6. DENSIFICATION BY ULTRA-HIGH PRESSURE SINTERING (UHP)

Different sintering cycles were used in an attempt to optimise the sintering conditions for the LPSSiC system under ultra-high pressure. A summary of the different runs can be found in Table 3.10. The sintering was carried out at about 1550°C (much lower temperature than the hot pressing and gas pressure sintering), under a pressure of 5.5 GPa for about fifteen minutes.

After the first ultra-high pressure sintering experiment (Run 1, samples UHP4R1 and UHP15R1, in Table 3.11), one could see that the samples were only partially sintered. A solid piece could not be recovered after sintering due to a high level of delamination. After RUN2, the samples (UHP4R2 and UHP15R2) appeared to be more sintered, but there was still a lot of delamination. RUN 3 produced more recoverable (intact) samples (UHP4R3 and UHP15R3). The four compositions of 10 mass-% sintering additives: \(3Y_2O_3:5Al_2O_3\) (UHP3Y5Al), \(4Y_2O_3:2Al_2O_3\) (UHP4Y2Al), \(1Y_2O_3:1Al_2O_3\) (UHP1Y1Al), \(1Y_2O_3:4Al_2O_3\) (UHP1Y4Al) were then UHP sintered under the same conditions as RUN3. Another experiment with an even slower cooling rate was done in RUN 4 (UHP4R4 and UHP15R4).

Pieces of selected UHP materials were polished to a one micron finish, and Vicker’s hardness and indentation fracture toughness were measured. Selected materials were scanned under XRD. The materials were investigated further under light microscope and using a scanning electron microscope.

6.1 Density, phase and mechanical properties analysis

The densities, phase content, hardness and fracture toughness of the ultra-high pressure sintered materials were measured and results are
summarised in Table 6.1. According to this table, the densities of all the UHP materials, are all close to the theoretical densities $\rho_{\text{theory}}$ (page 92, Table 3.7), the calculation of which was based on the assumption that silica present in the starting material is not removed during sintering. In addition, XRD results indicate the presence of yttrium silicates in the grain boundary phases of the materials analysed, which implies that evaporation of silica during ultra-high pressure sintering did not take place in an appreciable amount. The presence of extremely high pressures, lower temperatures, short sintering times, and the sealed compacted powder by a metal encapsulation possibly prevented formation of SiO during UHP sintering. The yttrium silicate phases observed in the UHP materials, were similarly observed in the hot pressed materials.

Only qualitative phase analysis using XRD could be done on the ultra-high pressure sintered materials. This is because the X-ray diffraction peaks are broader than the hot pressed samples peaks, as shown in Figure 6.1.

These broad peaks are possibly due to the very fine grain structure in the materials (examples of this can be seen in Figures 6.8, 6.11 and 6.12) and may be due to high strain in the material, as a result of a high rate of plastic deformation during UHP sintering. These broad peaks led to very high scatter in quantitative Rietveld calculations done on the XRD data.
The hardness of the UHP materials was expected to be higher than that of the hot pressed materials, because of the finer grain size expected in the ultra-high pressure sintered materials. The 10 mass-% UHP materials, UHP3Y5Al and UHP4Y2Al, had similar hardness values of average 20 GPa, similar to the hardness of the as-hot pressed materials (20GPa). The UHP1Y4Al material does appear to have a higher hardness than the other 10 mass-% UHP materials, as illustrated in Figure 6.2. This may be because of the residual alumina (shown in Table 6.1) in the grain boundary of this high alumina-content material. Alumina is a harder phase compared to yttrium silicates, which would explain why this UHP material has higher hardness than the other 10 mass-% UHP materials. Similar arguments for the influence of the different grain boundary phases on the hardness of LPSSiC materials are given in Chapter 5, in section 5.2.1.
Figure 6.2 Hardness of the UHP materials sintered with different compositions.

The 4 mass-% 1Y4Al materials: UHP4R1, UHP4R3 and UHP4R4, all have similar hardness values for the different UHP sintering cycles used, and they appear to have a higher hardness (average 23GPa) than the 10 mass-% and 15 mass-% materials (illustrated in Figure 6.3). This is most probably because the 4 mass-% additive materials have the lowest grain boundary content, which is the softer component. These results show, that the grain boundary phase of these materials have a decisive negative influence on the hardness.
In general, the lower fracture toughness values were observed in the ultra-high pressure sintered materials compared to the hot pressed and gas pressure sintered materials. The fracture toughness values of the 10 mass-% UHP materials, on average $3.3 \pm 0.2$ MPa.m$^{1/2}$, are however similar to the fracture toughness of the lower alumina content hot pressed materials. The ultra-high pressure sintered material with the highest fracture toughness was the material with 15 mass-% sintering additives, 15R1, with a fracture toughness of $3.8 \pm 0.1$ MPa.m$^{1/2}$. The 4 mass-% materials all had lower fracture toughness values, on average $3.0$ MPa.m$^{1/2}$, than the 10 mass-% and 15 mass-% UHP sintered materials. It seems that lower grain boundary content in the UHP sintered materials leads to lower fracture toughness and higher hardness.

**Figure 6.3** Hardness as a function of sintering additive content
Table 6.1 Results for the UHP materials (for details on nomenclature of UHP samples see Tables 3.14 and 3.15 in Chapter 3)

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>$\rho_{\text{theory}_1}$ (g/cm³)</th>
<th>$\rho_{\text{theory}_2}$ (g/cm³)</th>
<th>Grain boundary phase composition</th>
<th>HV10 (GPa)</th>
<th>$K_{\text{lc}}$ (MPam⁰⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHP1Y4Al</td>
<td>3.26</td>
<td>3.27</td>
<td>3.34</td>
<td>$Y_2\text{SiO}_5$, $\text{Al}_2\text{O}_3$</td>
<td>21.94 ± 0.40</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>UHP3Y5Al</td>
<td>3.29</td>
<td>3.28</td>
<td>3.35</td>
<td>$Y_2\text{SiO}_5$, $\beta-Y_2\text{Si}_2\text{O}_7$, $\text{YAlO}<em>3$, $Y</em>{4.67}(\text{SiO}_4)_3\text{O}$</td>
<td>20.42 ± 0.74</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>UHP1Y1Al</td>
<td>3.26</td>
<td>3.29</td>
<td>3.36</td>
<td>$Y_2\text{SiO}_5$, $\beta-Y_2\text{Si}_2\text{O}_7$, $\text{Al}_2\text{O}_3$</td>
<td>------------</td>
<td>---</td>
</tr>
<tr>
<td>UHP4Y2Al</td>
<td>3.30</td>
<td>3.29</td>
<td>3.37</td>
<td>$Y_2\text{SiO}_5$, $Y_4\text{Al}_2\text{O}<em>9$, $Y</em>{4.67}(\text{SiO}_4)_3\text{O}$</td>
<td>20.04 ± 0.26</td>
<td>3.3 ± 0.2</td>
</tr>
<tr>
<td>UHP4R1</td>
<td>3.20</td>
<td>3.22</td>
<td>3.30</td>
<td>------</td>
<td>23.00 ± 1.12</td>
<td>3.3 ± 0.1</td>
</tr>
<tr>
<td>UHP4R2</td>
<td>3.20</td>
<td>3.22</td>
<td>3.30</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>UHP4R3</td>
<td>3.20</td>
<td>3.22</td>
<td>3.30</td>
<td>------</td>
<td>22.82 ± 0.57</td>
<td>2.9 ± 0.1</td>
</tr>
<tr>
<td>UHP4R4</td>
<td>3.20</td>
<td>3.22</td>
<td>3.30</td>
<td>------</td>
<td>23.18 ± 0.49</td>
<td>2.8 ± 0.01</td>
</tr>
<tr>
<td>UHP15R1</td>
<td>3.32</td>
<td>3.32</td>
<td>3.39</td>
<td>$\text{Al}_2\text{O}_3$, $Y_2\text{SiO}_5$</td>
<td>20.95 ± 1.06</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>UHP15R2</td>
<td>3.33</td>
<td>3.32</td>
<td>3.39</td>
<td>$\text{Al}_2\text{O}_3$, $\text{YAlO}_3$, $Y_2\text{SiO}_5$</td>
<td>------</td>
<td>---</td>
</tr>
<tr>
<td>UHP15R3</td>
<td>3.33</td>
<td>3.32</td>
<td>3.39</td>
<td>$\text{Al}_2\text{O}_3$, $\text{YAlO}_3$, $Y_2\text{SiO}_5$</td>
<td>17.35 ± 0.40</td>
<td>---</td>
</tr>
<tr>
<td>UHP15R4</td>
<td>3.32</td>
<td>3.32</td>
<td>3.39</td>
<td>------</td>
<td>20.01 ± 0.34</td>
<td>3.3 ± 0.3</td>
</tr>
</tbody>
</table>
6.2 Microstructural characterisation

The 10 mass-% sintering additive-content materials UHP1Y4Al, UHP3Y5Al and UHP4Y2Al, as well as the 4 mass-% content material UHP4R3 and the 15 mass-% content material, UHP15R3, were investigated under the light microscope and scanning electron microscope. In optical light microscopy bright field and dark field emission modes were used, and under SEM, backscatter mode was used.

In all the materials large elongated silicon carbide grains, were seen scattered through the material. The 10 mass-% material with higher Al₂O₃-content seemed to show more of these elongated, large grains, with favoured orientation of the main axis in the same direction as which delamination was observed, perpendicular to the vertical direction of pressing. This is illustrated in Figures 6.4. This is evidence that the pressure distribution during sintering was not completely isotropic.

In addition to these elongated grains, another feature observed in all UHP materials were regions of segregated grain boundary phase. These segregations and their morphology became especially clear when viewed under dark field emission optical light microscopy analysis, as shown in Figure 6.5.
Figure 6.4 FESEM micrograph of UHP1Y4Al material

Under FESEM, the large SiC grains and regions of segregated grain boundary phase were investigated further. Due to the extremely fine, intergrown nature of the SiC grains (less than 0.5 µm) in the UHP materials, quantitative microstructural analysis was not possible. Nevertheless, qualitative microstructural analysis is given in the form of micrographs (see Figures 6.5 to 6.14 in this section).
a) Bright field optical light microscope image of region in UHP1Y4Al material

b) Dark field optical light microscope image of same region as in a)

**Figures 6.5** Bright (left) and dark field (right) optical light microscope images showing the same region in the UHP1Y4Al material, illustrating grain boundary segregation observed
In general in the ultra-high pressure sintered materials, there are large patches of grain boundary material only and large patches of SiC only. i.e. the material is inhomogeneous. Fine pores are also visible (as shown in Figure 6.6 below), and larger “elongated” pores were especially observed in the UHP4R3 and UHP15R3 materials, as shown in Figure 6.6 (additional Figures are given in Appendix G).

![FESEM micrograph of UHP4R3](image)

**Figure 6.6** FESEM micrograph of UHP4R3

In all of the 10 mass-% materials, large segregations of yttria-rich grain boundary were observed, which were not found in the green state of the samples, nor in the hot pressed or gas pressure sintered samples. Therefore it is unlikely that these segregations are a result of non-homogeneous mixing, but are a result of the densification technology.

In the UHP3Y5Al material, very fine grain size (less than 0.5 µm), as illustrated in Figures 6.7 and 6.8, was observed. In this material, segregations of grain boundary material ranged in size from a few micron
up to 40 µm, and were scattered throughout the material, as shown in the Figure 6.7.

![Image](image1.png)

**Figure 6.7** FESEM micrograph of UHP3Y5Al

An even closer look at one of these segregations, shows that they all have similar structures, as seen in Figure 6.9. The segregated region has

![Image](image2.png)

**Figure 6.8** FESEM micrograph of UHP3Y5Al
an elongated and irregular shape, which contains a core region and a thin rim, which have different compositions. The heavier elements (based on atomic number) appear as the brighter ("whiter") phase in the micrograph. Energy dispersive X-ray (EDX) analysis of the phases in the segregation regions, show that the central white phase consists of Y and O, and therefore is most likely Y\(_2\)O\(_3\). The surrounding thin layer of intermediate grey colour contains Y, Si and O and is therefore probably one of the Yttrium silicate phases, as detected by XRD and shown in Table 6.1.

Figure 6.9 FESEM micrograph of segregated grain boundary region in the UHP3Y5Al material

Similar "core-rim" structure segregations were observed in the UHP15R3 and UHP4R3 materials. The UHP4R3 segregations were however much smaller than those in the 10 mass-% and 15 mass-% materials (ca. 4 – 5 \(\mu\)m), and the Y\(_2\)O\(_3\) core was very small (as illustrated in Figure 6.10), which is because the composition of this material is high in alumina (1Y\(_2\)O\(_3\): 4Al\(_2\)O\(_3\)). Smaller core-rim segregations, similar to that shown in Figure 6.10, were also observed in the high alumina content 10 mass-% and 15 mass-% UHP materials.
Figure 6.10 Core–rim structure observed in the UHP4R3 (4 mass-
% sintering additive content material).

The ultra-high pressure sintering is a non-equilibrium sintering process: the entire sintering cycle, including heating, sintering time and cooling takes approximately 45 minutes. The resultant microstructure was a non-equilibrium one. The low reaction kinetics at low temperatures could explain the formation of the “core-rim” structures observed in all of the UHP materials, where \( \text{Y}_2\text{O}_3 \) was found to be the undissolved core material, and the yttrium silicates, as equilibrium phases, predicted by the yttria-alumina-silica phase diagram, Figure 5.3, precipitated on the yttria\(^{169}\). The high pressure may have contributed to the observed agglomeration and segregation of yttria.

Although the morphology of these segregations are unique to the ultra-high pressure sintered materials, the segregation of the more Y-rich phases was also observed in the \( \text{Y}_2\text{O}_3 \)-rich gas pressure sintered and post-sintering heat treated materials (given in Figure 5.10). The fact that \( \text{Y}_2\text{O}_3 \) is always found to be segregated in the inner part of the
segregations in the ultra-high pressure sintered materials, is also evidence for the poor wetting behaviour of Y-rich phases of silicon carbide (which was also observed in gas pressure sintering and discussed in section 5.1).

The UHP4Y2Al material’s microstructure, appeared to be more homogeneous than the UHP3Y5Al microstructure. The UHP4Y2Al material’s microstructure contained more grain boundary phase visibly spread out throughout the microstructure, as shown in Figure 6.11. However, large SiC grains and some smaller segregated grain boundary core-rim structures were still visible in the material.

![Figure 6.11 FESEM micrograph of UHP4Y2Al](image)

In the UHP1Y4Al material, grain boundary segregated pools are also observed as in Figure 6.10, but they are smaller than in the other 10 mass-% UHP materials. The silicon carbide structure in the UHP1Y4Al material (shown in Figures 6.4 and 6.12), appears to be more intergrown than the UHP4Y2Al material (shown in Figure 6.11). This is related to the higher Y2O3-content in the UHP4Y2Al material. The inner part of grain boundary segregated pool, which consists of Y and O, is much smaller in this material, compared to the outer rim, illustrated in Figure 6.13. This makes
sense since this material has the least $Y_2O_3$ content compared with the other two 10 mass-% UHP materials.

Figure 6.12 FESEM micrograph of UHP1Y4Al

Figure 6.13 FESEM micrograph of segregated grain boundary region in UHP1Y4Al
Another interesting feature in the highest alumina sintering additive composition materials (UHP1Y4Al and UHP15R3), is the presence of a high number of large SiC grains scattered throughout the material, surrounded by cracks. This is shown in Figure 6.14 and illustrated for the UHP15R3 material in Figure G7 (Appendix G). The coarser SiC grains in the UHP1Y4Al material appear to be larger and more elongated than in the UHP3Y5Al and UHP4Y2Al materials. This is in agreement with the observations in the hot pressed and gas pressure sintered materials, where higher grain growth was observed in the higher alumina content materials. These cracks observed around the large SiC grains are not observed in the UHP3Y5Al and UHP4Y2Al materials.

The cracking can be attributed to high residual tensile stresses in the material. The higher thermal expansion of the grain boundary material surrounding the large area of SiC, which has lower thermal expansion, results in this surrounding material being placed under residual tensile stress after cooling. The rapid cooling hence could lead to the observed crack formation.
SUMMARY

As expected, sintering at lower temperature (ca. 1550°C) using ultra-high pressure, resulted in a very fine grained, non-equilibrium microstructure. However, the hardness values of the UHP LPSSiC material were not higher than that of the HP and GPS materials. The higher alumina content 10 mass-% material UHP1Y4Al, had a higher hardness than the other 10 mass-% materials, probably due to higher hardness of the grain boundary component in this material. Hardness of the UHP LPSSiC materials increased, and fracture toughness decreased with decrease in grain boundary content. This shows the significant influence which the softer grain boundary content has on the mechanical properties of these UHP LPSSiC materials.

The fine-grained intergrown microstructures meant that quantitative microstructural image analysis could not be done on the UHP materials.

Figure 6.14 UHP1Y4Al material large grains observed with crack surrounding them (also observed in the UHP15R3 material, Figure G7).
High strain in the materials contributed to the broadening of the XRD peaks. A mixture of yttrium silicates, as observed in the HP materials, and aluminates, as seen in the GPS and heat treated materials, were observed in the UHP materials. YAG was not observed in any of the UHP materials.

Special features observed in all the UHP microstructures were large SiC grains scattered through the material and core-rim structures of segregated grain boundary regions. These core-rim structures probably arise because the sintering temperature is not high enough and sintering time not long enough, for all the sintering additives to dissolve and homogenise. The Y$_2$O$_3$ in particular precipitates as a non-equilibrium phase, with the equilibrium yttrium silicate phases precipitating onto the Y$_2$O$_3$, forming the rim of the structure. The core region was observed to become smaller as the Y$_2$O$_3$ content in the material decreased.

In the high alumina content materials, a higher number of large SiC grains were observed. These coarse silicon carbide grains had cracks circling them. This must be due to high residual tensile stresses in the material after rapid cooling.