample.

This B-AR sample heated at 2 °C/ min has a shoulder peak in densification rate, peaking at 0.79 relative density with the rate reducing rapidly from 1880 °C. The shouldered peak implies there are multiple onset temperatures for different mechanisms for densification, as the possible energy reduction from the lower temperature densification mechanisms was reaching exhaustion from the peak at 1820 °C/ 0.79 relative density, a second mechanisms activated from 1880 °C. Although by this point the relative density is greater than the 0.84 peak of the other runs, a relative density of 0.87 meant final stage sintering was well under way and still resulted in a continuing decline in densification rate

up to 2000 °C. Faster heating rates did not reach their peak densification rate until > 1880 °C, so the activation of this second rate simply continues to accelerate the densification until 0.84 relative density.

Table 6.2 Densification onset and peak densification rate information for grade B ZrB₂ hot-pressed at varying heating rates from both as-received (AR) and oxidised powder.

	1.0 wt%O (AR)			2.2 wt%O		
Heating Rate (°C/ min)	2	5	10	2	5	10
Densification Onset (°C)	1730	1770	1800	1850	1850	1870
Densification Rate Peak Temperature(°C)	1820	1885	1935	1940	1990	> 2000
Relative Density at Peak	0.79	0.84	0.84	0.84	0.84	> 0.76

The set of oxidised powder in Figure 6.11 show a later onset for densification than the AR powders. Extended time for coarsening granted by slower heating rates would be expected to delay the onset of densification by, however there is little difference in the onset temperature between heating rates of 1850 – 1870 °C. The precise onset of each increase in densification rate is further obscured by the smaller peak from neck growth from 1400 – 1700 °C.

The two possible diffusion pathways for densification in ZrB₂ are grain boundary diffusion and volume diffusion[136]. Grain boundary diffusion occurs at lower temperatures due to a lower activation energy and has been shown to be the rate determining mechanism in densification of ZrB₂ below 2000 °C[61]; this onset can therefore be attributed to the onset temperature of 1730 °C. The second recurring onset temperature of 1850 °C must therefore be due to volume diffusion. This implies that rapid, intermediate stage densification is not possible solely from grain boundary diffusion, but volume diffusion is required for densification due to the over-coarsened nature of the microstructure of the 2.2 wt%O oxidised powders. Faster heating rates used by Lonergan *et al.* will have resulted less coarsening during heating and therefore greater potential densification from grain boundary diffusion, potentially giving rise to the discrepancy between the reported transition to lattice diffusion at 2000 °C rather than the 1850 °C onset observed at the slowest heating rates in the present work.

Grain boundary diffusion requires the accumulation of vacancies diffusing from high concentration at the neck between particles, allowing the grains to rotate to lower energy orientations. The vacancy concentration is higher with higher curvature of the neck, leading to a greater driving force for grain boundary diffusion. Rapid surface transport in the oxidised powders will have reduced the curvature of this neck region while widening the neck[55]. This simultaneously reduces the driving force for grain boundary diffusion while the thick neck presents a more geometrically stable structure. Slowing densification until the activation energy requirement for volume diffusion of vacancies provides an additional diffusion path. These coarse microstructures were permitted to form by slow heating rates,

so rapid heating would likely still result in densification from grain boundary diffusion dominating up to 2000 °C, as reported by Lonergan *et al.* [61].

The lower value of 1730 °C than previously recorded for densification onset in ZrB₂ of 1750 °C from the Monteverde *et al.*[29] hot-pressing study is due to the onset discussed here being the onset of densification rate increase, rather than density increase. However, the measured onset temperature of 1730 °C does match the onset of densification in ZrB₂ during spark plasma sintering (SPS) at heating rates of 300 °C/ min[76], and 50 MPa. The higher heating rate and pressure of the SPS study will have resulting in less time for surface transport mechanisms during heating and increased the densification rates at the onset compared to hot-pressed ZrB₂, giving a more accurate identification of the initiation of densification mechanism, picked up by changes in the sintering rate in this study.

The onset temperature for volume diffusion in the 2 °C/ min AR and all oxidised powder samples predicts that volume diffusion is possible below 2000 °C. The lack of shouldered peaks at higher heating rates for AR powders implies that the rate controlling mechanism is still grain boundary diffusion below 2000 °C, whereas the later on-set temperatures in the oxidised mean volume diffusion is the dominant mechanisms. This agrees with Lonergan *et al.*, who showed that when hot-pressing below 2000 °C the dominant mechanisms was grain boundary diffusion, and volume diffusion above 2000 °C[61].

While this separation of densification mechanism onset may have implications on achieving typical dense, strong UHTCs with fine grains, this optimisation is outside the scope of this work which is focused on manipulation of initial stage sintering to promote neck growth between powder particles and preventing densification.

6.4 Conclusions

Analysis of the densification behaviour for the ZrB₂ powders provides additional context to results of processing and physical properties in the previous chapters, where hot-pressing was limited to just a few different temperatures.

Oxide contaminants cause densification by rearrangement from melting boron below 1000 °C and sintering of zirconia from 1000 – 1400 °C. Initial stage sintering is then shown to begin from 1300 °C, with an additional onset from 1500 °C required for substantial neck growth.

Initial neck growth is a combination of multiple coarsening and densification mechanisms, and the precise contribution of each is not clear. However, the degree to which neck growth causes densification depends on the oxide contamination of powders. Rapid densification was only observed

from 1500 – 1700 °C where sintering aids were used to reduce these oxide contaminants, but this was also limited to neck growth as the rate peaked well before final stage sintering. Boria vapour phase transport and surface zirconia providing fast diffusion pathways for coarsening prevents densification from 1500 – 1700 °C and can delay the onset of rapid intermediate stage densification when powders are further oxidised.

The previous chapter has shown pressure to assist the formation of necks without significant densification up to 1700 °C, a result that is also observed from the densification rates calculated here. The large, low oxygen content grade A powders were also previously observed to have poor neck formation up to 1700 °C, which is evident from a further lack of densification between 1500 – 1700 °C. This is in apparent contradiction to the removal of oxides causing rapid densification in the milled powder. However, the grade B milled powder will have higher curvature from the small particle size, resulting in higher sintering stresses which drive neck growth by plastic flow.

Intermediate stage sintering is defined by a rapid increase in density by grain boundary and volume diffusion. The onset temperature for grain boundary diffusion is shown to be from 1730 °C, in good agreement with the established literature onset temperature for densification of ZrB_2 . A second onset temperature for ZrB_2 densification by volume diffusion is shown to be 1850 °C. With the additional impact from this mechanism often disguised by fast heating rates, it is shown that volume diffusion is required for densification of ZrB_2 where increased oxide contamination has caused excessive coarsening during initial stage sintering and neck growth.

Final stage sintering is defined by the slowing of densification rates as the available driving force is consumed by reduced surface area from densification, and curvature gradients from coarsening. This is shown to consistently occur from 0.84 relative density, regardless of other powder and processing parameters for the ZrB_2 samples studied. The exceptions to this transition were where separate mechanisms for densification were isolated in the case of slow heating rates, or entirely prevented in the case of 5.3 wt%O grade B, and 2.1 wt%O grade A powder.

7 Substructure Channel Design

7.1 Introduction

Transpiration cooling of hypersonic vehicles requires a uniform film of inert gas to cool the material at the leading edge, and to provide protection from corrosion by the atmosphere during the extreme environment of atmospheric re-entry. Partially sintered ZrB_2 has been demonstrated as an effective material for this purpose[5], however low strength, damage tolerance, and thermal shock resistance remain problematic[6]. A requirement of the transpiration cooled material is high thermal conductivity to transport heat away from the leading edge, the temperature through the thickness of the material will, therefore, also be increased. This is problematic, as another engineering problem to overcome is attaching the transpiration cooled layer to the core structure of the vehicle. The temperature at this join will need to be low enough to accommodate the use of metals in the core framework of vehicles.

A proposed design to introduce a dense, or composite, substructure as a joining layer between the partially sintered UHTC and the metal structure of the vehicle, as shown in Figure 1.1, could solve these issues. This combination would allow the mechanical properties of the substructure to augment the porous ZrB_2 . Supplying coolant via channels would then also actively cool the substructure, reducing the temperature of the material at the eventual metal-ceramic join.

The design of the channel arrangement will then allow for control of the fluid distribution across the partially sintered surface layer. This is a desirable function of transpiration cooled systems as they will have a greater cooling requirement closer to the leading edges where temperatures are greatest. Variation of the permeability of the partially sintered layer could achieve this affect, a higher permeability from higher porosity or pore size would increase fluid flow. However, these changes would also reduce the mechanical properties of the UHTC, as discussed in 'Chapter 5: Properties of Porous ZrB_2 '.

There is therefore the question of what effect these channels will have on the fluid flow through the partially sintered layer, and if the flow can be tuned to cooling requirements by tailoring the channelled substructure. Any effects should be tuned such that the fluid flux at the material surface produces an even film rather than jets of fluid, illustrated in Figure 7.1.

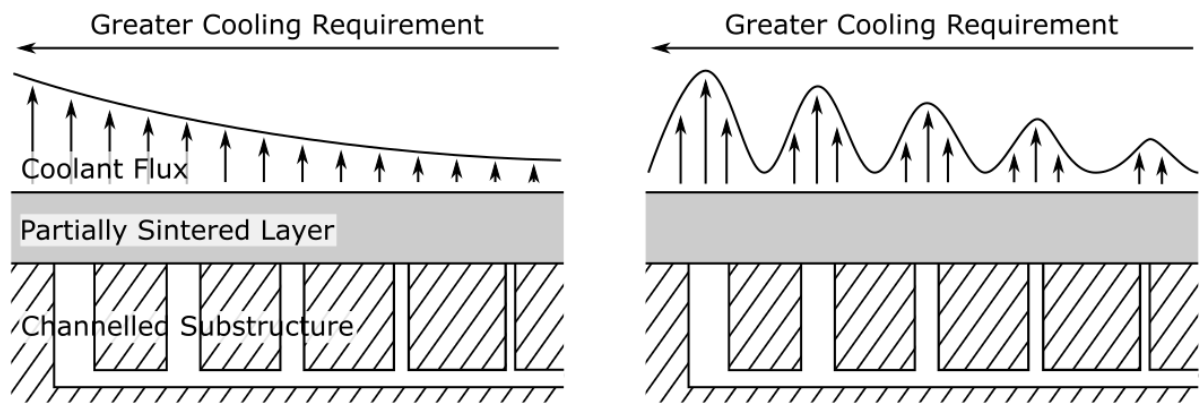


Figure 7.1 Illustration of the desired coolant control (left) and the possible undesired effect of a channelled substructure (right).

Any channel arrangement will be defined by its' channel size and shape, spacing, and unit cell geometry. This chapter will therefore explore how the distribution of coolant to the surface of the partially sintered material is affected by changes in channel array porosity, channel diameter/ spacing, and channel shape, and how the overall permeability of a layered system affected by changes to channel design. By investigating these parameters with finite element analysis, the aim is to develop design criteria for fabrication of dense, or composite, channelled UHTC substructures for further real-world testing.

7.2 Modelling of Gas Flux using Finite Element Analysis

Flow through a permeable layer was modelled in Abaqus/CAE (Dassault Systemes, France). The variables for a two layered structure made up of a permeable surface layer and channelled substructure are: permeable layer thickness, the porosity or specific area of the channels, and the geometry of the channels and their arrangement. These were modelled in 2D and 3D followed by experimental validation. Definitions of specific geometry and channel arrangement variables are case specific so are presented alongside the results in 'Chapter 7.3: Results & Discussion'. This section will detail the parameters and methods used for the finite element analysis (FEA) as well as the details of the experimental validation.

7.2.1 Finite Element Analysis

Abaqus models for heat flow were used in place of Darcy permeability for their matching equations. Darcy's law assumes an incompressible fluid flowing through an inter-connected network of pores, driven by the pressure gradient, expressed in equation 7.1. Darcy is used which assumed low flow rates and flow is assumed to be laminar, with the fluid flux dependant on the permeability of the porous media and viscosity of the fluid[102].

To adapt the heat flow equations, thermal conductivity is replaced with permeability divided by fluid viscosity, and temperature with pressure as shown;

$$q_{fluid} = \frac{\kappa \Delta P}{\mu t} \quad 7.1$$

$$q_{heat} = \lambda \frac{\Delta T}{t} \quad 7.2$$

$$\lambda = \frac{\kappa}{\mu} \quad 7.3$$

Where:

q = Flux of the fluid or heat

κ = Darcy permeability of the material

μ = Viscosity fluid

ΔP = Pressure difference across the thickness

t = Thickness

λ = Thermal conductivity

ΔT = Temperature difference across the thickness

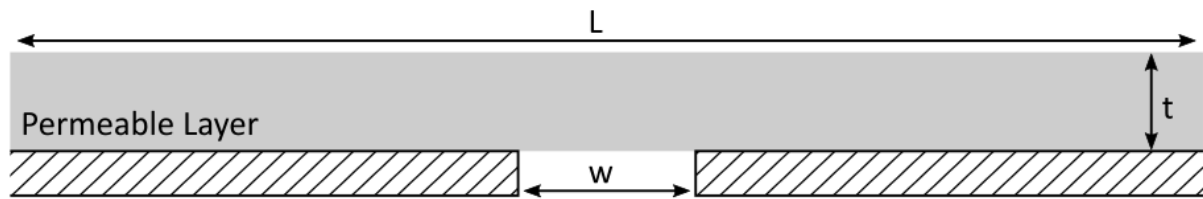


Figure 7.2 Dimension definitions for single hole FEA.

2D models were first studied as fluid being introduced to the permeable layer by a single channel, modelled as a slit with width w , as illustrated in Figure 7.2. The thickness was then increased incrementally, defined by the ratio of the permeable layer thickness, t , to slit width, w . The dimensions of each single hole model are recorded in Table 7.1.

Table 7.1 Dimensions of 2D single hole FEA.

Slit Width (w)	Permeable Layer Thickness (t)	Permeable Layer Length (L)	t/w
1	0.1	10	0.1
1	0.2	10	0.2
1	0.5	16	0.5
1	1	20	1
1	2	20	2
1	5	80	5
1	10	160	10
1	50	800	50
1	200	1600	200

Only flow through the permeable layer was modelled. Pressurised substructure channels were represented by the area over which fluid would be able to flow into permeable layer from the channel. In the case of 2D models this is a line segment, with width w, at the base of the permeable layer as shown in Figure 7.3.

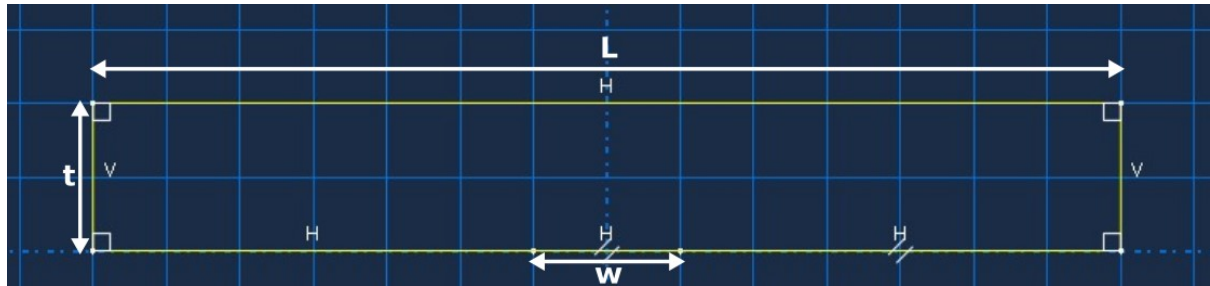


Figure 7.3 Image of 2D part creating in Abaqus for fluid flow modelling. The partially sintered layer, with width L and thickness t, is shown with a line segment partitioned to represent the channel, with width w, by which fluid will flow into the permeable layer.

Arrays of channels were then modelled for a variety of cases, defined by the dimensions in Figure 7.4. Each system is first defined by the porosity of the substructure due to the channels, Φ , defined in 2D by the channel width, w, and channel spacing or unit cell width, L, as in the equation;

$$\text{Channel porosity} = \Phi = \frac{w}{L} \quad 7.4$$

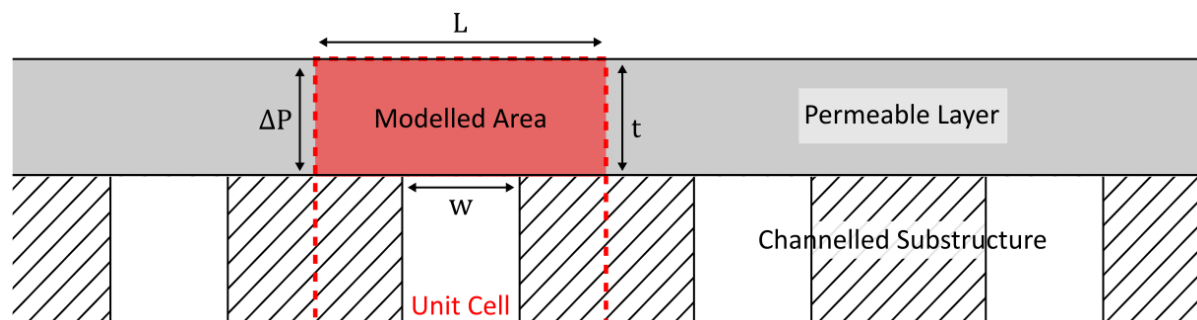


Figure 7.4 Unit cell for 2D channel arrays. The spacing, L, porous layer thickness, t, and channel width, w, are defined for FEA

Four different channel porosity cases are considered: 1, 5, 10, and 20 %. The secondary definition of each case is the size and spacing of the channels, relative to the permeable layer thickness, i.e., narrow channels spaced closely together can have the same channel porosity (Φ) as wide channels spaced far apart. This variation in spacing is therefore defined as the ratio of channel width to layer thickness, t/w , or channel spacing to layer thickness, t/L . Each channel porosity case is modelled from a t/w ratio from 0.5 to 200. This variation in spacing, channel size, and thickness is demonstrated in Figure 7.5, showing how either layer thickness or channel size can be held constant.

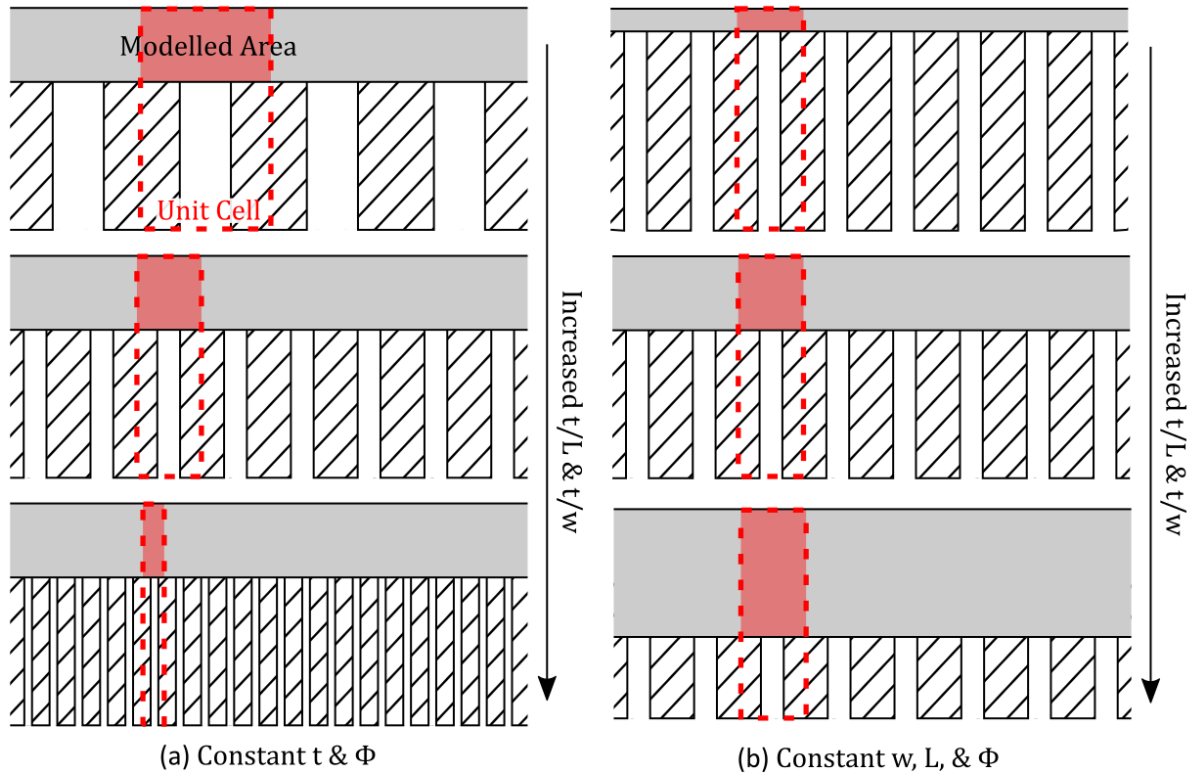


Figure 7.5 Illustration of how varying the channel arrangement definition of slit width (w) and unit cell width (L) ratio to thickness (t) appears in 2D while maintaining constant thickness (a) or constant slit and unit cell width (b).

The desired result is to compare the variation in t/w and t/L for constant t and Φ . However, for practical purposes the unit cell width, L , and slit width, w , are fixed for each porosity case when modelled in Abaqus and the arrangement ratios t/w and t/L varied by adjusting the thickness, t .

As each model is defined by the ratio of the slit width to the thickness ratio, t/w , for equal channel porosity, a thickness of 2 with a spacing of 1 is considered equal to a thickness of 4 with a spacing of 2, and so on. In practice, this thicker layer would lead to lower surface flux for equal permeability according to Darcy's Law for permeable flow, equation 7.1.

As the changing the t/w definition is achieved by modifying t , models are normalised by modifying κ/μ such that the resultant flux is comparable between cases, t appears constant and therefore the expected surface flux should the substructure be removed is unchanged. This is achieved by setting

κ/μ for each model to equal the thickness and the pressure difference set to 1. In the case with no substructure, with pressure applied uniformly across the bottom surface of the permeable layer, this produces a one-dimensional result with fluid flux equal to 1 at the surface of the permeable layer, as shown in Figure 7.6a, regardless of t .

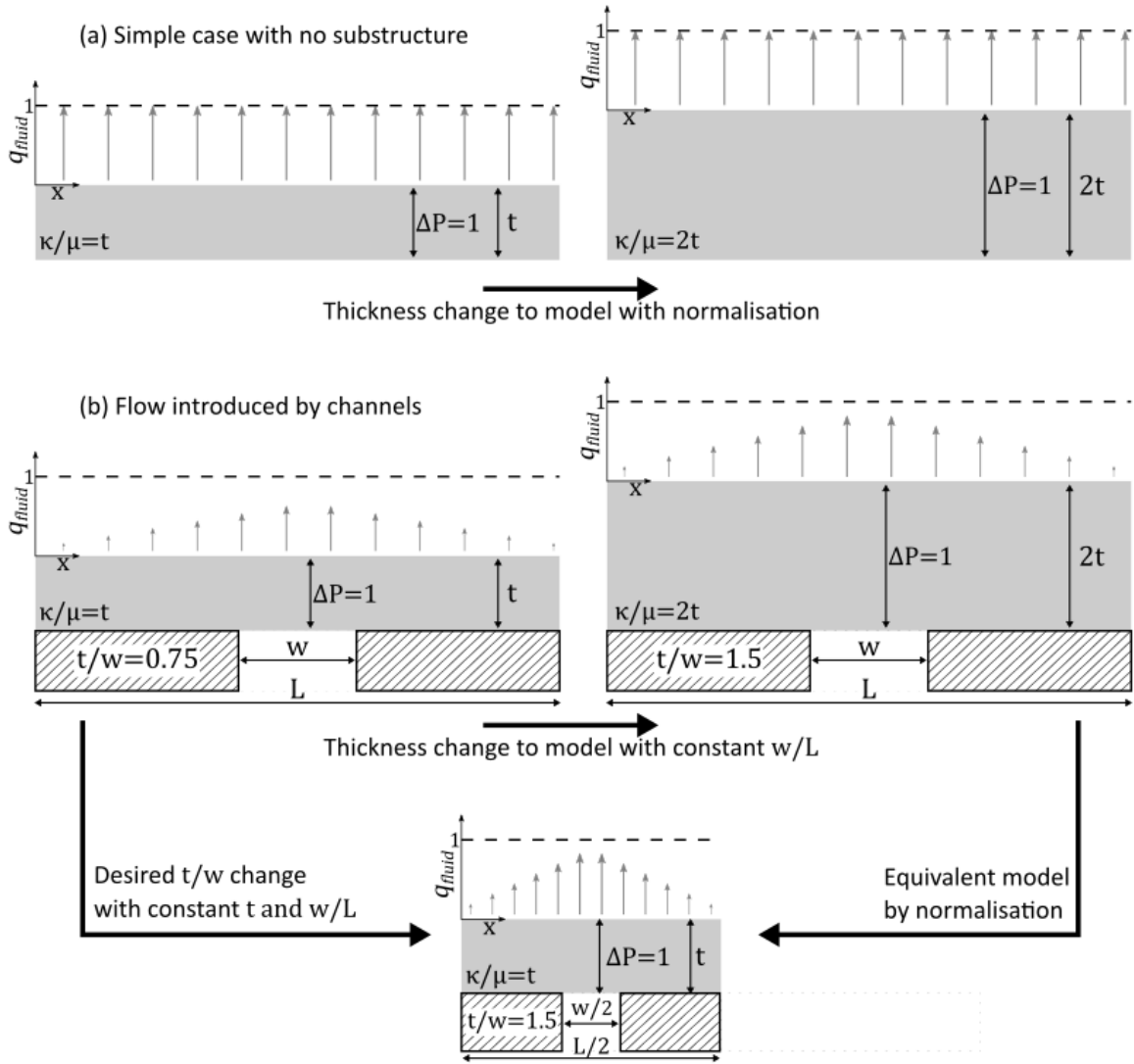


Figure 7.6 Illustration of thickness/size normalisation for FEA fluid flow models for; (A) the simple case without a substructure, and (B) when flow is introduced via channels. The ratio of permeability and fluid viscosity, κ/μ , is set equal to the thickness, t , for the normalisation. The pressure difference, ΔP , is set to 1 the fluid flux, q_{fluid} , at the surface is then 1 for the simple case, independent of thickness.

Variation in the t/w ratio is now comparable as the thickness is normalised and the surface flux is calculated relative to the case where the substructure is removed being equal to 1 at all points. This thickness normalisation for changes to the t/w ratio is demonstrated in Figure 7.6b.

This normalisation is demonstrated to be valid in Figure 7.7, where the same $t/w = 1$ model is scaled up 10, and 100 times to show that by changing the property κ/μ by the same factor as the thickness, the calculated results for fluid flux are identical. For real expected values of coolant flux, the expected

surface flux can be calculated for real values of permeability, viscosity, pressure, and thickness for the simple uniform case without a substructure from the equations for Darcy permeability. This expected flux could be multiplied by the relative flux predicted by the model for that t/w case to calculate the coolant fluid flux expected at the surface of the permeable layer.

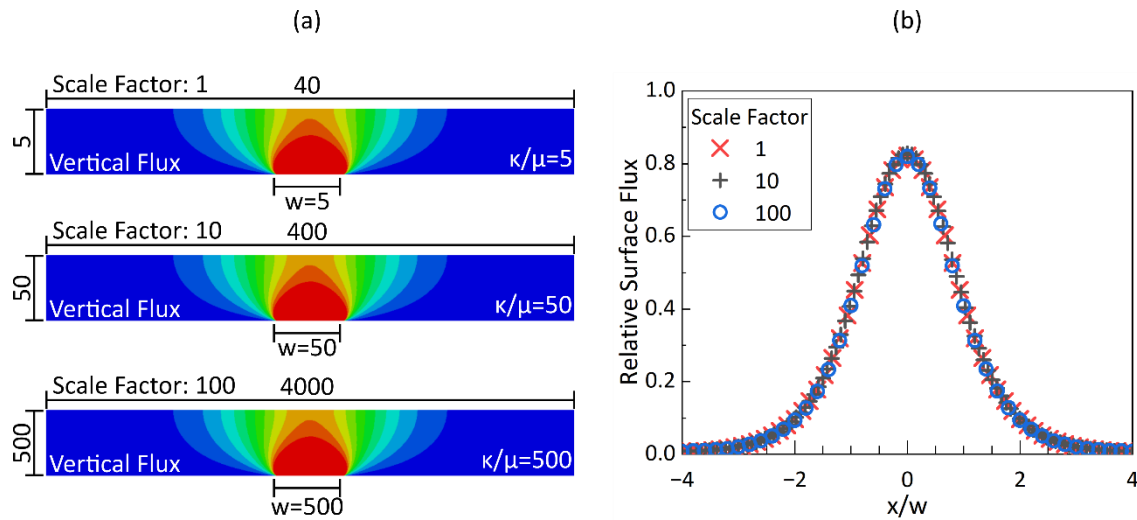


Figure 7.7 Models with matching t/w ratios but different thickness. (a) $t/w = 1$ for all three scales of model defined as by the scale factor 1, 10, and 100 with dimensions labelled on the fluid flux FEA result. The κ/μ scaled by the same factor to normalise the change in scale. (b) The measured surface flux along the top surface of the permeable layer, plotted against the lateral position divided by the hole width (w) to maintain the scale of each model.

Once this permeability property is set, to model the part in Abaqus, a solid homogeneous section is created with the defined material property. This section is then applied to the created part, and an assembly is created with the permeable layer part added. A steady state heat transfer step is then created after the initiation, with a time period of 1 and minimum increment of 1×10^{-5} .

For this step, boundary conditions are defined to represent the pressure from the coolant fluid flow. Where the channel would introduce the fluid at the back surface of the permeable layer, the pressure is defined by setting the boundary condition temperature to 1.0. To represent the pressure at the open top surface of the permeable layer, a second temperature boundary layer is set to equal 0, as shown in Figure 7.8. This mean that the surface flux measured at the top surface should equal 1.0 for the simple case with no substructure, so the flux calculated by the model is a relative flux compared to this case. It is important to note that for real scenarios the expected flux from the permeability and thickness would need to then be calculated, and then multiplied by the predicted relative flux.

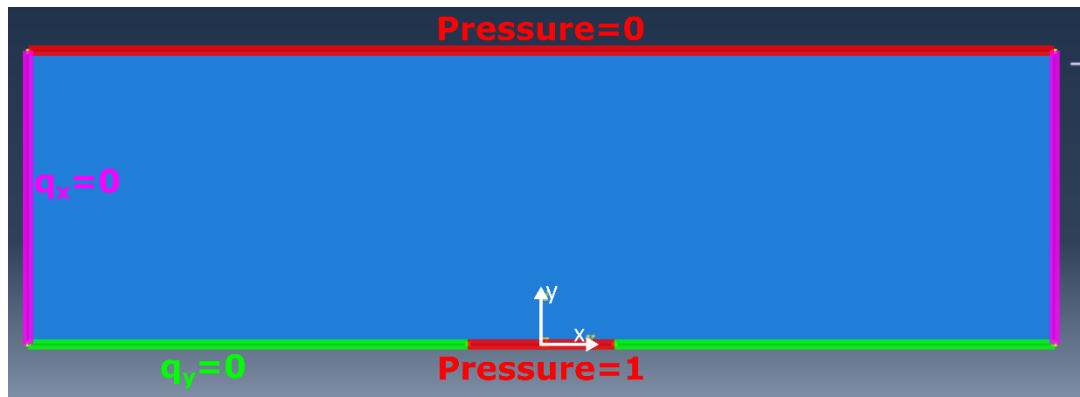


Figure 7.8 Image from Abaqus FEA set-up for boundary conditions. The fluid flux (q) boundary conditions are a result of the free boundary.

The sides of the part were seeded according to the requirements of the geometry to be finely meshed where pressure gradients were high but then to have greater spacing away from the channel entrance. The line segment with the boundary conditions for introduction of fluid were seeded with no bias to have 100 nodes along their length. The remainder of the bottom edge was then seeded with a single bias each side of the slit to make the seed size coherent with the slit line segment where they joined and increasing in size towards the outer edge of the unit cell. The vertical sides of the part were then seeded depending on the thickness, t . To avoid excessively small mesh sizes that would result in longer calculation time or breaching the node limit for the version of Abaqus used, a single bias was used to seed these edges such that the mesh was fine as at the bottom surface, but large at the top surface. The top surface was then seeded to match the larger seed spacing of the vertical sides. The parts were then meshed with the following parameters; Quad-dominated, technique: Free, Advancing front algorithm. The effects of these seed and meshing parameters are shown in Figure 7.9 for three unit cells of equal porosity but greatly different permeable layer thickness, resulting in a t/w ratio of 2, 20, and 200.

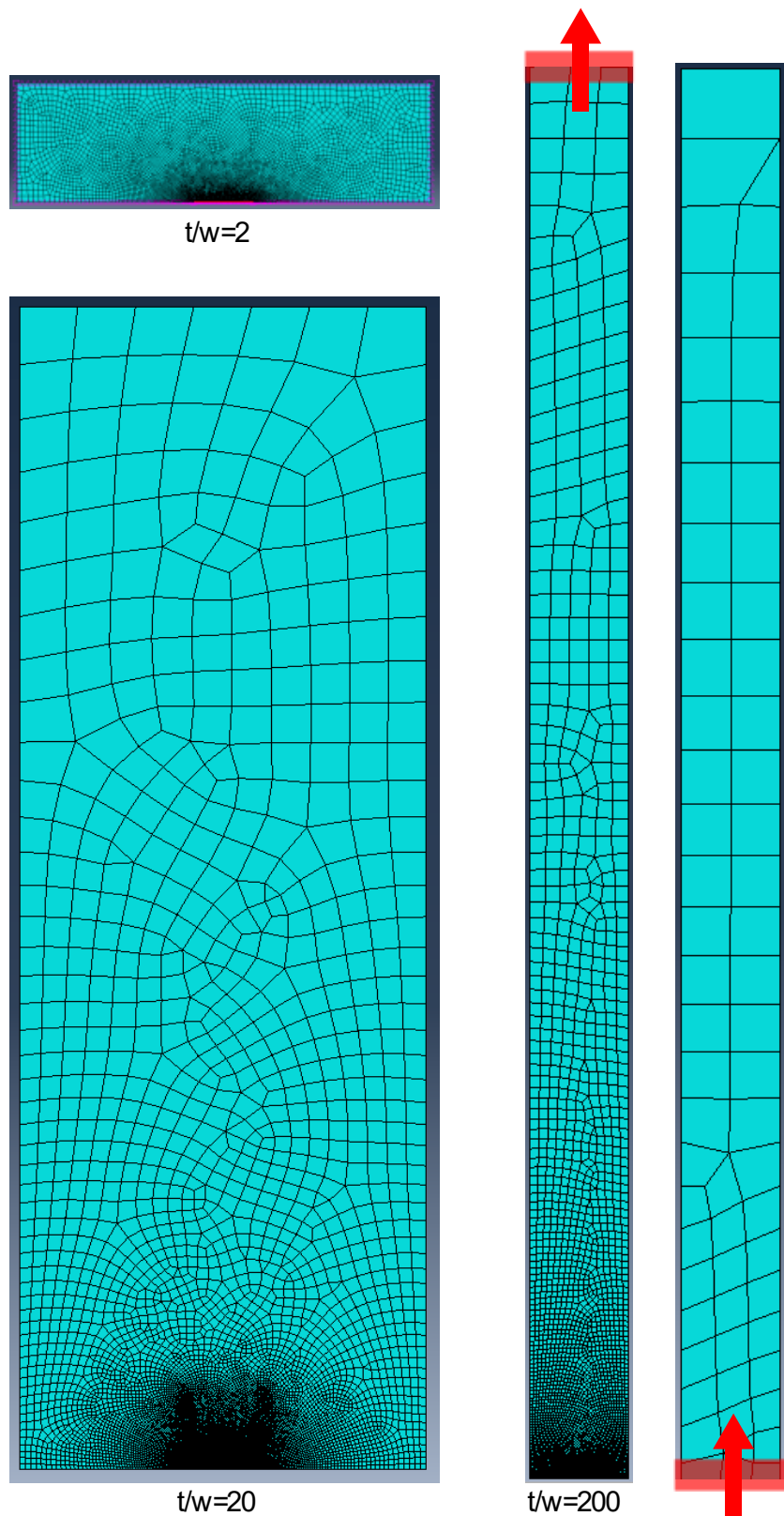


Figure 7.9 Meshing examples for three parts of equal channel porosity with thickness, t , of 20, 200, and 2000 and equal width, w , of 1 to achieve varied t/w ratios for analysis. The $t/w = 200$ case has been split, indicated by the red line and arrow, to fit a single page.

FEA for 3D channelled substructures was performed exactly as with 2D but with additional definitions of channel geometry and arrangement. Four different styles of channel geometry were used, detailed in Figure 7.10. Each design was made with 10 % channel porosity, defined in 3D as;

$$\frac{\text{Channel Cross Section Area}}{\text{Unit Cell Cross Section Area}} = \Phi \quad 7.5$$

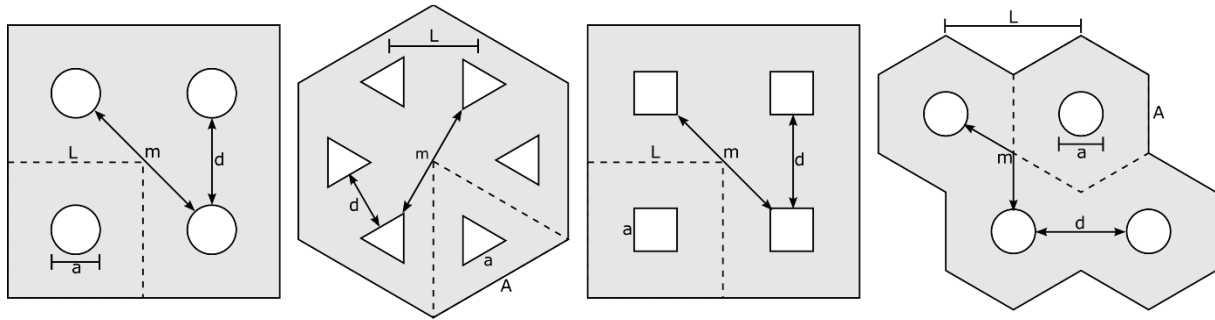


Figure 7.10 2D section of 3D unit cells for typical channelled substructures. The unit cell porosity is defined by the characteristic unit cell length A , and channel dimension a . m is the maximum distance between channel edges, and d the minimum distance. Where the unit cell dimension is equal to the distance between nearest channel centres, L , A is omitted.

As with the 2D series, the ratio of the permeable layer thickness to channel size and spacing was varied. As there is no common variable for channel geometry, the t/L ratio was varied for each 3D case from 0.1 to 8.

3D unit cells were made by extruding the unit cell geometry to the thickness required for the specified t/L ratio. The channel area can then be partitioned onto the base of the unit cell. The same boundary conditions are then applied as in the 2D case, with the pressure set to 1 at the channel and 0 at the top surface, as shown in Figure 7.11. The geometry of each unit cell is given by the following equations for channelled porosity, where r is the channel radius. For print the geometries expected from robocasting, is useful to relate the channel porosity and dimensions to filament width, n . For the PrintTri pattern, the line spacing is the height of the triangular unit cell, H .

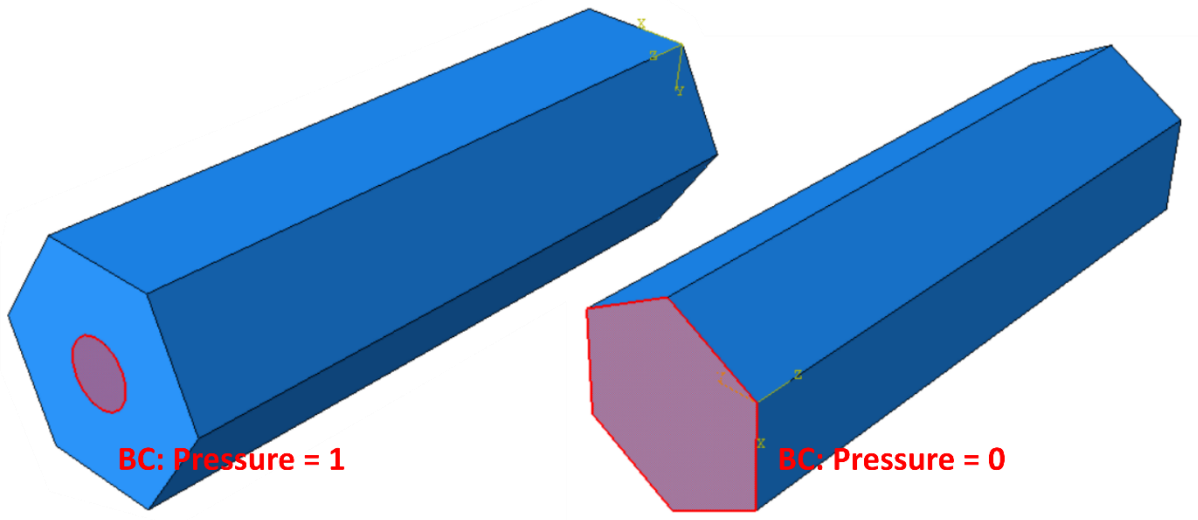


Figure 7.11 3D model example for Hex channel arrangement. Partition for the channel area is shown for the boundary condition of pressure in the channel (left), and at the top surface (right).

The 3D parts were then meshed with the same principles as 2D, with finer mesh close to the channel. The 3D models had the same issues as 2D when working with high aspect ratio models like that of $t/w=200$ case in Figure 7.9. This problem was exacerbated in 3D as the number of nodes is far higher with the extra dimension. If the limit of 250,000 nodes was reached the model would be split along lines of symmetry. The definitions and arrangements of each 3D pattern shown in Figure 7.10 is defined by the porosity in Table 7.2.

Table 7.2 Arrangement label and geometry for the four 3D channel arrangements measured.

Label	Arrangement	Channel Porosity, Φ
Square	Cylindrical channels in a square unit cell	$\frac{\pi r^2}{L^2}$
Hex	Cylindrical channels in a hexagonal unit cell	$\frac{2\pi r^2}{3\sqrt{3}A^2} \equiv \frac{2\pi r^2}{\sqrt{3}L^2}$
Print Square	Square channels in a square unit cell	$\frac{a^2}{L^2} \equiv \frac{(L-n)^2}{L^2}$
Print Tri	Triangular channels in a triangular unit cell	$\frac{a^2}{A^2}; a = A - \sqrt{3}n; A = \frac{2\sqrt{3}H}{3}$

7.2.2 Experimental Validation

For experimental validation of the FEA results, the permeability of a 30 % porous ZrB_2 disc, 80 mm in diameter with thickness 14.45 mm, was measured with the experimental setup described in 'Chapter

3.4.6: Permeability'. This permeability was then used as a reference for the case where no channelled substructure is present.

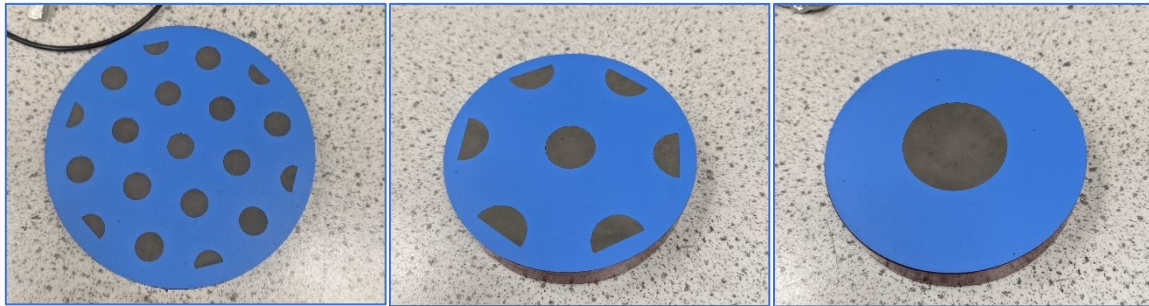


Figure 7.12 Example photos of vinyl stickers used as masks for 80 mm discs during permeability measurements.

Due to the high permeability of channelled substructures expected, as calculated by the Hagen–Poiseuille equation, the thickness of the substructure is expected to have little effect. Therefore, these substructures were represented in the validation by vinyl stickers, an example of which is shown in Figure 7.12. The holes in the stickers were arranged as cylindrical channels in a hexagonal array. The permeability of the ZrB_2 disc was measured with a selection of the vinyl stickers with a channel porosity of 10 % and 20 %. The channel size, spacing, and resultant t/L ratios are shown in Table 7.3. Between each permeability measurement, the ZrB_2 was washed with acetone to remove as residue. For comparison to the FEA, additional 20 % porous 3D Hex channels were modelled.

Table 7.3 Dimensions for vinyl stickers of 10 % and 20 % specific channel area.

Hole Radius (mm)	10 % Channel Porosity	11.50	5.76	2.88	2.30	1.64	1.15	0.89
	20 % Channel Porosity	16.27	8.15	4.07	3.25	2.33	1.63	1.25
Hole Spacing (mm)		69.28	34.70	17.33	13.85	9.90	6.92	5.33
Sample Thickness/ Spacing		0.21	0.42	0.83	1.04	1.46	2.09	2.71

7.3 Results & Discussion

The results from the progression of modelling from a single slit in 2D, 2D channel arrays, and 3D channel geometry are presented in this section alongside a discussion of the results. The experimental validation is compared to 3D models with a discussion of errors and assumptions made during modelling and validation. While presenting the results, the meaning of the ratios t/w and t/L are reiterated as they are case specific, alongside examples of the FEA raw data and summary figures.

7.3.1 Single Hole

The first case studied is the 2D single hole case. Figure 7.13 shows the model for a very large channel compared to the thickness of the permeable layer, defined by the slit width (w) and thickness (t) ratio

$t/w = 0.1$. The data shows that in the central region above the hole the relative surface flux is 1.0, the flux would be no different if the substructure was removed. This is mirrored in the pressure distribution in the material between the surface and the substructure, with flat, straight contour lines of equal spacing between each surface. The surface flux then decays away from the edge of the slit. The pressure can be seen to drop away rapidly in the horizontal direction and, likewise, the fluid flow rates.

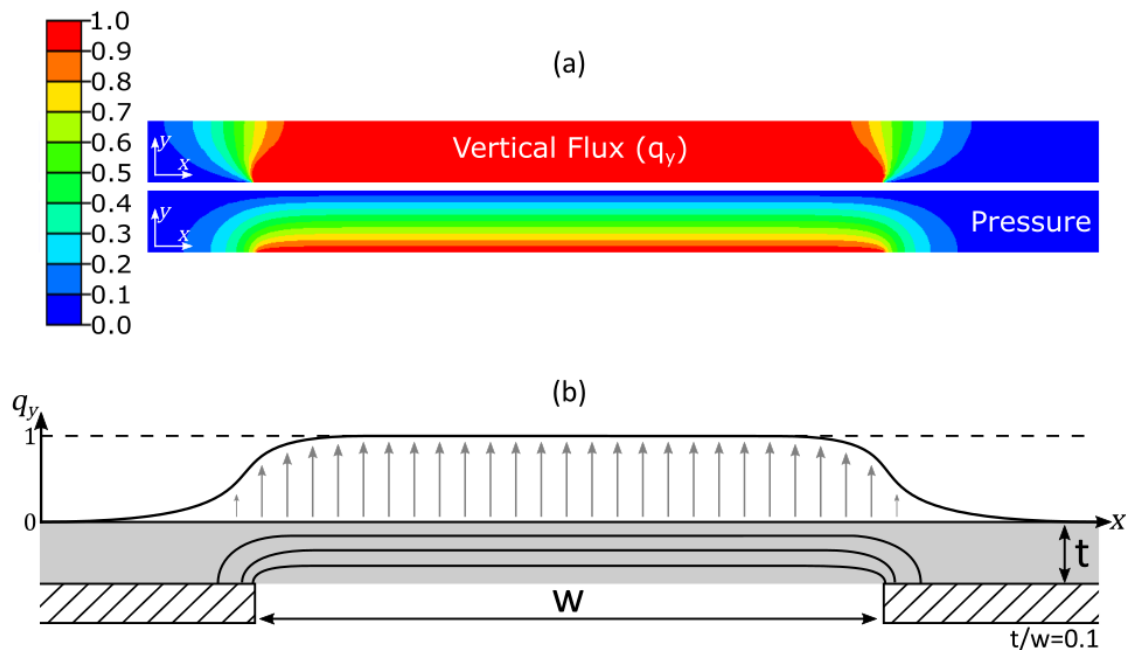


Figure 7.13 Example of FEA pressure and flux data for the single-hole case where the ratio of layer thickness, t , to channel width, w , $t/w=0.1$. (a) Raw FEA output data for vertical flux and pressure through the permeable layer. (b) Schematic data representation showing channelled substructure, pressure contour throughout the permeable layer, and the surface flux (q_y) plotted above the permeable layer relative to if the substructure was removed and flow unrestricted.

Figure 7.14 then shows a case where the thickness of material is equal to the slit width, $t/w = 1$. This still shows the highest surface flux is centred directly above the slit, but this maximum relative flux is now 0.82, decaying away from the centre and away from the slit edge. The pressure contours arc round much more across the width of the slit compared to Figure 7.13. The changes from $t/w = 0.1$ to $t/w = 1$ are continued and exaggerated in Figure 7.15 for $t/w = 10$, where the thickness is 10 times greater than the slit width. The pressure drops quickly away in all direction from the slit into the permeable layer, meaning high pressure gradients are only seen very close to the slit opening, reducing the maximum relative surface flux to 0.40. The surface flux distribution can be seen to spread widthways from the slit at the material surface though, despite its reduced peak the measured surface flux extends for many times the width of the slit itself. The shape of this surface flux distribution is plotted for the surface directly above the slit for varying t/w ratios from 0.1 to 50 in Figure 7.16.

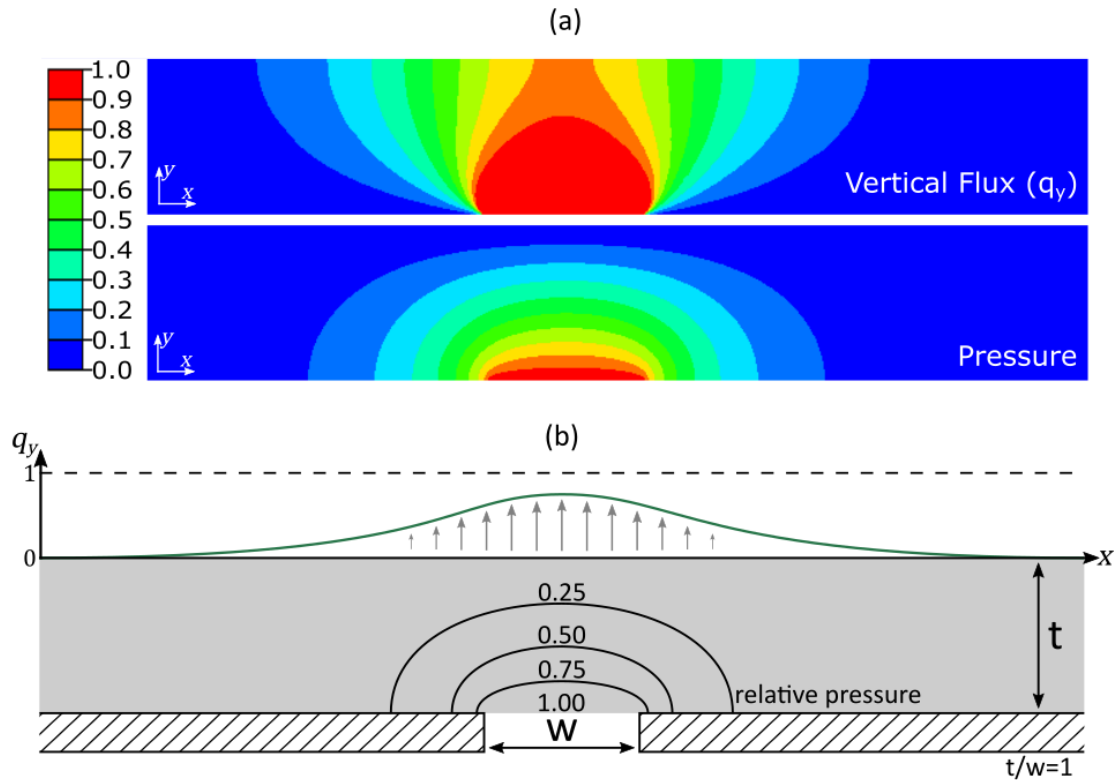


Figure 7.14 Example of FEA pressure and flux data for the single-hole case where the ratio of layer thickness, t , to channel width, w , $t/w=1$. (a) Raw FEA output data for vertical flux and pressure through the permeable layer. (b) Schematic data representation showing channelled substructure, pressure contour throughout the permeable layer, and the surface flux (q_y) plotted above the permeable layer relative to if the substructure was removed and flow unrestricted.

Figure 7.16a shows the relative surface flux close to the single hole, at the top surface of the permeable layer, for varying ratios of t/w . It can be seen when t/w is low then the flux at the surface above the hole is equal to the expected flux should the pressure be applied equally across the back of the permeable layer. This flux then reduces near the edge of the slit and decays rapidly with increasing distance from the edge. This low t/w is represented in Figure 7.13, as t/w increases the width of the slit is reduced relative to the thickness of the permeable layer. Figure 7.16 shows that this leads to a reduction in the maximum surface flux measured above the hole and a wider surface area over which flux is recorded. The flow is less concentrated above the hole and spreads further in relation to the slit width. This is represented in Figure 7.15 showing varying t/w ratios by both increasing the thickness of the permeable layer and reducing the width of this pressurised slit below the material.

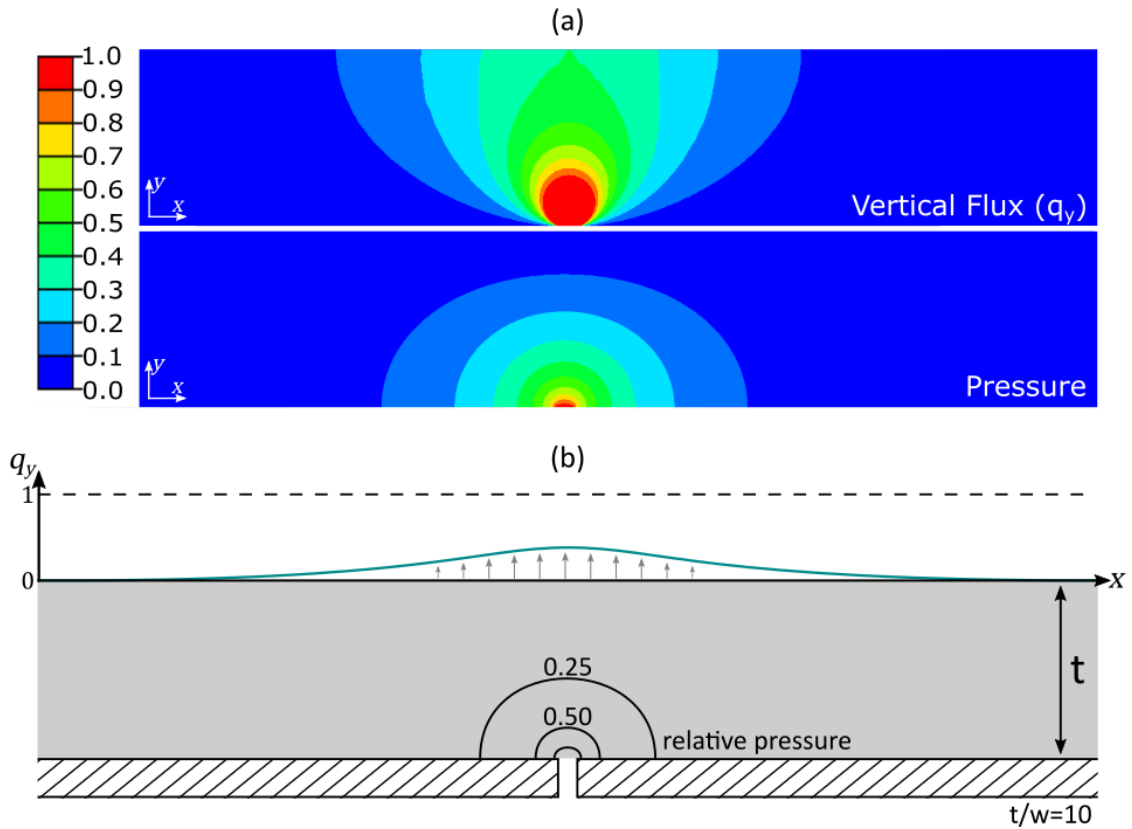


Figure 7.15 Example of FEA pressure and flux data for the single-hole case where the ratio of layer thickness, t , to channel width, w , $t/w=10$. (a) Raw FEA output data for vertical flux and pressure through the permeable layer. (b) Schematic data representation showing channelled substructure, pressure contour throughout the permeable layer, and the surface flux (q_y) plotted above the permeable layer relative to if the substructure was removed and flow unrestricted.

Figure 7.16b then plots the maximum measured surface flux above a single slit at surface of the permeable layer for each of the t/w cases. This summarises the data seen in Figure 7.16a and shows a reduction in maximum surface flux as either the thickness of the permeable layer is increased, or the width of the slits is reduced. This highlights the requirement for a single slit dimension < 0.2 for the maximum surface flux to equal 1.0, without dissipation of pressure laterally through the layer. How this pressure interacts with neighbouring channels will be assessed in the following sections.

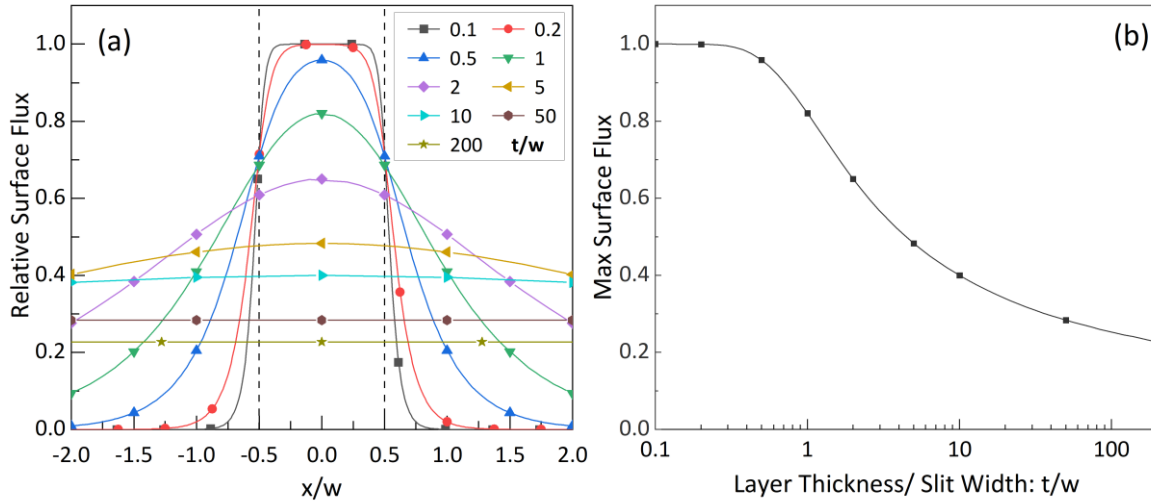


Figure 7.16 (a) Surface flux for each FEA single-hole case. Surface flux is plotted against distance from the centre of the pressurised slit (x), normalised by with slit width (w). (b) Maximum measured surface flux from (a) for each t/w single hole case.

7.3.2 2D Channels

For the application of transpiration cooling, fluid will be introduced through a permeable layer via multiple channels in a dense substructure. This is modelled as a unit cell of permeable material above one of these channels as defined in Figure 7.4. How varying the channel arrangement affects the appearance of channel width, spacing, and permeable layer thickness for a fixed specific channel area if visualised in Figure 7.5. This can either be viewed as making the permeable layer thicker to increase t/w , or changing the size and spacing while keeping thickness constant. For simplicity in this work and for direct comparison between relative surface flux for each t/w case, each model will be considered to have equal permeable layer thickness, with the spacing and size of channels varied depending on desired t/w ratio and specific channel area.

An example of the unit cell calculation for a channel porosity of 20 % and a t/w ratio of 0.2 is shown in Figure 7.17. Each channel behaves as the models for the single whole case, seen previously in Figure 7.13 and Figure 7.16. The relative flux directly above the slit is equal to 1.0, as though no substructure were present, but decays quickly along the horizontal axis away from the channel edge. The channels are too far apart for any overlap as the fluids permeates to the surface, resulting in separate jets of fluid and therefore does not satisfy the criteria for transpiration cooling.

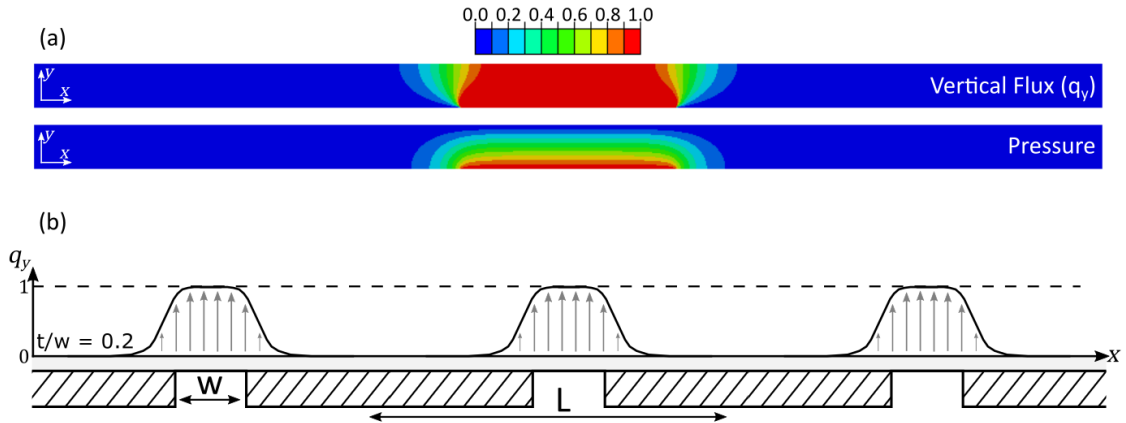


Figure 7.17 Example of FEA pressure and flux data for the 2D channel case with 20 % channel porosity and the ratio of layer thickness, t , to channel width, w , $t/w=0.2$. (a) Raw FEA output data for vertical flux and pressure through the permeable layer. (b) Schematic data representation showing channelled substructure, pressure contour throughout the permeable layer, and the surface flux (q_y) plotted above the permeable layer relative to if the substructure was removed and flow unrestricted.

Figure 7.18 then shows a second unit cell FEA example with a t/w ratio of 1, the same as the single hole case in Figure 7.14. The surface flux is still clearly non-uniform, concentrated above the channels by which the fluid is introduced. The maximum surface flux produced has reduced from 1.0 to 0.82, fitting with the trend seen for the single hole arrangements. However, the spacing between channels is small enough for the minimum relative flux at the surface of the permeable layer to be greater than zero; the system is no longer behaving as multiple single holes.

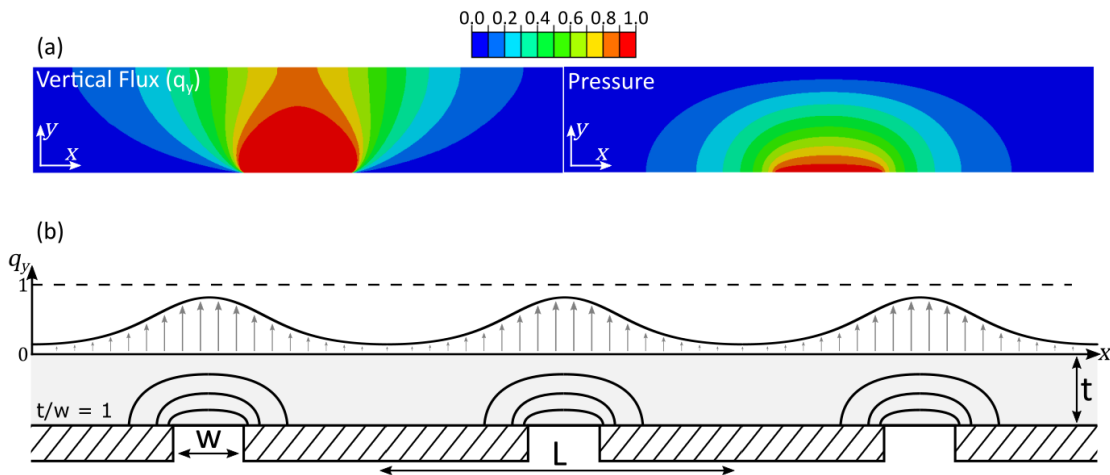


Figure 7.18 Example of FEA pressure and flux data for the 2D channel case with 20 % channel porosity and the ratio of layer thickness, t , to channel width, w , $t/w=1$. (a) Raw FEA output data for vertical flux and pressure through the permeable layer. (b) Schematic data representation showing channelled substructure, pressure contour throughout the permeable layer, and the surface flux (q_y) plotted above the permeable layer relative to if the substructure was removed and flow unrestricted.

This complimentary mixing of fluid between channels continues and is further enhanced for the cases shown in Figure 7.19. Here, two more examples where the t/w ratio is further increased such that the fluid is introduced via smaller slits spaced closer together while maintaining the same 20 % porosity of channels. The flow at the surface is entirely uniform across the unit cell for $t/w = 4$ in Figure 7.19b. The maximum surface flux increased by changing $t/w = 2$ to $t/w = 4$ from 0.68 to 0.70.

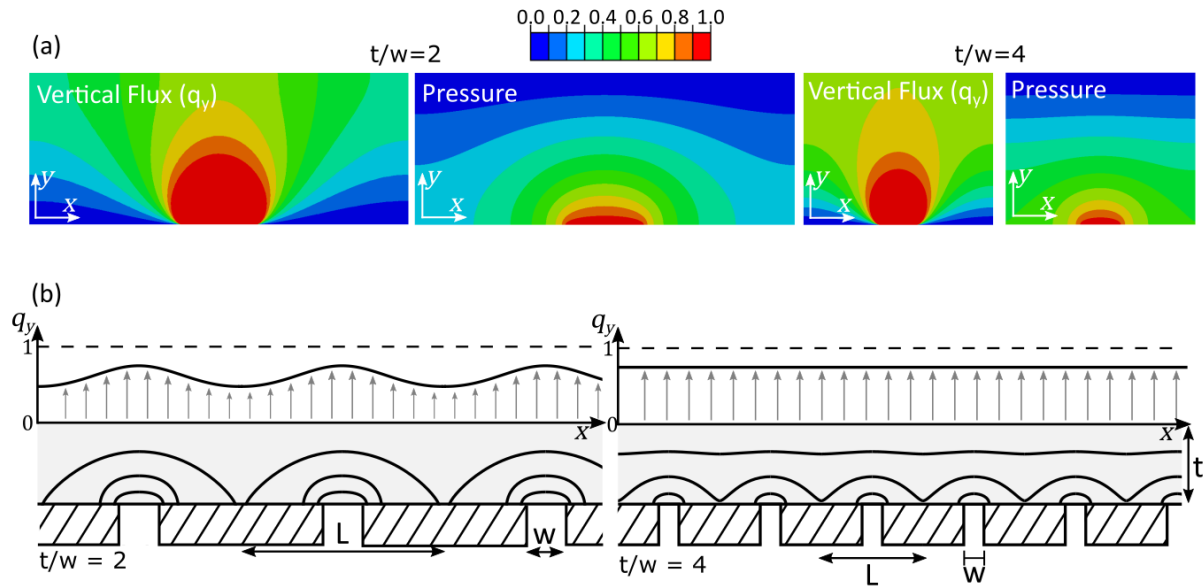


Figure 7.19 Example of FEA pressure and flux data for the 2D channel case with 20 % channel porosity and the ratio of layer thickness, t , to channel width, w , $t/w=2$ and $t/w=4$. (a) Raw FEA output data for vertical flux and pressure through the permeable layer. (b) Schematic data representation showing channelled substructure, pressure contour throughout the permeable layer, and the surface flux (q_y) plotted above the permeable layer relative to if the substructure was removed and flow unrestricted.

The example data shown in Figures 7.17, 7.18, and 7.19 is then plotted with relative surface flux versus x/L in Figure 7.20 for 1, 5, 10, and 20 % channel porosity. Where L is the length of the unit cell as defined by the slit width and porosity in Figure 7.4. As the channel porosity is increased, the peaks of relative surface flux broaden for equal t/w ratios. This is expected as the slit will be wider, taking up more of the substructure area. This then leads to greater interaction between channels for arrangements with higher specific area, i.e. for the 1 % arrangement the surface flux decays to 0 at the unit cell edges for the $t/w = 10$ case, whereas for both the 10 % and 20 % cases $t/w = 10$ shows an almost perfectly even distribution of surface flux across the unit cell area, and therefore across the entire surface.

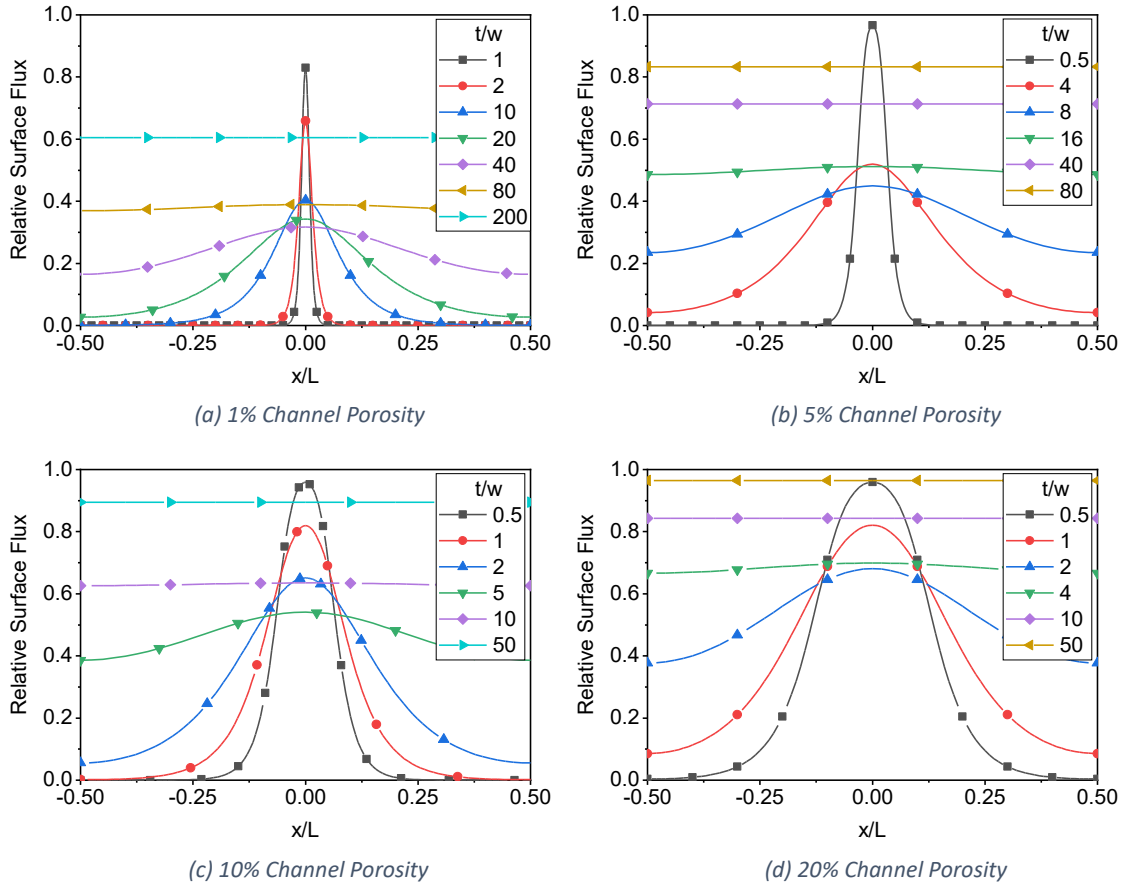


Figure 7.20 Relative surface flux across the unit cell top surface for multiple t/w scenarios for channel systems with 1, 5, 10, and 20 % channel porosity, layer thickness t , and channel width w .

However, for each channel porosity the same trend is observed. As t/w is increased, the maximum flux reduces but the minimum rises as slits are narrowed and moved closer together. There is a t/w value for each case where the maximum surface flux observed starts to increase towards 1.0 and then surface flux becomes evenly distributed across the entire unit cell width. As the even distribution is of interest to the application of transpiration cooling, the minimum and maximum surface flux for cases ranging from $t/w = 0.1$ to 200 for the 1, 5, 10, and 20 % specific channel area are compared in Figure 7.21.

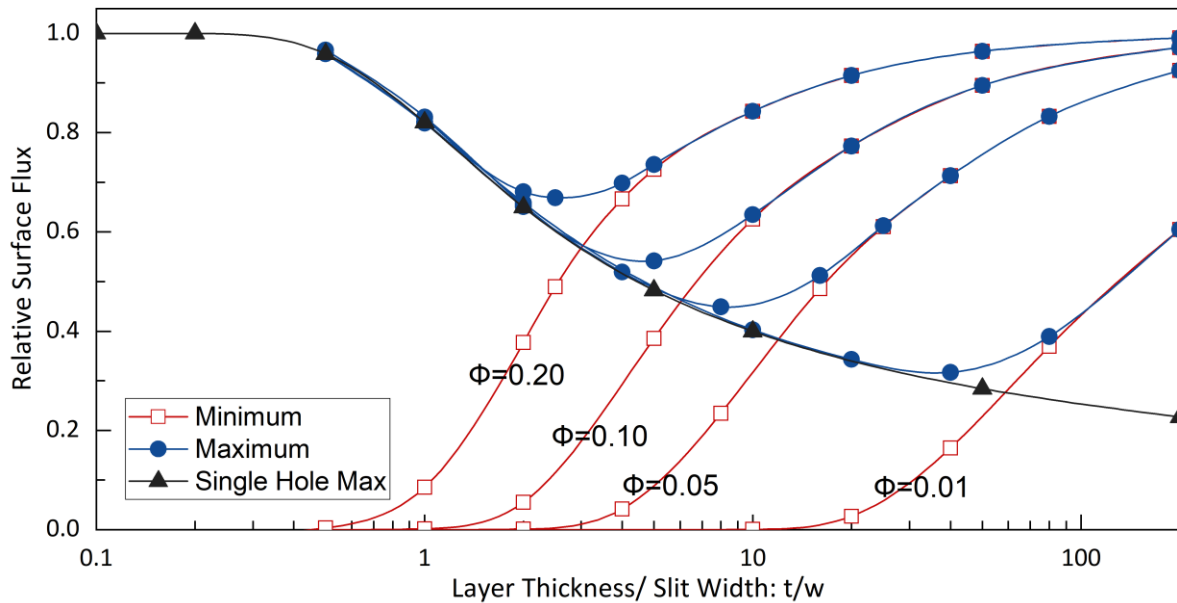


Figure 7.21 Maximum and minimum recorded surface flux from Figure 7.20 for the four different channel porosity, Φ , compared to the single hole case, Figure 7.16b.

These four cases are plotted in comparison to the single-hole case, as shown in Figure 7.16b. Figure 7.21 further illustrates each channel porosity initially behaving as an array of widely spaced single holes at low values of t/w , where the spacing between channels is large in comparison to the thickness of the permeable layer. Then, as the ratio of thickness to slit width is increased, fluid flow between channels constructively interferes to increase the minimum value of relative surface flux. Begins to occur around $t/w = 0.6$ for $\Phi = 0.2$, $t/w = 2$ for $\Phi = 0.1$, $t/w = 4$ for $\Phi = 0.05$, and $t/w = 20$ for $\Phi = 0.01$. As seen for each case in Figure 7.20, the minimum surface flux is then rises until the minimum and maximum are equal, and the flux is evenly distributed across the surface, a flat line in Figure 7.20.

This comparison of maximum and minimum surface flux can be summarised by their ratio for each case. Figure 7.22 plots the ratio of min/max surface flux against t/w ratios for each of the channel specific area case. This shows more clearly the sudden increase in minimum flux as the fluid from neighbouring channels overlaps, and repeats the result seen in Figure 7.21 of lower channel porosity arrangements needing greater t/w ratios for an even surface flux. After the point at which the

minimum is equal to the maximum surface flux, Figure 7.21 then shows an increase in uniform surface flux as the ratio t/w is further increased for each porosity of channelled substructure.

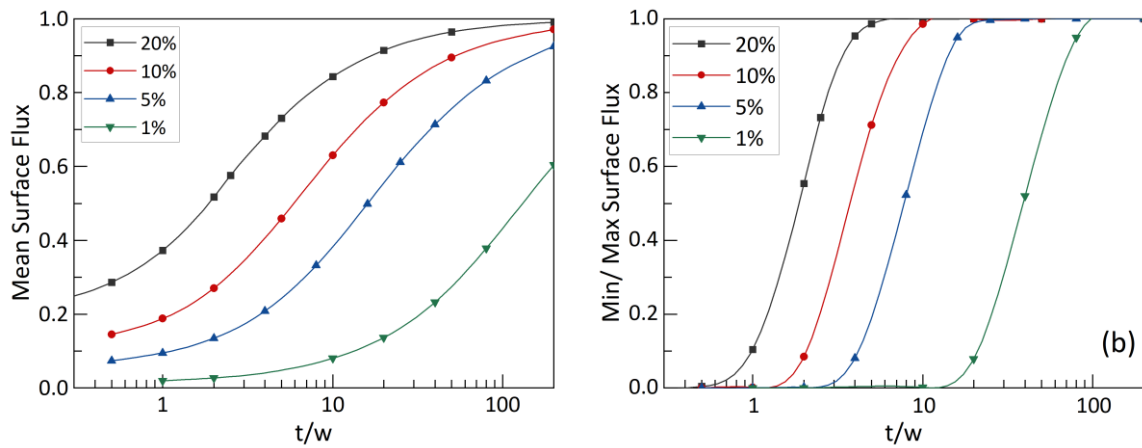


Figure 7.22 Mean surface flux for 1, 5, 10, and 20 % channelled substructures vs. t/w (a). The ratio of minimum/ maximum surface flux for each porosity of channel substructure plotted against t/w (b).

The uniformity of surface flux is not the only factor of interest in this system; the total resistance to flow is also of importance. This can be calculated by integrating the flux across the unit cell surface and dividing by the unit cell width to find the mean surface flux of the unit cell surface. Recalling the definition of the relative surface flux from section 7.2.1, a mean surface flux of 1.0 would mean there is no change to the permeable layer from the addition of a substructure, whereas reductions in mean surface flux equate to a reduction in the permeability of the layer due to the way the fluid is introduced via channels.

Figure 7.22 shows this mean surface flux across a unit cell as t/w is increased for each measured channel porosity of substructure. For equal t/w , the mean flux is higher for the higher specific area of channel, each trend tending towards a relative flux equal to its specific channel area at very low values of t/w . This extreme case would see fluid limited only above the wide channels, limiting the amount of fluid flow to the area of the channels in an even more extreme example than shown in Figure 7.17.

Each case shows the mean flux slowly increasing with t/w from the lower values, followed by a more rapid increase that coincides with the surface flux becoming more evenly distributed in Figure 7.22. Finally, the 0.2, 0.1, and 0.05 channel porosity cases then slow their increase as they tend towards 1.0. The 0.01 case should also follow this tendency but at much higher values of t/w .

The average surface flux constantly increases with t/w for each porosity case. It is also clear that greater porosities lead to a greater mean surface flux. Each case is tending towards 1.0 relative surface flux for high t/w systems, and to a relative flux equal to the porosity of the channelled substructure for extremely low t/w (<0.1). This result suggests that by reducing the channel width for a constant

specific channel area the substructures' inhibiting effect on fluid flow through the permeable layer is reduced.

As the function of the substructure layer is to improve mechanical properties of the system, being able to reduce the channel porosity while maintaining a high overall permeability is desirable for transpiration cooling. This result then goes some way to defining the first criteria for designing substructure channels, increasing t/w ratios for improved permeability. If considering only the partially sintered permeable layer, for a set pressure, the surface flux can only be controlled by the thickness of the material. Reducing the thickness will increase fluid flow through the layer, but with decreased effectiveness as the t/w ratio will also be decreased. This variation with t/w then allows for the ability to tailor the surface flux depending on the cooling requirements.

While comparing to a single hole, the t/w ratio is useful as a single hole does not have a defined unit cell for the L dimension. For arrays of channels, however, the t/L ratio can also be used, Figure 7.23 shows how the channel porosity can be changed while maintaining either constant t/w or constant t/L ratios. Comparing t/w has shown the transition from single hole behaviour to combined channel effects in Figure 7.21, and to build on the comparison and trends between specific area cases as the channel arrangement is adjusted, Figure 7.24 re-plots the data from Figure 7.22 against the alternative definition t/L .

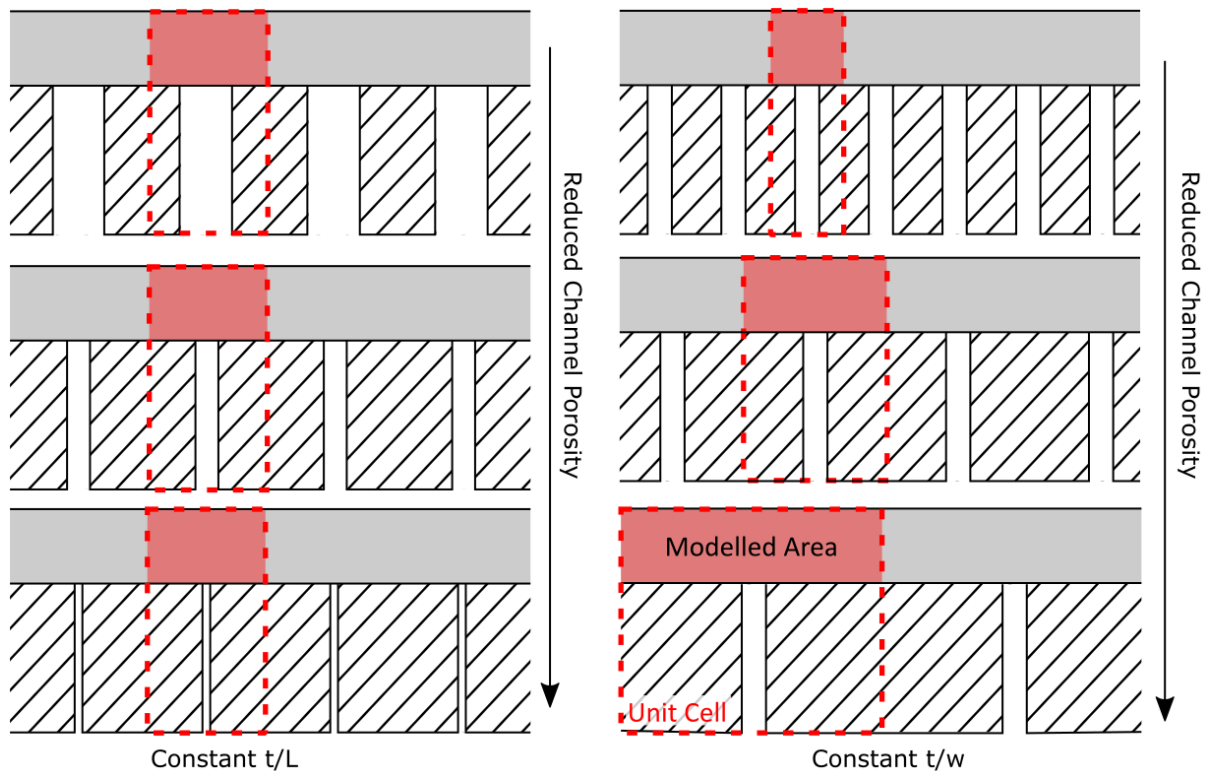


Figure 7.23 Demonstration of the different channel arrangements when considering constant spacing vs. constant width for a fixed thickness of permeable layer across different channel porosities.

The general trend observed for the mean surface flux in each channel porosity case is the same for t/L as plotted against t/w in Figure 7.24 and Figure 7.22. Each has the shallow gradient that steepens as the flow becomes uniform with increasing min/max ratio, tending towards 1.0 at high t/L . The difference between each curve is less extreme when plotted against t/L , however. Each has similar gradient and curve shape as t/L is increased, with the main difference between each specific porosity case being the magnitude of the mean surface flux. This similarity in trend between the cases is reflected in the min/max surface flux ratio plotted in Figure 7.24. The ratio measurement for uniformity of surface flux is identical for each specific channel area case as the t/L ratio is increased from 0.01 to 10, with the surface flux completely even when $t/L > 1$.

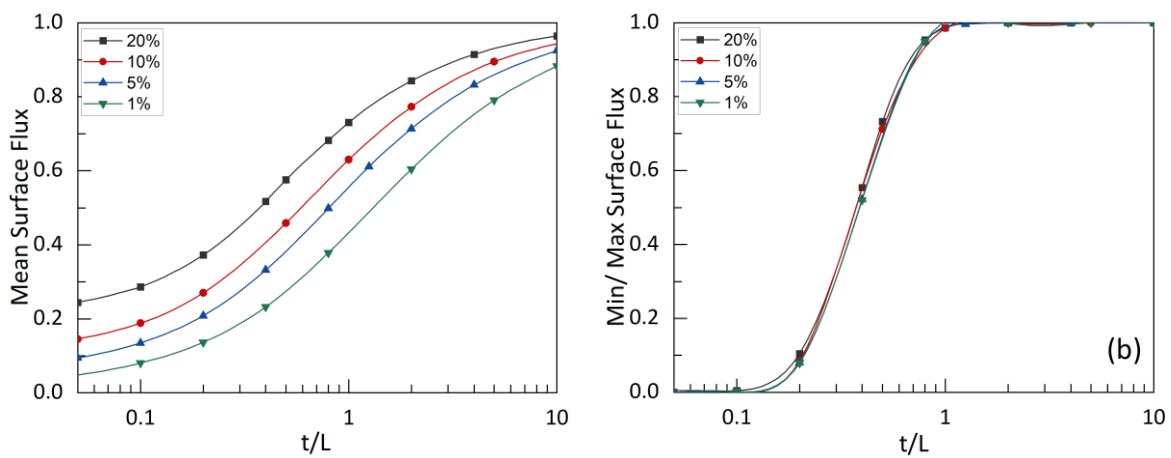


Figure 7.24 (a) Mean surface flux for 1, 5, 10, and 20 % channeled substructures vs. t/L . (b) The ratio of minimum/ maximum surface flux for each porosity of channel substructure plotted against t/L .

This then shows that the magnitude of surface flux is dependent largely on the porosity of the channel substructure, which will also increase with increased t/L ratios. The uniformity of surface flux, however, is entirely dependent on the t/L ratio and independent of specific channel area.

7.3.3 3D Channels

The 2D modelling shown in the previous section was then expanded to realistic 3D substructures defined by the unit cells, Figure 7.10. The more complicated nature of geometry definitions between different 3D structures means there are several dimensions which could influence how the flow interacts between channels. The channels themselves are defined by their characteristic size, a , which is either an edge length or diameter. The arrangement dimensions are then identified as the centre to centre spacing between closest neighbours, L , the minimum edge to edge distance between channels, d , and the maximum edge to edge spacing between channels, m , as well as the characteristic side length of the unit cell, A , and the characteristic channel dimension, a . Each of these dimensions is defined for the channel arrangements in Figure 7.10. As there is no consistent channel dimension

definition between different shapes of substructure channels, the t/w ratio is not considered in three dimensions, in favour of definitions of channel spacing L , m , and d .

An example of the finite element analysis outputs for vertical surface flux the vertical direction and pressure distribution is shown for a cross section of each unit cell in Figure 7.25. Qualitatively, for the examples selected the pressure is centred around the channel openings. The vertical flux spreads out with a maximum hot-spot directly above the channel, and dead-spots with low surface flux in the corners of the unit cell. As with 2D, the minimum, maximum, and average surface flux will be measured, and between the different channel arrangements for varied thickness to spacing ratios.

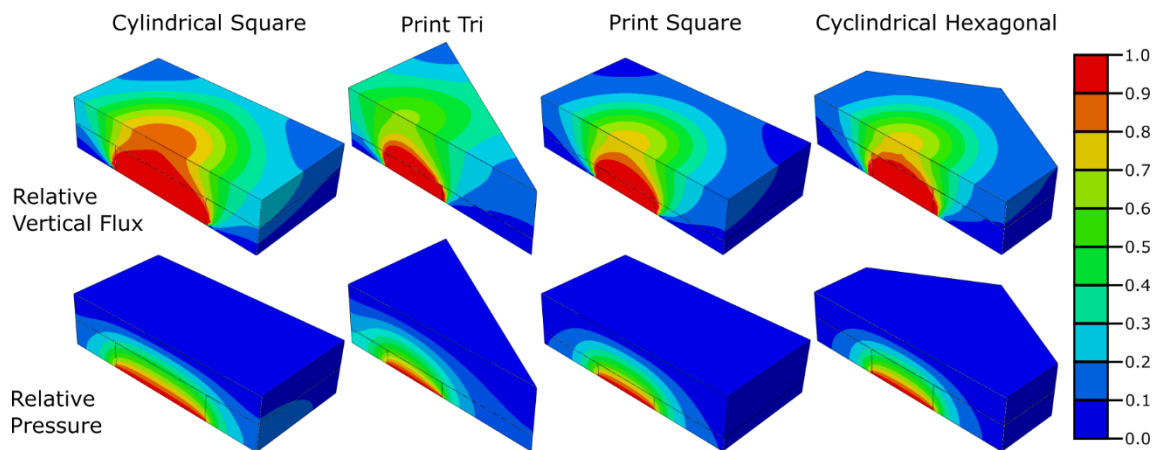


Figure 7.25 Example sectioned FEA analysis data from each type of 3D channel structure unit cell for $t/L=0.2$.

The results of varying the t/L ratio of the four 3D channel geometries are compared with the 2D case for 10 % channel porosity in Figure 7.26. The minimum and maximum surface flux are plotted, as in Figure 7.21 only against t/L rather than t/w . The first key difference between the 2D and the 3D models are the consistently higher maximum surface flux in 3D when $t/L < 0.5$. In this region, the minimum flux is also lower in 3D than the 2D case. The two square arrays are very similar for the cylindrical and square channels for all values of t/L . The maximum flux for each is similar to the hexagonal array but with minimum flux consistently lower. The maximum flux for the triangular channel print pattern is clearly higher than the other 3D cases when $t/L < 0.7$, and the minimum consistently lower until $t/L > 1.5$.

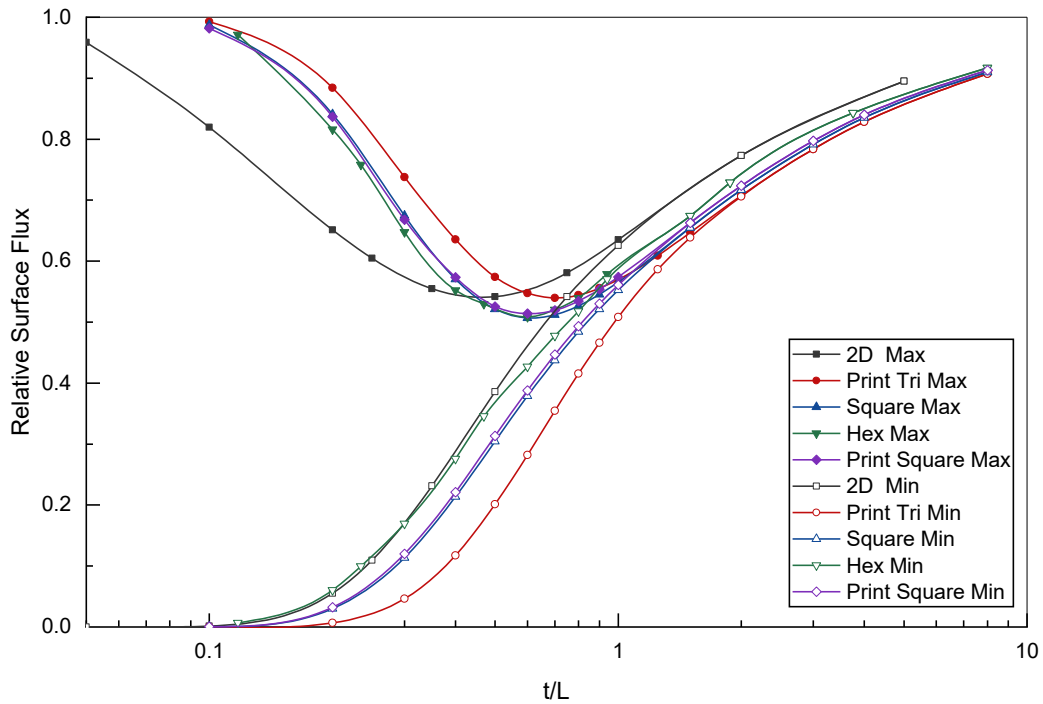


Figure 7.26 FEA data from each 3D model case for 10 % specific channel area; Maximum and Minimum surface flux vs. t/L . compared with the 10 % 2D case.

Figure 7.27 then shows the mean surface flux for each of these 3D models, along with the ratio of min/max surface flux plotted against the t/L spacing ratio. Each 3D model shows good agreement with each other for the mean flux vs. t/L , but each is slightly lower in magnitude than the comparison to the 2D 10 % specific area case.

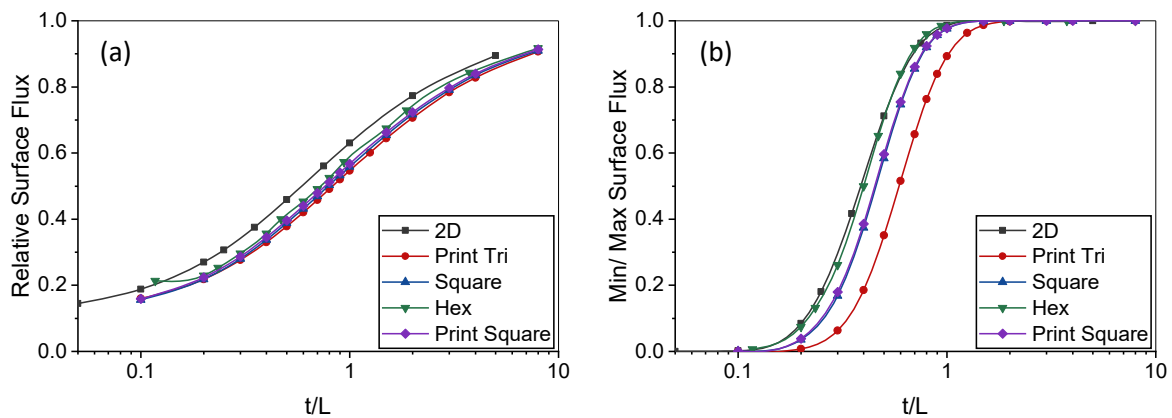


Figure 7.27 FEA data from each of the modelled 3D channel structures for a 10% specific channel area showing mean surface flux vs. t/L (a) and the ratio of minium/ maximum surface flux vs. t/L (b).

Figure 7.27 also shows the Min/Max ratio vs. t/L . The hexagonal array of cylindrical channels (Hex) shows best agreement with the 2D model, and there is a good match between the square arrays of cylindrical (Square) and square channels (Print Square). These square arrays are shown to require a tighter spacing from the greater t/L ratio to achieve uniform surface flux compared to the hexagonal

array of cylindrical channels. The printed triangular pattern for channels is even further displaced from the 2D and hexagonal arrays, again meaning that to achieve an even surface flux the channels would need to be smaller, spaced closely together, or require a thick permeable layer to spread the fluid, i.e. $t/L > 2$. This is in keeping with Figure 7.26 which showed the maximum surface flux to be consistently higher, and minimum to be consistently lower for the printed triangular pattern.

These trends of results indicate that minimising the average distance between the open channel areas of neighbouring unit cells will improve fluid coverage, which can be achieved through a combination of channel and unit cell geometry. The effect of these geometric definitions on the flow properties of the system can be highlighted to show why this printed triangular channel array is less effective than the other 3D geometries.

To show this, the min/max ratio is re-plotted against the other spacing measurements, m and d . By plotting the min/max ratio against the minimum distance between channels in Figure 7.28, despite requiring a greater t/d compared to the 2D case, all 3D models develop an even surface flux at the same t/d ratio other than the print tri arrangement. Again, this triangular arrangement requires finer channels and closer spacing to achieve even surface flux. This result is then repeated when replotted using the maximum distance between channels, m . Other than the triangular arrangement remaining separate, there is now excellent alignment with each of the other 3D model with the 2D for the distribution of surface flux. This means that whether the fluid exits the permeable layer as separate jets or an even film is dominated by the maximum distance between the channel edges, there is then some aspect of the triangular channel geometry that is particularly problematic when requiring even flow at the surface.

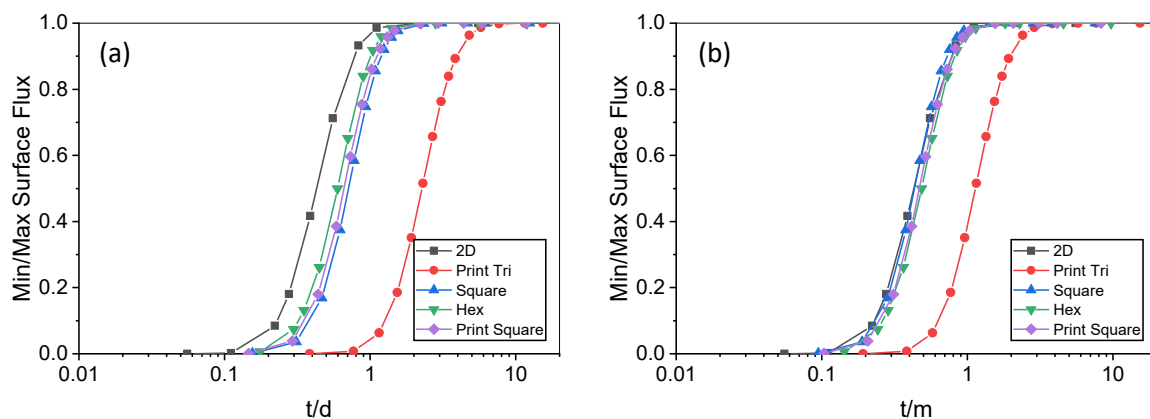


Figure 7.28 The ratio of minimum to maximum observed flux for vs. the spacing of channels defined by the minimum distance, d , between channel edges (a) and maximum distance, m , between channel edges (b).

The triangular arrangement is significantly worse than the other channel arrangements because of this difference between the minimum and maximum distances between channel edges. There are relatively thin walls between each channel along the triangle edge, but a large area towards the tip of each triangular unit cell far from the channel, and from the fluid being introduced. Thin channel walls along the flat edges means a high flux is reached very quickly in those areas as the channels constructively interact, but the large maximum distance then takes longer to reach the same levels of flux at the surface. This comparison between the shortest and longest distance between channel edges can be compared for each 3D channel arrangement as a function of specific channel area. As the print pattern channels are similar shapes to the unit cell the ratio will not change with increasing channel porosity. The cylindrical channels will have a greater disparity between the minimum and maximum distances as the channel porosity is increased, this change is plotted in Figure 7.29 which shows the cylindrical hexagonal array is superior until > 35 % channel porosity, far greater than is likely for such a system.

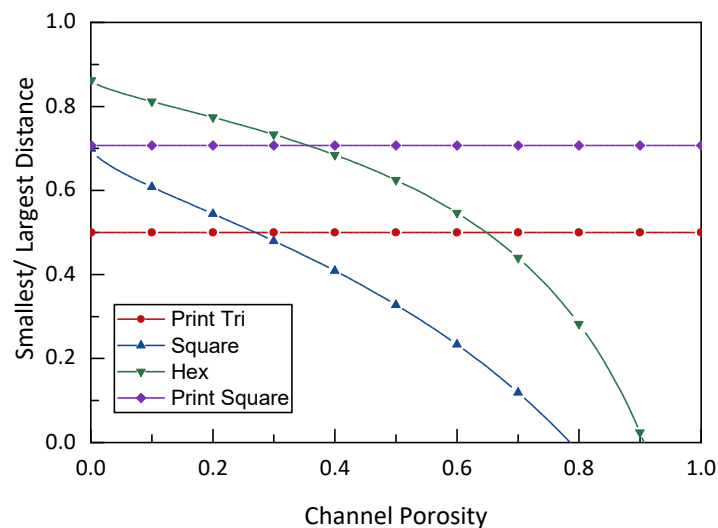


Figure 7.29 Ratio of largest and shortest distance between channel edges vs. porosity of channelled substructure.

7.3.4 Experimental Validations

The 3D models give an idea of how different channel arrangements will affect fluid flow through the permeable layer. However, due to the many variables defining a 3D system and the limits of modelling gaseous fluid flow using incompressible models for Darcy permeability, there are diminishing returns on what these models can inform and predict when it comes to real world channel design. The remainder of this discuss the results of experimental validation of the trends from the FEA models.

First, the permeability of a 30 % porous ZrB_2 disc was measured as described in 'Chapter 3.4.6: Permeability'. This disc was made by hot-pressing grade A ZrB_2 powder at 1700 °C under a constant

load of 24 MPa. After grinding two parallel surfaces, the disc had a diameter of 80 mm and thickness of 14.45 mm. As the experimental set-up deals with compressible fluid flow in porous media, the full Darcy-Forcheimer equation must be used;

$$-\frac{dP}{dx} = \frac{\mu}{\kappa_D} v + \frac{\rho}{\kappa_F} v^2 \quad 7.6$$

This is the same as Darcy permeability, with the addition of the kinetic term, where ρ is the density of air and κ_F the Forcheimer permeability coefficient[102].

The experimental data for measuring permeability in the disc is shown in Figure 7.30 alongside the calculated $\Delta P/t$ and fluid velocity. To calculate Darcy and Forcheimer coefficients of permeability, a second order polynomial was fitted, with κ_D and κ_F calculated from the viscosity and density of air, these values, and results of which, are shown in Table 7.4.

The values for the Darcy and Forcheimer coefficients measured are consistent with the Ifti *et al.*[6] study into similar hot-pressed ZrB_2 , with the Darcy coefficient $2.67 \times 10^{-14} \text{ m}^2$ compared to $2.59 \times 10^{-14} \text{ m}^2$ measured by Ifti for the same powder hot-pressed at the same temperature. 24 MPa was used for the sample in this study compared to 12 MPa in the Ifti study, and therefore resulted in a lower porosity of 30 vol%. Measuring a higher permeability despite a lower porosity suggests there is error in the method as a lower volume of porosity would restrict fluid flow, however the initial Ifti *et al.* study discussed in 'Chapter 4.2.2: Initial Permeability Assessment' also showed little change to permeability when pressure was the defining variable in porosity. The Forcheimer coefficient of $4.05 \times 10^{-7} \text{ m}$ is large in comparison to the Ifti study, but not in comparison to the range of values measured, spanning three orders of magnitude from 1.39×10^{-9} to $1.97 \times 10^{-7} \text{ m}$. Considering the porosity changes discussed in 'Chapter 4: Porous ZrB_2 By Hot-Pressing' resulted in an order of magnitude change in permeability, the consistency of values give confidence that the accuracy of the method is good enough for direct comparison between samples measured this way.

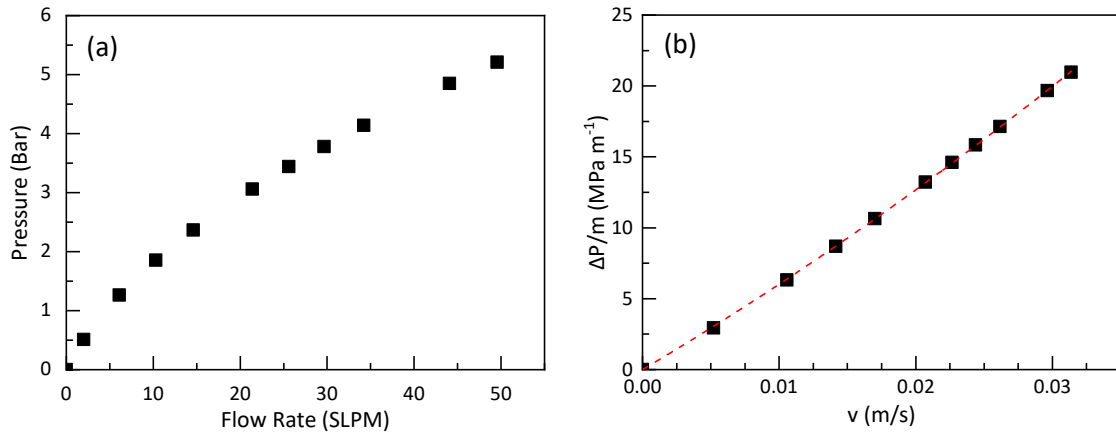


Figure 7.30 Measured volume flow rate and pressure (a) and calculated velocity and ΔP (b) for the 14.45 mm thick ZrB₂ disc with no substructure.

For the FEA model, the pressure drop across the substructure is assumed negligible. Therefore, the thickness of the substructure is assumed to have no impact on behaviour. In keeping with these assumptions for validation, the channelled substructure can be replaced with vinyl stickers, removing the need to manufacture and join UHTC channelled structures to assess their impact on the fluid flow.

Table 7.4 Permeability coefficients and constants from measurement of the ZrB₂ disc.

Coefficient	Unit	Value
μ	m ² s ⁻¹	1.52×10^{-5}
ρ	gm ⁻³	1.29×10^{-3}
κ_D	m ²	2.67×10^{-14}
κ_F	m	4.05×10^{-7}

As described in 'Chapter 7.2.2: Experimental Validation', vinyl stickers with varying arrangements of holes were used to mask the back surface of the 80 mm ZrB₂ disc. The thickness of the disc, coupled with the spacing of the circular holes, leads to t/L ratios as discussed in the FEA models. With each sticker applied, the flow rate was then measured with varied pressure across the disc.

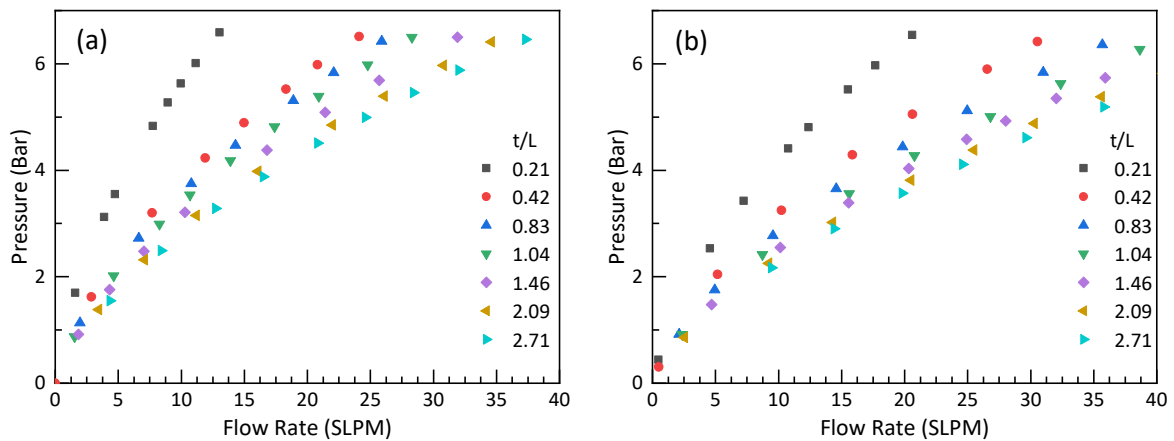


Figure 7.31 Measured pressure and flow rate with masks of 10 % (a) and 20 % (b) channel porosity.

The measured results of pressure vs. flow rate are shown in Figure 7.31 for a substructure of 10 % and 20 % specific channel area. Data shows that lower the t/L ratio, the steeper the curve, requiring greater pressure to achieve the same mass flow rate for both specific channel area cases. The calculated fluid velocity and pressure differences across the disc are plotted in Figure 7.32, where the same trends are observed. The permeability coefficients calculated from the polynomial fit are recorded in Table 7.5.

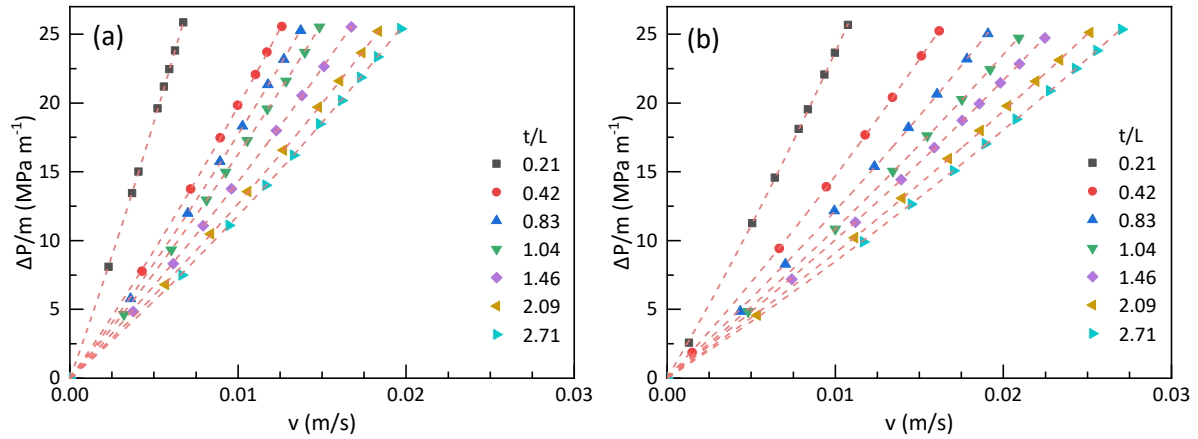


Figure 7.32 Calculated pressure difference and flow velocity with masks of 10 % (a) and 20 % (b) channel porosity

The calculated Darcy permeability is then compared to the equivalent FEA models. For this, the mean relative flux is taken as relative permeability of the permeable layer in the FEA model, as reduction in permeability would have an equal effect as the introduction of the channelled substructure. The relative permeability is calculated for experimental data by comparison to the permeability calculated when no vinyl sticker substructure is in place. The results of this comparison are plotted against the t/L for hexagonal channel array for the 10% and 20% specific channel area FEA and vinyl sticker cases in Figure 7.33.

Table 7.5 Darcy and Forcheimer permeability coefficients as calculated from the experimental data for the masked ZrB_2 disc. Masks are defined by the channel porosity, 10 or 20 %, and the t/L ratio.

t/L	10%		20%	
	κ_D (10^{-14} m^2)	κ_F (10^{-7} m)	κ_D (10^{-14} m^2)	κ_F (10^{-7} m)
0.21	0.45	0.20	0.73	0.44
0.42	0.87	0.55	1.15	0.86
0.83	0.97	0.65	1.37	1.19
1.04	1.06	0.67	1.53	1.41
1.46	1.19	0.71	1.64	1.65
2.09	1.33	1.01	1.79	2.14
2.71	1.43	1.12	1.91	2.40

Figure 7.33 shows the experimental data has the same trend as the FEA model but is offset; the FEA predicts a higher fluid flow for the same channel arrangements in the experimental validation. The relative permeability increases with increasing t/L arrangements of vinyl stickers, and the difference

between the magnitude of permeability for 20 % channel porosity is greater than 10% for both FEA and experimental data.

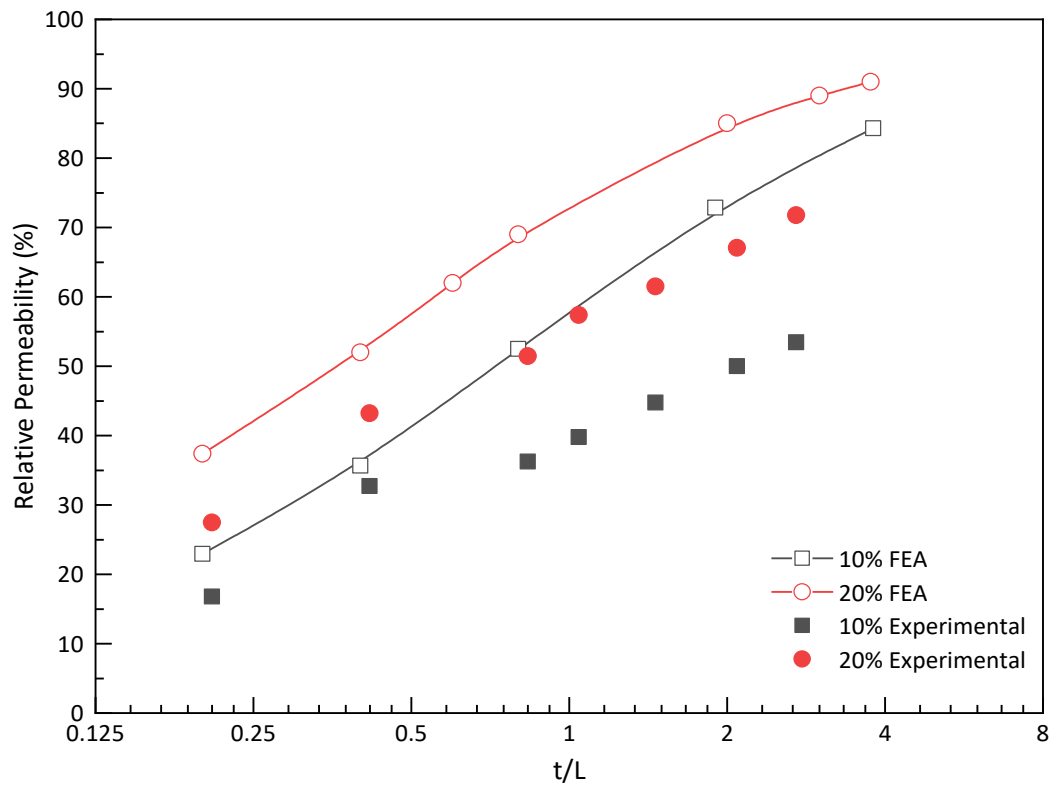


Figure 7.33 Measured permeability of porous ZrB_2 with various substructure channel arrangement plotted with the corresponding FEA model data.

Although the validation does not agree with the magnitude of FEA models, the trend still corroborates the design criteria of smaller channels spaced closer together to improve fluid flow. The limit of how high the t/L ratio can go will be dependent on manufacturing techniques used to make the channels. Fluid flow can always be increased by reducing the thickness of the permeable layer; however, this also reduces the absolute spacing required between channels to achieve an even surface flux.

The validation also does not make any attempt to assess the flow distribution across the top surface, whether it is evenly spread or jets. It would be possible to measure the distribution with a hot-wire test as demonstrated by Ifti *et al.*[6]. This highlights the desire to further testing of real systems to fully tailor properties to cooling requirements.

7.3.5 Assumptions and Errors

The FEA models and experimental validation apply a pressure to the back surface of the partially sintered layer, at the hole locations. It is assumed that is pressure drop over the substructure would be negligible compared to the pressure drop over the partially sintered layer. This disparity and the factors affecting the pressure drop across each layer of the structure are illustrated in Figure 7.34

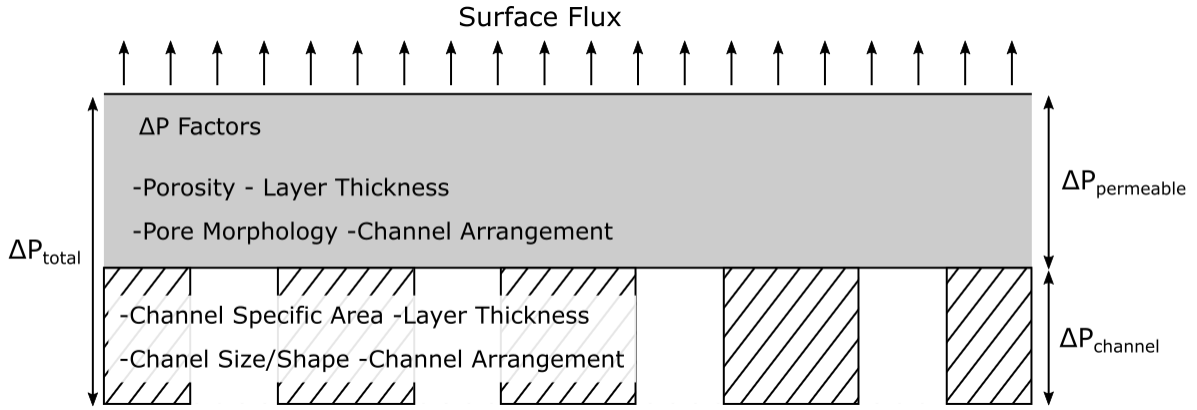


Figure 7.34 Illustration of separation of pressure difference across the channelled substructure and the permeable layer. The key factors affecting the pressure drop across each layer is displayed.

The pressure drop across a real channelled structure would depend on the channel size and length, according to the Hagen–Poiseuille, equation 7.7. This can be adjusted for cylindrical channels with definitions of specific channel area, Φ , and flux, q , in equations 7.8 and 7.9. This substitution leads to the pressure drop across a specific channel arrangement, $\Delta P_{channel}$, defined by the thickness of the channelled layer, $t_{channel}$, specific channel area, channel radius for the fluid viscosity and flux in question, equation 7.10. Comparing this with Darcy's law for the pressure drop of a permeable layer, $\Delta P_{permeable}$, with thickness $t_{permeable}$ in equation 7.11 results in equation 7.12.

$$-\frac{dP}{dx} = \frac{8\mu Q}{\pi R^4} \quad 7.7$$

$$q = \frac{Q}{A} \quad 7.8$$

$$A = \frac{\pi R^2}{\phi} \quad 7.9$$

$$\frac{\Delta P_{channel}}{t_{channel}} = \frac{8\mu q}{\phi R^2} \quad 7.10$$

$$\frac{\Delta P_{permeable}}{t_{permeable}} = \frac{\mu q}{\kappa} \quad 7.11$$

$$\frac{\Delta P_{permeable} \kappa}{t_{permeable}} = \frac{\Delta P_{channel} \phi R^2}{8 t_{channel}} \quad 7.12$$

This allows for direct comparison of the pressure drop across each layer of material as a function of several design variables and partially sintered layer permeability. This ratio is outlined in equation 7.13, where the variable C is used as a function of the relative thickness and permeability of the two layers, the arrangement of the channels defined by the specific channel area and channel radius. The effective permeability of the partially sintered layer has been shown throughout these results to be a

function of the channel spacing, specific area, and permeable layer thickness, so rather than use the measured permeability of the material, κ , the new relative permeability, κ^* , must be used.

$$\frac{\Delta P_{permeable}}{\Delta P_{channel}} = \frac{t_{permeable}}{t_{channel}} \frac{\phi R^2}{8\kappa^*} = \frac{C(t_p, t_c, \Phi, R)}{\kappa^*(\kappa, t_p, \Phi, L)} \quad 7.13$$

Comparison therefore can be used to correct the pressures assumed in the FEA models, where only ΔP_p was considered. The total pressure drop across both layers can be calculated by substituting equation 7.13 into the definition for total pressure: $\Delta P_{total} = \Delta P_p + \Delta P_c$, as shown in equation 7.14.

$$\Delta P_{total} = \Delta P_{permeable} + \Delta P_{channel} = \Delta P_p + \frac{\Delta P_p \kappa^*}{C} = \Delta P_p \left(1 + \frac{\kappa^*}{C}\right) \quad 7.14$$

To test this for real systems a worst-case scenario is considered for a hybrid of 5mm total thickness, with 1mm partially sintered material above 4 mm of channelled substructure with a specific channel area of 1 %. The smallest realistic channel radius considered is 50 μm in a hexagonal array, meaning a spacing, L , of 952 μm and a t/L ratio of 1.05. Figure 7.24 predicts a mean relative surface flux of 0.4 for 1 %, $t/L = 1.05$. Using a relatively high prediction for κ of $4 \times 10^{-14} \text{ m}^2$, $\kappa^* = 0.4\kappa = 1.6 \times 10^{-14} \text{ m}^2$. Applying these conditions to calculate $C(t_p, t_c, \Phi, R)$ gives $7.5 \times 10^{-13} \text{ m}_2$. Applying to equation 7.14 yields $\Delta P_{total} = 1.05 * \Delta P_{permeable}$.

For any system with greater channel specific area, lower permeability of partially sintered ceramic, larger channel radius, or thicker partially sintered layer, the result will be even more favourable towards the assumption. Applying the same principle to a 10 % specific channel area of 100 μm pores in a hexagonal array with the same layer thicknesses and permeability yields $\Delta P_{total} = 1.0006 \Delta P_{permeable}$, so for most cases the assumption that $\Delta P_{channel}$ is negligible is correct. It is certainly correct for the 10 % and 20 % specific channel area cases considered for experimental validation.

7.4 Conclusions

In conclusion, the models define a set of variables to be used in design of channelled substructures beneath a permeable layer in transpiration cooling. The channel spacing to permeable layer thickness ratio is determined to be the critical factor in whether a coolant fluid will be uniformly distributed or leave the permeable layer surface as separate jets. The 2D models predict this thickness/ spacing ratio must be greater than 1, but for 3D each different channel geometry will have its own factors and requires further experimental testing to validate.

The models predict that the addition of a substructure will reduce the overall fluid flow through the top permeable layer to varying degrees, depending on the specific channel area and the spacing and size of the channels. Resistance to flow is reduced by reducing the channel size and spacing while maintaining specific channel area. As such, it is possible to tailor the fluid flow to the requirements of transpiration cooling by altering the channel arrangement variables as well as the permeable layer thickness.

The trend of reduced resistance to flow with reduced channel size and spacing is confirmed by experimental validation. While the magnitude of flow calculated from experimental results is below those of the FEA models, the ability to control flow by channel arrangement is confirmed. The FEA model is limited by not including the compressibility of flow in calculation, as such further physical testing would be beneficial for desired real channel arrangements.

A real channel system would provide additional resistance to flow, which would be made worse by the proposed narrow channels for better delivery into the permeable layer. The effect of this additional resistance to flow is discussed and the correction factor derived, this effect is calculated to be negligible for channels larger than a $\sim 50 \mu\text{m}$ diameter.

Due to the low permeability of ZrB_2 ($\sim 1 \times 10^{-14} \text{ m}^2$) and the typical thicknesses and channel sizes expected for the transpiration cooled systems, the takeaway point for designing the substructure is to make the channels and channel spacing as small as possible with the techniques available. This will aim to ensure both an even surface flux and lower overall resistance to fluid flow of the two-layer system.

8 Conclusions and Future work

8.1 Conclusions

The strength and thermal conductivity of 25 – 40 vol% porous partially sintered ZrB_2 can be improved, without increasing the density, by oxidising powders prior to sintering. The improvements in physical properties were due to enhanced neck growth between grains in the initial stage of sintering. Increasing pressure during hot-pressing also promoted neck growth, increasing both strength and density, without significant changes to pore size or permeability. Increasing thermal conductivity is beneficial for dissipation of heat laterally away from a leading edge but could cause an increase in temperature through the thickness of the TPS. The specifics of desired properties must be bespoke for each TPS design, but the control of microstructure demonstrated allows for control of properties, Layering of UHTCs using the principles demonstrated in modelling will allow for further tailoring of thermal protection.

Surface transport mechanisms were accelerated in oxidised powders, increasing the pore size and permeability, potentially allowing for higher density ZrB_2 to be used in transpiration cooled systems. However, the increased elastic modulus from increasing density may be counterproductive due to reduced thermal shock resistance. Thermal shock will also need addressing in dense substructure layers, along with any thermal expansion mismatch between materials.

Partially sintered ZrB_2 hot-pressed at 1700 °C from as-received powders densify below the intended application temperature of 2000 °C. Reducing the pore area by increasing the powder size reduced the speed of densification, while surface transport from increased oxygen completely prevented rapid densification at 2000 °C.

Slow heating rates during hot-pressing allowed for a separation of onset temperatures for densification by grain boundary and volume diffusion. This showed that volume diffusion was required to densify ZrB_2 with increased oxygen content. Further increasing the oxygen content and powder size then prevented any densification beyond 80 % relative density up to 2000 °C/ 24 MPa. The large microstructures seen in samples held at 2000 °C shows that coarsening will continue to enlarge pores without densification at application temperatures; this will change the permeability. Therefore, for reliable properties, ZrB_2 for transpiration cooling should be treated at 2000 °C to achieve final pore sizes. This may give less control over permeability and physical properties than otherwise suggested, meaning control of fluid delivery requires the adaptation of the combined effect of substructure channels and surface layer thickness.

Modelling and experimental validation of the introduction of flow to the permeable layer through channelled substructures concluded that the overall resistance to fluid flow was reduced by reducing channel size and spacing. The resistance to fluid flow from the channels themselves was negligible due to the low permeability of partially sintered ZrB_2 compared to potential channel diameters.

The distribution of surface flux can therefore be controlled by varying the channel size and spacing in the substructure, while ensuring the permeable layer thickness is greater than the channel spacing for an even distribution of surface flux.

The results of modelling suggest that evenly distributed fluid flow can be achieved with channels spacings in the order of millimetres with channel sizes achievable by common methods for shaping ceramics, such as robocasting. This is a key result as it allows for rapid prototyping of channel structures and does not require significant investment into the control and fabrication of micro-channelled structures. However, the specifics of what constitutes ideal properties and therefore processing conditions for leading edge transpiration cooling applications is yet to be defined.

8.2 Future Work

Further development of UHTCs for transpiration cooled thermal protection systems following from this study will mostly centre around the fabrication and characterisation of layered UHTC hybrids. The design criteria outlined suggest that even surface fluxes are achievable with millimetre thick surface layers and channel spacing, allowing for a wide range of ceramic processing methods to create channels for tailored cooling properties. These design criteria require further validation, particularly for evenness of surface flux and set criteria for tolerable variation under application specific conditions.

Work will then be required to join these two layers, assessing the importance of any mismatch in thermal expansion as they will experience an extremely high range in temperatures. Experimental assessment of thermal shock is also required to confirm predicted trends based on calculations of flexural strength and elastic modulus, and the effect of a bilayer construction.

With regards to the partially sintered ZrB_2 , the range of oxygen content and powder size studied was limited. For bespoke control of permeability, further characterisation of samples made from a wider range of oxygen content is desired. Translation of processing to pressureless sintering could also be beneficial for near-net-shape forming of leading-edge components.

Identifying the individual effects of vapour-phase transport and surface diffusion would also allow for further optimisation of processing, potentially simplifying powder preparation if only boria or zirconia

were required for the desired surface transport effects for target properties. Further assessment of the effect of each of these mechanisms, coarsening rates, and quantification of neck growth is desired.

The high temperature mechanical and thermal properties desires further assessment, and further work is also required to assess the impact of extended high temperature holds on microstructural stability. It was shown that densification was slow but microstructural coarsening at 2000 °C could increase pore and grain sizes, affecting both strength and permeability.

9 Bibliography

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