Sintering of ZrC by Hot Isostatic Pressing (HIP) and Spark Plasma Sintering (SPS); effect of impurities.

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Abstract
Carbides are generally used as structural materials for high temperature applications. Particularly, ZrC because of low activation, neutronic transparency, cubic structure (isotropic behaviour) and good thermal conductivity, is one of the candidates under consideration for structural materials in the core of new high temperature nuclear reactors (Generation IV).

Just a few studies about densification of monolithic ZrC exist. They mainly involve natural sintering or hot pressing at high temperature (until 2700°C). Unfortunately those processes induce grain growth [1,2,3,4] and do not lead to fully densified ZrC.

The aim of this study is to compare the characteristics and the properties of ZrC sintered by HIP and by SPS. Fully dense ZrC can be reached either by HIP or by SPS, grain size being more or less controled. Microstructural observations and mechanical testing of several ZrC grades shows that powder impurities play an important role in the quality of the grain boundaries and consequently in the mechanical properties. In particular, the porosity falls from 17% to 3% just by reducing the free carbon content in starting ZrC powder. The densification process of dense monolithic ZrC was improved by combining a HIP at 1600°C (titanium canning) followed by a post-HIP at 1900°C (no canning required). Four-point bending tests are in progress to confirm the improvement of fracture strength.

Introduction
In new concepts of future nuclear reactors such as Gas Fast Reactors (GFR- Generation IV) the core structure materials have to face high temperatures (>1000°C) and high level of dose (>80 dpa). Consequently, to fit those drastic conditions, the choice focused on ceramics and specifically on nitrides and carbides, exhibiting a high thermal conductivity and a cubic structure suggesting no anisotropic swelling due to irradiation. In that framework, Zirconium Carbide (ZrC) is one of the candidates. But densification of monolithic ZrC is a technical challenge due to its high fusion temperature (Tf=3445°C) and the strong covalent boundary, whichbridles diffusion.

In the present work, sintering investigation of ZrC densification has been run by two techniques, involving “a priori” very different densification mechanisms: Hot Isostatic Pressing (HIP) and Spark Plasma Sintering (SPS). This paper presents and compares the impurities effects on densification and microstructure of ZrC sintered by HIP or SPS. A conclusion highlights the main results and gives perspectives for the continuation of the study.

1. Experimental procedure.

1.1. Process parameters
ZrC fusion temperature is very high (~3445°C). Such as the main part of the transition metal monocarbides, it exhibits a cubic structure NaCl type allowing stoechiometry from ZrC_{0.6} to ZrC_{1}. In most of the studies, ZrC is densified by natural sintering at very high temperatures (until 2800°C) [1,2] or by hot pressing from 10 to 1500 MPa [3,4]. The materials obtained by these techniques are not dense (<95% theoretical density) and exhibits very large grains, most of the time higher than 10 µm with grain size heterogeneities.

In the present work HIP and SPS fabrication process have been used:
The HIP press is an ACB brand, which can work under pressure up to 200MPa and at temperature as high as 1900°C (below 1600°C, a titanium canning is used, above 1600°C, a tantalum canning is necessary).
The SPS device is a SPS-2080 from Sumitomo, which can provide a maximum uniaxial sintering pressure of 100MPa. A current up to 8000 amperes is sent through the sample and, by creating electric spark, allows a densification in very short times (typically a few minutes). In those conditions the temperature at the
edge of the sample can reach 2000°C (measured on the
graphit matrix by a pyrometer).

Table 1 presents the characteristics of the two powder
grades that have been densified by HIP process. The
first powder is a ZrC_{0.93} commercial grade (Commercial
Powder, CP grade B from HC STARCK). It contains a
lot of free carbon and hafnium impurities. The second
powder has been developed especially in the scope of
this study by HC. STARCK (Special Powder, SP). The
stoichiometry is close from the CP powder (ZrC_{0.94}) but
the free carbon and Hafnium content has been
considerably lowered.

The ZrC sintering conditions by both HIP and SPS are
presented in Table 2. Some samples were heat treated
twice by HIP in order to eliminate the closed porosity if
open porosity is less than 0.1% (“post-HIP”). The post-
HIP step is performed without canning the HIPed
sample.

<table>
<thead>
<tr>
<th>Chemical analysis (weight%)</th>
<th>CP</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr + Hf</td>
<td>87.6 %</td>
<td>87.7 %</td>
</tr>
<tr>
<td>C total</td>
<td>11.6 %</td>
<td>11.3 %</td>
</tr>
<tr>
<td>O</td>
<td>0.3 %</td>
<td>0.8 %</td>
</tr>
<tr>
<td>free C</td>
<td>1.1 %</td>
<td>0.4 %</td>
</tr>
<tr>
<td>Hf</td>
<td>2.0 %</td>
<td>0.1 %</td>
</tr>
<tr>
<td>Granulometry</td>
<td>50%</td>
<td>4 µm</td>
</tr>
</tbody>
</table>

Table 1: ZrC Powder characteristics.

2. Results

Table 3 shows the relative densities of ZrC samples
densified with sintering conditions described in
section 1. All the samples are fully densified (>95 %
theoretical density) except ZrC_{HIP}(1600°C,CP) which
exhibits almost 18% porosity left. Those results clearly
highlight the effects of the starting powder grade on the
densification efficiency. In particular, for similar
sintering conditions (HIP, 1600°C, 200MPa), the
relative density can increase from 82.6% up to 96.9%
just by reducing the impurities in the starting powder.

2.1 ZrC densified by HIP

The microstructure of ZrC_{HIP}(1900°C,CP) is
represented on the SEM micrography of Figure 1. It
exhibits small grains (3-5 µm) suggesting a quite
limited grain growth and residual intergranular
porosity. A lot of grains have been pulled out during the
mechanical polishing, which may sign very weak grain
boundaries and then a mediocre mechanical behavior.
This is confirmed by a Vickers hardness of 18.3 GPa
whereas the basic reported value is 27 GPa. Four points
bending tests also confirm the expected poor bending
strength (310MPa while 490MPa in literature) and the
large result dispersion.

The following section deals with the microstructural
observations and is focused on the best densified
specimen ie

ZrC_{HIP}(1900°C,CP),
ZrC_{HIP}(1600°C,SP) +_{post HIP}(1900°C)
ZrC_{SPS}(1800°C, CP)
ZrC_{SPS}(1800°C, CP)

2.2 Characterization tools

Densities have been determined by hydrostatic
weighting. The microstructure of the samples was
investigated (i) by Scanning Electron Microscopy (SEM)
on their cross section after polishing, (ii) by Transmission Electron Microscopy (TEM) after
mechanical grinding and ion milling of specimens.
Mechanical characterization was achieved on
ZrC_{HIP}(1900°C,CP) using 4-point bending test at room
temperature followed by Weibull statistical analysis
from 32 fractured beams [5].
Vickers microhardness analysis have been run on a
Leica VMHT 30 A, loaded at 300g during 15s.
Fig 1: SEM micrography of ZrCHIP(1900°C,CP)

Fig 2 TEM micrography of ZrCHIP(1900°C,CP)

Fig 3: SEM micrography of “ZrCHIP(1600°C,SP) + post HIP(1900°C)”.

Figure 3 shows the microstructure of “ZrCHIP(1600°C,SP) + post HIP(1900°C)” (the microstructure of ZrCHIP(1600°C,SP) + post HIP(1800°C), not presented here, is very similar despite a bit higher residual porosity). This sample exhibits an optimal microstructure showing no grain pulling out, a mainly intragranular porosity and grains of 4 to 8µm in diameter suggesting a beginning of grain growth. This microstructure is in agreement with the achievement of the densification step.

2.2 ZrC densified by SPS

The microstructures of SPS sintered ZrC are presented on microographies of Figure 4 and 5. In spite of quite similar densities (see table 3), the two sintering conditions lead to very different microstructures.

Fig 4: SEM micrography of ZrCSPS(1800°C, CP)

Fig 5: SEM micrography of ZrCSPS(1950°C, CP)

ZrCSPS(1800°C, CP) exhibits small grains with diameter ranging from 3 to 5µm suggesting a limited grain coarsening. Residual porosity is exclusively intergranular and grains seem to be few linked. This typical microstructure corresponds to the beginning of intergranular bridging: the densification step is under progress.

On the other hand, ZrCSPS(1950°C, CP) sample exhibits large grains (~10µm in diameter), well defined grain boundaries and mainly intragranular porosity. The residual intergranular porosity together to some non-spherical shaped intragranular porosity suggests that grain growth is under progress and that the microstructure can be further improved.

3 Discussion

Either HIP or SPS sintering process enables to reach 99% of ZrC theoretical density.

By HIP, the sintering optimisation consisted, in a fist time, in decreasing the free carbon content in the starting ZrC powder: indeed, preliminary characterisations highlighted a carbon segregation at grain boundaries that should explain the limited grain coarsening (carbon is known to bridle chemical diffusion) and consequently the mediocre mechanical strength (Hf impurities are probably of importance too).

In a second time, two HIP steps were combined to reach the maximum density: the first at 1600°C and the second at 1900°C. In the same way, this process results in a decrease in fabrication cost because (i) Ti
Canning is sufficient for the first HIP (much cheaper than Ta canning) and (ii) no canning is required for the second HIP.

By SPS, high density are easily reached but the optimal microstructure is obtained in ZrC$_{SPS}$ (1950°C, CP). The presence of free carbon in the starting powder does not obviously affect the densification whereas this is dramatic in the HIP process. This difference could be explained by the sintering mechanisms occurring in SPS process: (i) temperature at grain boundaries should be higher than the measured temperature and thus, higher than HIP temperature (ii) as sintering results probably from spark electric heat between particles, the diffusion at grain boundaries should be very peculiar. Further TEM investigations will precise where is the carbon in SPS specimen.

In addition, microstructures of dense HIPed and SPS sintered ZrC (“ZrC$_{HIP}$ (1600°C, SP) + post HIP (1900°C)” and “ZrC$_{SPS}$ (1950°C, CP)“) are very different. Despite final comparable grain size, HIP densification leads to faceted grains with straight grain-boundaries whereas SPS sintering results in mainly round shaped grains. Again, the densification mechanisms relative to HIP and SPS process should be involved.

4 Conclusions

Despite ZrC high refractivity and strong covalent boundary, fully densified samples (99 % theoretical density) have been obtained both by HIP and by SPS. Nevertheless a sintering temperature as high as 1900°C is necessary in the two fabrication process.

By HIP, a free-impurities powder (in particular carbon and hafnium) must be processed to achieve high density. Two sintering steps are necessary to obtain a dense material with cohesive grain boundaries (1600°C then 1900°C). By this double HIP it’s possible to avoid Ta canning, which reduces the cost of the process. Presence of impurities in the starting ZrC powder does not apparently have bad consequences on SPS sintering. Despite very high density, the microstructure suggests that it can be further improved through, eg, the reduction of intergranular porosity. Sintering efficiency (density), impurity effects (free carbon) and final microstructure (grain shape) seem to be very different from HIP or SPS process. CEA and CNRS launched in 2004 a common investigation program dedicated to the understanding of mechanisms involved during SPS sintering through the comparison of HIP and SPS process. Finally, to evaluate the potential use of ZrC as structural component in future nuclear systems (Gas Fast Reactor), an irradiation program is planned in Phenix reactor that will allow to precise the under-irradiation behaviour of the most promising materials.

5 Acknowledgements

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6. References

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