Reaching full density of 100Cr6 PM steel by capsule free hot isostatic pressing of high-velocity compacted material

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ABSTRACT

Spherical gas atomised 100Cr6 steel powder, processed with the MMS-Scanpac® process to 95% density (agglomeration, followed by conventional pressing, low temperature sintering and re-strike using high velocity adiabatic compaction) has been fully compacted using capsule-free hot isostatic pressing. The material is characterised at different steps of the process and the results are discussed in this paper. Sintering steel powder with high content of carbon requires carbon control at sintering. By continuously measuring the atmosphere at sintering the ingoing gases are adjusted so that carbon control is achieved. Computational work has been made in order to determine how the sintering atmosphere should be adjusted based on the oxygen release and moisture content in the furnace at sintering.

KEYWORDS: Capsule free HIP, high velocity compaction, 100Cr6, carbon control

INTRODUCTION

Producing components through powder metallurgy have some general advantages that should be taken into account. One advantage is that powder materials offer a better chemical homogeneity due to a finer solidification structure. At conventional casting segregation will occur due to the solidification range, with different compositions of first and last solidified material. To some extent this can take place in a powder grain as well but the diffusion distances are much smaller. A powder droplet will also experience a much higher cooling rate which will practically freeze the melt giving less segregation. Another advantage is the possibility to directly shape a component with little need of machining. The high level of material usage gives material and energy savings compared to the corresponding casted, forged, and machined product.

Producing fully dense PM components through HIP normally requires a capsule in order to give the product its shape. The integrity of the capsule is critical. If the capsule is leaking consolidation might not occur, or argon might be introduced in the material giving pores which limits the mechanical properties. After densification the capsule has to be removed by machining or acid pickling. The cost of capsule production and handling per component can so high that it is not motivated to produce small components through capsule based HIP.

The submitted paper will present a PM route to reach full density of products by capsule free HIP, the MMS-Scanpac® method. The method mainly focuses on components in the interval 50 gram to 5 kg. The steel powder 100Cr6 is used, which is a material for automotive and bearing applications and exhibit high fatigue and wear-resistance. The process starts with the agglomeration of gas atomised powder followed by conventional pressing. A low-temperature sintering is made, which produce a preform with a relative low density, approximately 75-80% of theoretical density. This preform is then given a re-strike using high velocity adiabatic compaction. This process step will raise the density to approximately 95%. At this state, the surface of the material is gas-tight which allows for a capsule-free hot isostatic pressing to fully compact the material. Further information about the process is given in [1].

The use of gas atomised powder like 100Cr6, prealloyed with a high concentration of strong oxide formers like chromium, manganese and silicon, requires sufficiently reducing sintering atmospheres in order to ensure a successful sintering. Oxygen in the powder or introduced early in the process will remain in the material and influence the mechanical properties of the final component. The 100Cr6 steel powder also contains high carbon content, approximately 1wt%. Carbon as a small interstitial atom is highly mobile and the material will decarburise at high temperature if a low carbon potential is present at the surface. In order to keep carbon in the material the carbon potential of the gas should meet the carbon potential of the material in order to keep the system at equilibrium.

Nitrogen/hydrogen gas mixtures are the dominating choice for sintering of steel powder parts. Hydrogen is a reducing gas that will remove surface oxides and assist the sintering and compaction. Hydrogen can also be decarburising since it reacts with carbon in the material forming methane. This reaction is limited since methane is relative unstable high temperature gas specie. On the other hand, oxygen in the sintering furnace in the form of water vapour can be decarburising since it allows for the formation of carbon monoxide, which is stable at high temperature. All furnaces contain some amount of oxygen. It can be remaining moisture in the furnace, or leakage from outer atmosphere. In order to keep carbon in the material the moisture content in the furnace should be monitored. Based on the moisture content a hydrocarbon such as methane can be added for carbon control.

The present work will present a method to produce fully dense components based on capsule free HIP. Material will be characterised and evaluated at different steps of the process. The use of high-alloyed materials at sintering requires a sintering atmosphere which is both reducing and offers carbon control, which will be discussed in the present work.

MATERIALS AND METHODS

Gas atomised 100Cr6 steel powder produced by Carpenter Powder Products has been used. The composition of the steel powder is given in Table 1.

Table 1. Composition of 100Cr6 steel powder

Grade	C	Si	Mn	Cr	Co
100Cr6	0.98	0.5	0.4	1.5	0.2

A component has been produced following the MMS-Scanpac® process [1]. Spherical gas atomised powder was agglomerated followed by conventional uniaxial pressing. The green body was then sintered in a continuous furnace. A sintering temperature of 1120ºC was used, with 4 hours sintering stage including delubrication, sintering, and cooling. Sintering was made in a H_2/N_2 gas mixture with CH_4 added for carbon control. At sintering, the dew-point (H_2O), CO, CO_2 and CH_4 concentrations were continuously measured. After sintering, the components were re-striked by high velocity adiabatic compaction. This gave a gas-tight surface which allowed for capsule-free HIP. Standard HIP-cycle has been used with 1000 bar and 1150ºC for three hours.

Thermodynamic calculations in this work have been made with Thermo-Calc version 4.1 [2]. The thermodynamic database TCFE7 and mobility database MobFe2 have been used. The samples have been characterised with SEM using EDS for element quantification.

RESULTS

Equilibrium calculation for 100Cr6 has been made based on the composition given in Table 1. The fraction of stable phases as function of temperature is presented in Figure 1a. The transformation temperatures from high to low temperature are as follows: liquidus 1452ºC, solidus 1332ºC, cementite start 910ºC, ferrite start 753ºC.

The stable oxides as function of oxygen activity for 100Cr6 at 1100ºC have been evaluated as well, as shown in Figure 1b. The oxygen activity is the square root of the partial pressure oxygen in the sintering atmosphere. The oxide that is stable at the lowest activity is the most stable oxide, which is quartz SiO_2. Other stable oxides are rhodonite $MnSiO_3$ and spinel type of oxide Cr_2MnO_4. An oxygen activity 10^{-9} at 1100ºC corresponds to a dry hydrogen gas mixture with -55ºC dew-point.

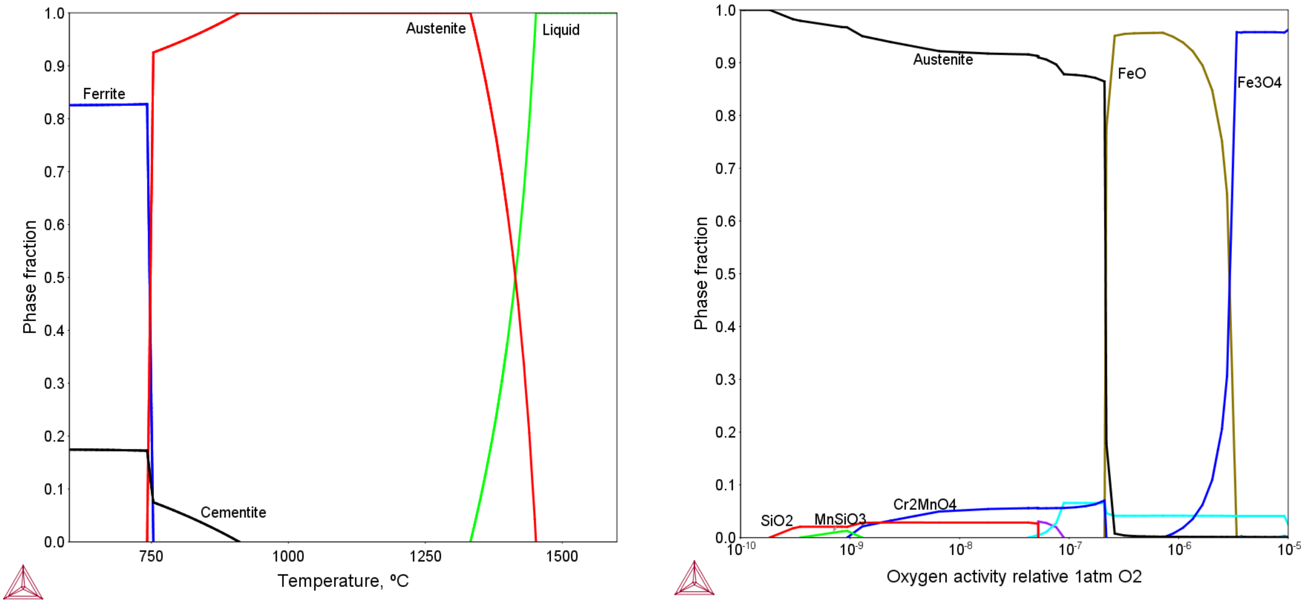
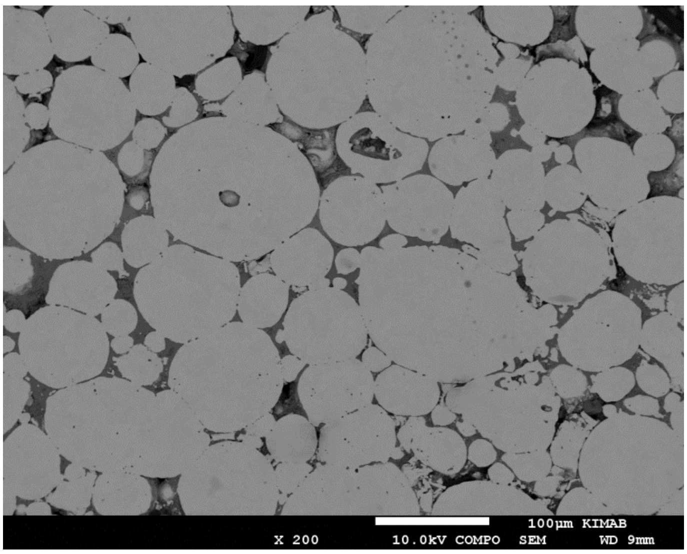


Figure 1. Equilibrium calculation for Fe-0.98C-0.5Si-0.4Mn-1.5Cr-0.2Co using TCFE7 database. a) Stable phases as function of temperature b) Stable oxides as function of oxygen activity at 1100ºC

The 100Cr6 steel powder has been low temperature sintered, and a sintered component is shown in Figure 2b. It is cylindrical with 5 cm diameter and 1 cm thickness. This material has been characterised with SEM, and a typical microstructure is presented in Figure 2a. As expected, a high amount of porosity is present and the original spherical gas atomised powder grains are shown. Some of the powder particles shows minor amount of deformation.



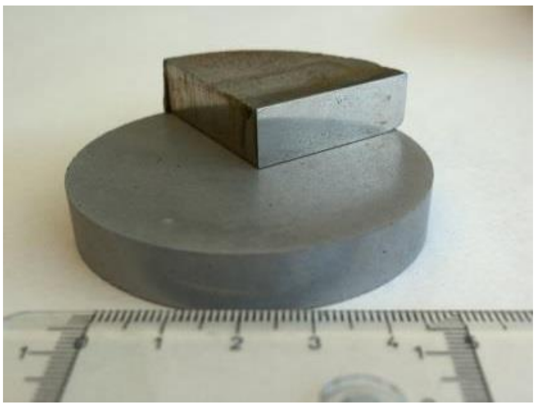


Figure 2. a) Backscattered image of low-temperature sintered specimen b) sintered specimen.

The material was re-strike, and then HIPed using standard heating cycle 1000 bar and 1150ºC for three hours. A micrograph of the final microstructure is shown in Figure 3. This figure is from the centrum of the HIPed sample showing a fully dense material with few oxides. The oxides are shown as black inclusions, and are typically smaller than 1 µm in size.

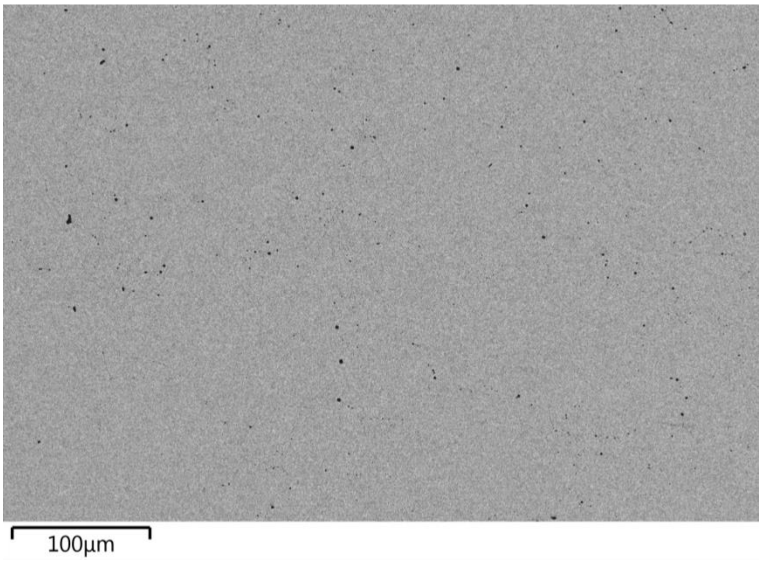
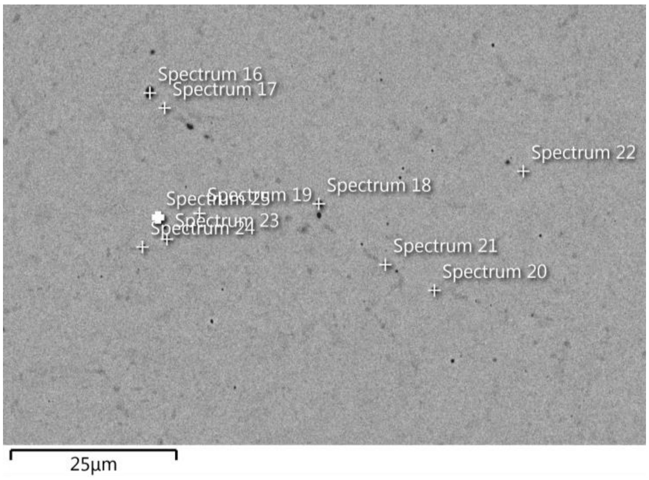


Figure 3. Micrograph of HIPed sample. Tiny oxides, less than 1 µm in size, are shown in black.

An additional micrograph of the HIPed material is shown in Figure 4, in higher magnification and with EDS analysis of oxides. The oxides are small and the measured spectrums are typically a mixture of oxide and surrounding matrix. A clear increase in silicon content is seen and the oxides are probably of quartz SiO_2 type. The concentrations are given in weight-percent, and an ideal atomic 1:2 relation for SiO_2 corresponds to 1:1.14 in weight.



Spectrum	O	Si	Cr	Fe
Spectrum 17	7.6	5.5	1.7	85.2
Spectrum 21	5.0	5.1	2.9	87.1
Spectrum 23	8.3	5.9	1.4	84.5
Spectrum 24	7.8	5.3	1.2	85.7

Figure 4. Micrograph and EDS analysis of the HIPed material. Concentrations are given in weight-percent.

The densities of the LT-sintered sample, re-striked sample, and HIPed samples at two different states, have been measured. The results are summarised in Table 2. One HIPed sample was hardened, and one sample was as-received after HIP. The state of the materials was verified by hardness measurements. The HIPed material gave 58 HRC at the surface and 54 HRC in the centrum of the component. The as-received material gave 20 HRC. The density was measured by Archimedes method, except the LT-sintered material which was estimated from its mass and volume. The theoretical density values are taken for a conventional steel of similar compositions [3]. It can be seen that the HIPed material gives over 99% of theoretical densities.

Table 2. Measured and theoretical densities for different process states.

Process state	**Measured density, g/cm^3**	**Theoretical density, g/cm^3**	**Fraction of theoretical density**
LT-sintered	~6.3	7.84	~80%
Re-strike	7.57-7.62	7.84	96.5-97.2%
HIP (ferritic + carbides)	7.79	7.84	99.4%
HIP + hardening	7.67	7.71	99.5%

(martensitic)			

The high carbon content of the steel powder requires carbon control at sintering. The possible rate of decarburisation without carbon control has been evaluated with Dictra software. A simulation has been made for 100Cr6, with 5 mm length from centrum to surface, 1100ºC for 1 hour, and a boundary condition with low carbon activity. The resulting carbon profiles at different times are shown in Figure 5a. With time the material decarburises through solid state diffusion of carbon to the surface. Carbon is a quick diffusing element and the process is rapid at 1100ºC. After 1 hour the outer 1 mm of the component has lost 50% of its carbon content. This illustrates the need for carbon control, which can be achieved by raising the carbon activity of the sintering gas.

Water vapour in the sintering gas will act decarburising, which can be compensated by the use of methane. Methane is a low-temperature stable gas specie and will decompose at high temperature giving carbon potential to the sintering gas. The increase in carbon potential, or carbon activity, with temperature for N_2/H_2 a gas mixture including methane is presented Figure 5b. The calculation is made with Thermo-Calc. The steel powder 100Cr6 contains 1% of carbon. The solubility of carbon in the steel will increase with temperature and as a consequence its carbon activity will fall with temperature, as shown in the figure. By optimising the methane content it is possible to have identical carbon activity in material and gas at sintering temperature. In a theoretical situation, without oxygen in furnace, approximately 0.14% methane is needed for carbon control. A furnace with oxygen, or moisture, will require additional methane. This is illustrated how different oxygen contents in the gas mixture can be compensated by additional methane. 0.5%O corresponds to -3ºC dew-point. The minor difference at around 800ºC is due to the additional carburising effect of CO, which is relative weak when comparing with methane.

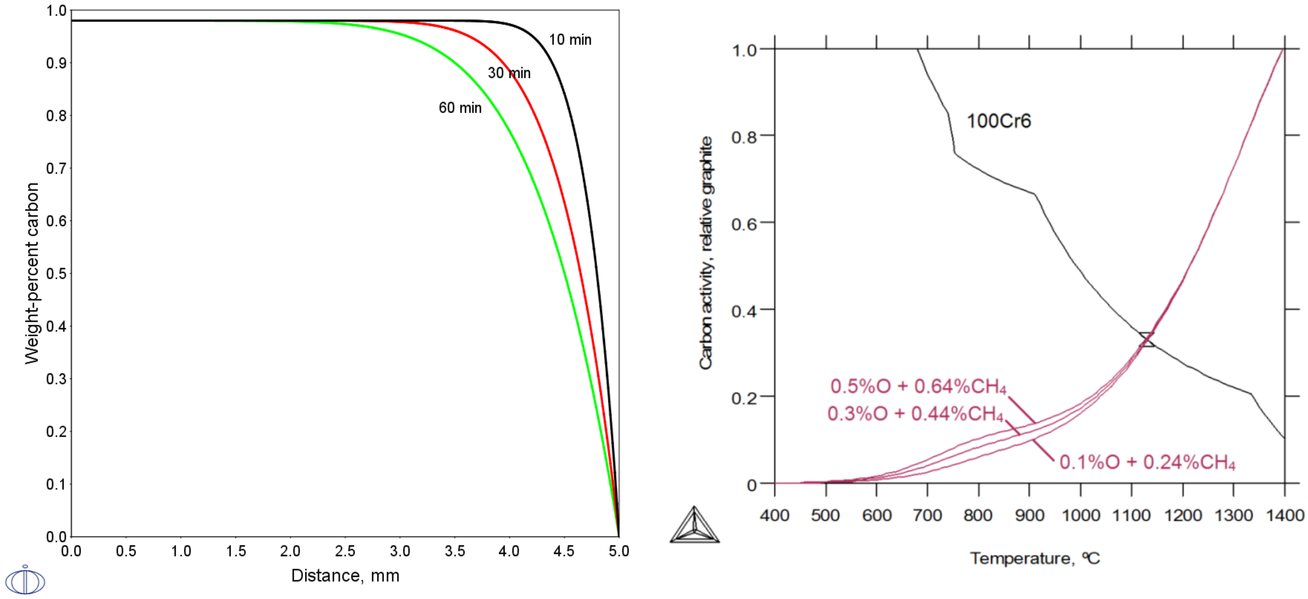


Figure 5. a) Decarburisation profiles simulated at 1100ºC after 10 minutes, 30 minutes, and 60 minutes. b) Carbon activity in 100Cr6 and three different atmospheres with carbon control.

The relation between dew-point *T* in K, and moisture content $y_{gas}^{H_2O}$ is given by the following relation:

$$y_{gas}^{H_2O} = 3.76 \cdot 10^6 exp\left(-\frac{46000}{RT}\right)$$

where *R* is the gas constant. The above expression has been evaluated based on thermodynamic data of water and water vapour. When making low-temperature sintering of 100Cr6, the dew-point was measured and additional methane content was added in the same amount. The ingoing steel powder contained 0.98C. Carbon analysis was made on the low-temperature sintered material, which gave 1.02C and 1.03C measured on two samples.

Discussion

A method to produce fully dense components through capsule-free HIP has been presented and evaluated. Based on agglomerated gas atomised powders traditional uniaxial pressing was used to produce a green part for sintering. The low-temperature sintering produces a preform that can be compacted to higher density through plastic deformation at an additional re-strike. This process gives a gas-tight surface which makes the preform suitable for HIP or high-temperature sintering to reach full density.

The use of gas atomised powders allows for a wide range of alloy types. High alloying contents can be used, since chemical segregation is limited to the size of the powder grain. In this study 100Cr6 steel powder was used, which contains high concentrations of strong oxide formers like chromium, silicon, and manganese. Some oxides were seen in the HIPed state, which were mainly of quartz type SiO_2. The present oxides were small, less than 1 µm in size, and should have little influence on the mechanical properties. The calculation showed that the most stable oxide was SiO_2, which was stable down to very low oxygen activities corresponding to a very dry hydrogen environment. Due to great stability of the oxide it will become very important to minimise the ingoing oxygen content in the process. By the use of gas atomised metal powder the ingoing oxygen content is low. In addition, the delubrication part will be important to ensure that all excess oxygen has left the material before sintering starts.

A sintering atmosphere with low oxygen content is also important for carbon control. Oxygen, in the form of moisture, will react with carbon and lower the carbon potential in the furnace. It was shown in this work that carbon diffusion at sintering temperatures is a rapid process and decarburisation can happen quickly. The surface of the sample is decarburised first, which will directly influence the properties of the component since the hardness of martensite falls with carbon content [4]. In order to ensure a neutral environment, a hydrocarbon such as methane should be added in the same amount as water vapour in the furnace. In this work the moisture content was continuously measured by a dew-point meter and based on this information methane was added. The sintered specimen had similar carbon content as the ingoing powder.

Conclusions

A method to produce fully dense components through capsule-free HIP, MMS-Scanpac® method, has been evaluated for 100Cr6 steel powder. Material has been characterised at different steps of this process showing the increase in density from low-temperature sintering, high-velocity compacted preform, to HIPed component. The final components showed 99.4 and 99.5% of theoretical density.

The HIPed material showed a fine microstructure with few oxides. The oxides were typically less than 1 µm in size. EDS quantification indicated Si-enrichment, and the oxide is most likely of SiO_2 sort. This is in agreement with thermodynamic calculations for this material at sintering.

The need of carbon control has been demonstrated by kinetic modelling of decarburisation at sintering. Simulation showed that after 1 hour at 1100ºC the outer 1 mm of the component has lost 50% of its carbon content. A method for carbon control was introduced, and how to correlate measurable dew-point data to required hydrocarbon such as methane to achieve carbon control was presented and evaluated.

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