Gravitational Defects from Sintering of Hard Metal

Marcus Maiorana

Master Thesis
Department of Theoretical Physics
Royal Institute of Technology, Stockholm, Sweden
Stockholm 2012
Abstract

Sintering is a manufacturing process for metal components and is used at Seco Tools AB to produce hard metal inserts for milling and turning. A metal powder is first compressed into the desired shape of the product and is then heated to some temperature below its melting point. During the heating process, grains of the powder "sinter together" which makes the material strong. The aim of this report is to investigate how gravity affects the shape of the body during sintering since the body becomes soft at high temperatures and might deform under its own weight. Bending of thin rectangular hard metal pieces has therefore been investigated during sintering. It has also been investigated how gravity affects edge deformation, since edge deformation is a problem in some inserts at SECO. The main results were that most inserts produced at SECO are too small for gravity to have an impact, and that gravity is not responsible for edge deformation. For completion, it has still been investigated what constitutive equation describes the deformation during sintering. It was found that hard metal is best described by a viscoelastic model. A future goal is to elaborate this result, so that simulations can be made to predict the deformation of hard metal products during sintering.
Acknowledgements

This work has been carried out at Seco Tools AB in Fagersta, Sweden. First of all, I would like to express my gratitude to my supervisor Dr. Martin Schwind for great guidance and many interesting discussions. I would also like to thank my other colleagues at Seco Tools for making my stay in Fagersta a pleasant experience. Thanks also to my examiner Professor Olle Edholm at KTH for his professional help during the project. I would also like to thank my aunt Marketta and her husband Jukka for providing a home for me in Fagersta. Finally I would like to thank Sara and my family for their support during the project.
Contents

1 Introduction 2

2 Background 3
   2.1 Euler Bernoulli beam theory . . . . . . . . . . . . . . . . . . . . . . . . . . . 4
   2.2 Other deformations . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 6

3 Experimental Procedure 7

4 Results 8
   4.1 Beam samples . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 8
   4.2 Insert Samples . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 11

5 Discussion 13
   5.1 Mechanisms of deformation . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 13
   5.2 The constitutive equation . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 14

6 Conclusion 16
1 Introduction

The work of this report has been carried out at Seco Tools AB, a manufacturer of cutting tool inserts used in turning and milling. Turning and milling are processes where a piece of metal is shaped by cutting it and the end product can be anything from a car component to a turbine blade. Fig. 1 shows how an insert is used in a turning process. In order to cut through a work piece made of some metal one must use a cutting tool insert made of some even more durable material. Hard metal, also called cemented carbides, is one such material and the bulk of the inserts made at SECO consist of tungsten carbides (WC) cemented by cobalt (Co). As the name suggests it can be compared to concrete where WC is the aggregate and cobalt is the binder phase. The insert is also coated with a few thin layers of some even stronger compound such as titanium carbide or aluminium oxide through the process of physical or chemical vapour deposition, though this is not considered in this report. The micro structure of a typical insert can be seen in Fig. 2 which shows a cross section of an insert.

![Figure 1: A high speed picture of a turning process. The light grey part in contact with the work piece is a hard metal turning insert from SECO.](image1)

![Figure 2: Typical micro structure of an insert. The grey regions are WC and the white are cobalt. The upper layer is the CVD coating.](image2)

The first step in the manufacturing process is to mix the constituents. The main constituents are WC and Co where Co makes up about 5 to 15 percent depending on the desired properties and WC makes up the rest. The WC grain size also plays an important role for the desired properties of the grade and it ranges from about a half to a few $\mu$m. There can also be small amounts of different additives such as chromium, titanium or tantalum. The chemical compound Poly Ethylene Glycol (PEG) is also mixed with the constituents to make the mixture gluey. The mixture is then spray dried into granules that are about a hundred $\mu$m large, and this is then pressed into the desired shape of the insert. After pressing the insert is referred to as a green body and is very brittle, and also very porous with a relative density of about 60%.
The green body is then put in a furnace where it is slowly heated to about 1500°C. This heating process is called sintering and transforms the insert in the following ways. In the interval 150 - 400°C the PEG is vaporized during decomposition. At 1100°C the insert starts to shrink significantly as densification occurs through reduction of pores. And at 1350°C an eutecticum is formed between WC, Co and C making the cobalt melt, thus reducing the remaining pores. During most of the process neighbouring WC grains grow together, despite the temperature being far below the melting point of WC. This is called sintering and an illustrating example is when ice cubes in water stick to each other and form a single ice cube. Once the insert is cooled the structure has become very strong.

During sintering, densification inevitably makes the insert shrink, but the the shape of the insert may also be distorted in other ways. These distortions are removed if necessary by grinding, which is a costly and time consuming process. The aim of this report is to investigate deformations caused by gravity, and the hypothesis is that the insert is so soft at high temperatures that gravity contributes to deformation. Another known reason for deformation is non-uniform packing densities in the green body, which leads to non uniform shrinkage. Also friction against the support is known to lead to anisotropy.

2 Background

The gravity force induces stress fields in massive bodies, so in order to calculate the deformation of a body one must know the relation between stress and strain - the constitutive equation. Hook’s law $E\epsilon = \sigma$ is probably the most well known relation and describes elastic materials. The opposite of an elastic material is a viscous material and in the simple linear viscous model the strain rate is proportional to the stress according to $\dot{\epsilon} = \sigma/\eta$ where $\eta$ is the viscosity. A viscous material is fundamentally different to an elastic material since there is no limitation on the actual strain. In an elastic material the micro structure can be thought of as being held together by many small springs while in a viscous material there is only friction force that prevents movement.

Some materials show both elastic and viscous properties, so called viscoelasticity, and Fig. 3 shows a typical strain curve for such a material. This behaviour is also known as creep and is typical for metals at high temperatures [1]. Experiments by for example Lee et al [7] has also shown such a creep behaviour during sintering of a $ZrO_2$ based ceramic, a material fairly similar to hard metal.

![Typical creep curve for metals at high temperature. A constant load is applied at $t_0$ and $\epsilon$ is the resulting strain. $\epsilon_0$ is the instantaneous elastic strain.](image)
A goal of this study is to find an adequate constitutive equation and in general it is
done through some uni axial tensile test, where elongation is measured while the stress
is controlled. Since the behaviour at temperatures up to 1500 °C is of interest such tests
require special analysis equipment. For simplicity this study will instead be focused
on the bending of a beam loaded only by its own weight as seen in Fig. 5a. The results
of such a measurement will however be more difficult to interpret because assumptions
must be made about the stress field in the beam to find the relation between stress
and strain. Euler-Bernoulli beam theory will be used to do this and a derivation of the
shape distortion is presented in the next section.

When an adequate constitutive equation has been found it can be used in Finite
Element Simulations (FEM) to predict the deformation during sintering. Such simu-
lations have been carried out with hard metal by Gasik et al [3] where a viscoelastic
model was used to simulate the deformation. The method was to use a standing cylin-
drical rod which was deformed by its own weight so that the radius at the bottom
became larger than at the top. The comparison between experiment and simulation
was not too convincing which motivates further studies in the area. Similar studies of
ceramic compounds have been carried out by Sanliturk et al [5] and there is also room
for improvement in the model used in that study.

The hypothesis in this study is that most of the deformation due to gravity occurs
during the liquid phase of sintering. This motivates the use of pre sintered hard metal
in our experiments, since the already sintered material is only slightly denser than hard
metal during liquid phase sintering [8]. The advantage of using pre sintered hard metal
is that there are no shrinkage defects to account for, which is the case when sintering
from a green body. This means that the effect of gravity can be isolated by using
samples made from pre sintered hard metal.

2.1 Euler Bernoulli beam theory

The main assumption in beam theory is that vertical cross sections of the beam re-
main straight and orthogonal to the centre horizontal line when the beam is de-
flected [6], as shown in Fig. 4. This im-
plies that the longitudinal strain of the
infinitesimal part of the beam in Fig. 4
can be written as,

\[ \epsilon = \frac{du}{dx} = \frac{(R - z)d\theta}{dx} - \frac{dx}{dx}. \]  (1)

Here \( du \) is the longitudinal elongation of
the bended sample and \( R \) is the radius
of curvature. \( R \) and \( \epsilon \) are both functions
of \( x \) and \( z \) but this will be suppressed.
The coordinate system has been chosen

\[ x \]

\[ z \]

\[ dx \]

\[ d\theta \]

\[ R \]

Figure 4: Illustration of bending of a beam.
Note how the vertical cross sections remain
straight lines after bending.
so that $x$ ranges from 0 to $L$, where $L$ is the length of the beam, and $z$ ranges from $-T/2$ to $T/2$, where $T$ is the thickness of the beam. In beam theory the centre line of the beam is assumed to be unstrained if forces are not applied longitudinally which is true in our situation. This means that $Rd\theta = dx$ which gives,

$$
\epsilon = \frac{Rd\theta - zd\theta}{dx} = -z \frac{d\theta}{dx} = -z \frac{R}{R} = -z \kappa,
$$

(2)

where $\kappa$ is the curvature. Now the constitutive equation must be used in this relation to find the stress field, and for simplicity the linear viscous model will be used. This constitutive equation however includes the derivative of the strain $\dot{\epsilon} = \sigma/\eta$ and can not be used directly. It will therefore be assumed that the stress field in the beam remains constant which allows for integration of the constitutive equation to obtain $\epsilon = t\sigma/\eta$. This is true for small deflections and its validity will be discussed in later sections. Using $\epsilon = t\sigma/\eta$ in Eq. 2 above gives the longitudinal stress,

$$
\sigma = \frac{-\eta z \kappa}{t}.
$$

(3)

Note that the stress is negative for $z > 0$ and positive for $z < 0$. This means that there is compressive stress in the upper part of the beam and straining stresses in the lower part of the beam and these different stresses is what makes the beam bend. The next step is to integrate the stress times $z$ over the vertical cross section seen in Fig. 5b. This is done because the integral will equal the momenta in the cross section,

$$
M = \int_A \sigma zdA = \int_A \frac{-\eta \kappa z^2}{t} dA = \frac{-\eta \kappa I}{t}.
$$

(4)

$I = \int_A z^2 dA$ is called the area moment of inertia and is equal to $BT^3/12$ for a square cross section. Rearranging gives,

$$
\kappa = \frac{-Mt}{\eta I}.
$$

(5)

The momentum can now be calculated using ordinary statics by requiring force and momentum equilibrium in the left part of the beam shown in Fig. 5b. First $N1 = N2 =

\[\]

Figure 5: a) A conceptual image showing the forces acting on the beam. b) The forces acting on the left part of the beam.
\( mg/2 \) is obtained from force equilibrium. By calculating the momentum equilibrium around the rightmost point the shear force \( T \) can be ignored and this gives,

\[
M = \frac{mgx^2}{L} - \frac{m gx}{2} = \frac{mgL}{2} \left( \frac{x^2}{L^2} - \frac{x}{L} \right) = \frac{BTL^2 \rho g}{2} \left( \frac{x^2}{L^2} - \frac{x}{L} \right), \tag{6}
\]

where it was used that \( m = \rho V = \rho BTL \). Since the beam is symmetric around the middle, the momentum and deflection will also be symmetric. For this reason the coordinate change \( x \rightarrow x + L/2 \) will be made, and Eq. 6 thus becomes,

\[
M = \frac{BTL^2 \rho g}{2} \left( \frac{x^2}{L^2} - \frac{1}{4} \right). \tag{7}
\]

Inserting this in Eq. 5 gives,

\[
\kappa = \frac{-Mt}{\eta I} = \frac{6 \rho g L^2 t}{\eta T^2} \left( \frac{1}{4} - \frac{x^2}{L^2} \right). \tag{8}
\]

The curvature will now be related to the deflection of the beam, and by assuming that the deflection is small, the relation \( \kappa \approx d^2w/dx^2 \) can be used [6], where \( w \) is the deflection in the \( z \) direction. Integrating \( \kappa \) twice gives,

\[
w = \frac{6 \rho g L^2 t}{\eta T^2} \left( \frac{x^2}{8} - \frac{x^4}{12L^2} + Ax + B \right). \tag{9}
\]

The boundary conditions \( w(0) = w(L) = 0 \) give \( A = L/12 \) and \( B=0 \), and the final result is thus,

\[
w = \frac{\rho g L^4 t}{2\eta T^2} \left( \frac{3x^2}{2L^2} - \frac{x^4}{L^4} - \frac{5}{16} \right). \tag{10}
\]

This is the deformation of the beam according to EB beam theory, and by changing units to the dimensionless length \( x \rightarrow x/L \) it can be seen that the shape of the deformation is always the same while the parameters only affect the amplitude. Finally the maximum deflection, which is found at \( x=0 \), will be written out,

\[
|w_{\text{max}}| = \frac{5 \rho g L^4 t}{32\eta T^2}. \tag{11}
\]

### 2.2 Other deformations

Investigation of beam bending will give information about the uni axial viscosity of hard metal. It will not however give any information about shear deformation since shear stresses are much smaller than the longitudinal stresses and are thus neglected in beam theory. This means that the value of the shear viscosity \( \eta_s \) will not be found.

Nor will any information about the expansion perpendicular to the strain be found and thus the corresponding Poisson ratio \( \nu \).
One might also expect other types of deformations due to gravity. A problem at SECO is edge deformation when sintering so called positive inserts. (A positive insert has an edge hanging out as shown in Fig. 6b and c and it is usually sintered standing upright so that the edge is hanging freely.) Intuitively it is reasonable that gravity contributes to edge deformation, however the stress induced in the tip of an edge is not very large and therefore suggests another mechanism for deformation. One hypothesis is that deformation occurs through surface transportation and that gravity in this way transports matter away from the edges. Another hypothesis is that non uniform packing densities in the green body lead to this kind of deformation. To investigate this, positive inserts will also be analysed.

### 3 Experimental Procedure

<table>
<thead>
<tr>
<th>Grade #</th>
<th>Cobalt (%)</th>
<th>WC type</th>
<th>WC grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>WC 8</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>WC 8</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>WC 8</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>WC 150</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>WC 80</td>
<td>0.7</td>
</tr>
</tbody>
</table>

This study will be limited to the behaviour at the liquid phase of sintering and already sintered material will therefore be used for the samples. The samples will be shaped from standard square pieces of hard metal (SNUN) using a diamond blade cutting machine. The samples to be considered consist only of WC and Co and the amount of cobalt and the WC grain size will be varied. Five different grades will therefore be used for the samples and are listed in Table. 1. Sample 5 also contains a small amount of chromium which reduces grain growth. Rectangular pieces will be

![Figure 6: a) The beam sample and the support. b) The self made positive insert, and c) the cylindrical positive insert.](image)
cut for the bending tests, with the dimension 10*4*0.5 mm. They will be placed on a support made from carbon, covered with Zirconium oxide which prevents the carbon from reacting with the samples. For the investigation of edge deformation, two different positive inserts will be used and they are approximately 10 mm wide and 5 mm high. The first sample has been shaped manually and the other sample is the cylindrical RPKT 1605 M 0T-M18 insert. These samples can be seen in Fig. 6.

In order to heat the samples the STA 449 F3 laboratory furnace from NETZSCH will be used and it measures both weight and temperature. The furnace is not much larger than the sample, which improves temperature homogeneity. An atmosphere of argon will be used to prevent chemical reactions. After heating, the samples will be measured using the confocal microscope Infinite Focus from Alicona. A confocal microscope is an optical microscope that uses focus variation to determine the height of a point, and by scanning over a sample it generates a 3D image that can be analysed. This will be used to generate the deflection profiles of the beams, and the edge profiles of the self made insert. For the cylindrical inserts however, a stylus measurement needle will be used instead of the confocal microscope. It is essentially a needle that is pulled along the surface of the sample and records the height. This turned out to give more consistent results, since it was difficult to focus on the edge with the optical confocal microscope. The reason being that the surface of the insert was shiny after sintering and in addition the sharp angle of the edge makes it difficult to focus on from above. This was also a problem with the self made positive insert but in that measurement the average profile of the edge could be extracted to give better results, which is not possible with a cylindrical insert.

4 Results

4.1 Beam samples

Figure 7: a) The deflection of a sample from grade 4 after sintering for 15 min at the respective temperature. The image is not made to scale. b) A graph showing the deflection and shrinkage of the sample as a function of temperature.

In order to justify the limitation of the study to liquid phase sintering, a sample
that was only pre sintered to 1100°C has first been used. The difficulty of using hard metal that has not been completely sintered is that it is brittle and thus difficult to cut through without breaking. However, after a pre sintering to 1100°C the material is strong enough to cut through and still very porous. A single sample has then been used, and has been heated several times at increasing temperatures. The sample has been measured in between the heating cycles and the results can be seen in Fig. 7a. It is clear that at temperatures above 1350°C the deformation is significantly larger and this motivates that gravity has most effect during liquid phase sintering. In Fig. 7b the relative density of the sample has also been plotted, which was obtained by simply measuring the length of the sample after each sintering cycle and using that

\[ \rho_{rel} = \frac{\rho}{\rho_0} = \frac{m/V}{m/V_0} = \frac{L_0^3}{L^3}. \]  

Table 2: Deflection of beam samples sintered one hour at 1500°C.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Cobalt (%)</th>
<th>WC size (µm)</th>
<th>Thickness (mm)</th>
<th>Deflection (µm)</th>
<th>Stuck on support</th>
<th>Weight-loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>6</td>
<td>3</td>
<td>0.49</td>
<td>164</td>
<td>No</td>
<td>0.43</td>
</tr>
<tr>
<td>1b</td>
<td>6</td>
<td>3</td>
<td>0.50</td>
<td>190</td>
<td>No</td>
<td>0.46</td>
</tr>
<tr>
<td>2a</td>
<td>10</td>
<td>3</td>
<td>0.50</td>
<td>242</td>
<td>Yes</td>
<td>0.86</td>
</tr>
<tr>
<td>2b</td>
<td>10</td>
<td>3</td>
<td>0.51</td>
<td>205</td>
<td>Yes</td>
<td>0.60</td>
</tr>
<tr>
<td>3a</td>
<td>15</td>
<td>3</td>
<td>0.48</td>
<td>540</td>
<td>Yes</td>
<td>0.80</td>
</tr>
<tr>
<td>3b</td>
<td>15</td>
<td>3</td>
<td>0.49</td>
<td>420</td>
<td>Yes</td>
<td>1.11</td>
</tr>
<tr>
<td>4a</td>
<td>6</td>
<td>1</td>
<td>0.52</td>
<td>185</td>
<td>No</td>
<td>0.34</td>
</tr>
<tr>
<td>4b</td>
<td>6</td>
<td>1</td>
<td>0.49</td>
<td>172</td>
<td>No</td>
<td>0.37</td>
</tr>
<tr>
<td>5a</td>
<td>13</td>
<td>0.7</td>
<td>0.51</td>
<td>258</td>
<td>No</td>
<td>0.63</td>
</tr>
<tr>
<td>5b</td>
<td>13</td>
<td>0.7</td>
<td>0.49</td>
<td>257</td>
<td>No</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Next the samples from the five grades shown in Table 1 have been investigated. These samples have been made from pre sintered hard metal and the samples have been rapidly heated to 1500°C and kept at this temperature for one hour. There are two samples of each grade and the maximum deflection of the samples can be seen in Table 2. One clear trend to be observed is that more cobalt results in more deflection, while grain size on the other hand has no clear impact. The shape of the deflection of most samples agreed surprisingly well with theory and Eq. 10 which can be seen in Fig. 8a. As mentioned above the shape of the deformation is always the same according to Eq. 10, while the amplitude of the deformation can vary. Therefore the maximum deflection is the only parameter needed to make the curve fitting, and with a maximum deflection of about 0.2 mm the viscosity constant \( \eta \) can be determined to be approximately 10 GPa. This result illustrates the order of magnitude of the strength of hard metal, though the results must not be stressed too far since it is not verified whether the linear viscous model is correct.
In some samples however, the shape of the deflection deviated slightly from the theoretical shape, but it should be mentioned that the samples had discrepancies from start due to the poor precision of the cutting machine. The uncertainty in the sample thickness was about ± 0.02 mm. Fairly large variations in the maximum deflection was also noted among samples of the same grades. This inconsistency could depend on the slightly different thickness and shape of the samples, yet by comparing samples 4a and 4b it can be seen that the thicker sample 4a has a larger amplitude, which is contrary to the expectation. Therefore the result seems to be sensitive to some other parameter, and this is most likely how much friction there is between the sample and the support. Friction against the support is a common problem during sintering and this has been shown by Olevsky et al [2]. Some samples were even stuck on the support after sintering and this has been recorded in Table. 1 since it reduces the accuracy of the measurement. The last column shows the weight loss during sintering and this most likely represents vaporization of liquid cobalt. The rate of decrease was seen to be constant during the time at 1500 °C, and in addition the more cobalt rich samples had a greater weight loss which supports this hypothesis.

To investigate how the amplitude is affected by sample thickness, a few samples with different thickness were sintered during one hour at 1500 °C and the result is shown in Fig. 9a. According to Eq. 10 the amplitude should be inversely proportional to the thickness squared, yet the best fit curve is not too convincing. As mentioned
before there is a large spread in the results and the model is not perfect either. One very interesting observation was however that the thickest sample was not deflected at all, and this will be analysed further in the next section.

In order to investigate the time evolution of hard metal a single sample was heated several times to 1430°C and measured in between. This is the same way the temperature dependence was investigated, except that this time the same temperature was used for all heating cycles. The results are shown in Fig. 9b, and it is clear that the deflection is a time dependent process which motivates the viscous model, though it is clearly not linear. The first two hours the deflection rate decreases exponentially while for longer times the deflection rate is almost constant.

4.2 Insert Samples

![Diagram of edge profiles](image.png)

Figure 10: Profile of the upper and lower edge of the self made insert, before and after sintering. The sample is made from grade three, and has been sintered for one hour at 1500°C.

In the investigation of edge deformation in positive inserts, there has been no indication that such defects would be caused by gravity. In Fig. 10 the edge profile of the self made sample can be seen, before and after sintering for one hour at 1500°C. The difference in the edge shape is no more than a few µm, which is also at the limit of measurement precision. In addition this sample is made from grade three which contains fifteen percent cobalt, and is thus the grade that is expected to deform the most. Since this sample was made from already sintered hard metal there are no density variations and hence shrinkage effects.

Another simple way to investigate the effect of gravity on inserts that have not been pre sintered at all, is to use two samples and put one of them upside down in the furnace. The RPKT 1605 M 0T-M18 insert made from grade 630 and pressed with the tool 950297-02-8-3 has been investigated, and it can be seen in Fig. 6c. The samples have been sintered from a green body, and in addition they have been kept at 1500°C for six hours. The edge profiles of two such samples can be seen in Fig. 11, and the differences between the upside down sample and the upright sample are remarkably small. The shape of the edges in fact deviate less from each other, than from the initial
green body. This indicates that shrinkage anisotropy has a larger effect than gravity on deformations in these samples. It should be mentioned that the green body has been scaled down 16 percent to account for the shrinkage, meaning that the actual edge radius is even larger. However, the measurement of the green body is not entirely rigid. As mentioned, these cylindrical samples were measured with a pin needle that moves along the surface of the sample, and since the green body is soft the needle peels off a thin layer of the surface.

In addition to this deformation there are significant variations over the edge of a single sample, which can be seen in Fig. 12. The sample has been rotated and measured along four different edges. Compared to these sample inhomogeneities and the anisotropic shrinkage from the green body, gravity has little impact on edge deformation.

Figure 12: The edge along four different sides of a single cylindrical insert. A close up reveals significant differences.
5 Discussion

5.1 Mechanisms of deformation

In order to predict the deformation of a sample it helps to understand what mechanisms that lead to deformation. To understand the micro structure one should recall that WC makes up about 90% of the mass and only a little less of the volume (since it has a higher density than cobalt). This means that the WC grains are tightly packed and in contact with each other while the cobalt simply fills the voids. The micro structure of three of our grades can be seen in Fig. 8. Since WC grains are extremely hard it is unlikely that the relatively small stresses induced by gravity would lead to deformation of single grains. It is more likely that grains slide against each other and that this results in deformation. According to Table. 2 it is clear that more cobalt leads to more deformation which is reasonable since more cobalt means more liquid during the liquid phase of sintering. And if there is more liquid the WC grains have more space to move around.

Figure 13: Micro structure of grade 2, 4 and 5 respectively. The images are generated with a scanning electron microscope. The grey regions are WC grains and the black regions are cobalt.

Let us now consider the sample in Fig. 7 that was used to investigate the temperature dependence. Cobalt makes up about 10% of the volume, so the sample could be considered to have a 10% porosity during liquid phase sintering. In Fig. 7b it can be seen that in the first interval, when the relative density goes from 62 to 83%, the deflection is still significantly less than during liquid phase sintering. This indicates that porosity alone does not lead to deformation. According to Uhrenius [8] the liquid cobalt can dissolve the boundaries between WC grains, and this could be the key to why most deformation takes place during liquid phase sintering. In contrast to the grains which are more or less perfect crystals, the WC in between grains is in an unordered amorphous phase which makes it easier to dissolve [8].

If the process of grain sliding is what allows for deformation one might also expect the grain size to affect the deformation, but this has not been observed. Grain size probably matters to some extent, but since the dependence is weak more samples are
needed to find some statistically reliable result. A reason why grain size does not matter much is that large and small grains have roughly the same shape, since the shape is affected by the crystal structure. It is thus understandable that a micro structure of small grains has the same properties as a micro structure of large grains, since they look the same if one zooms in enough. There is however more surface area and grain boundaries per unit volume when the WC grains are small which should be of some importance.

What could also matter is the distribution of grain sizes, i.e. if large and small grains are mixed. In such a grade the smaller grains would fill up the voids in between larger grains and this could affect the ability of movement for the larger grains. If the smaller grains are large enough to fill up a significant space in between larger grains this should decrease the mobility. Yet if the grains are too small it is possible that the effect would be the opposite. It is not clear however that this is what happens, and one must separate the concepts of adding small grains to a distribution of larger grains and simply changing the distribution, since the first also involves reducing the amount of cobalt. In reality the grades already consist of grains with a large variety of sizes which can be seen in Fig. 8. This makes it difficult to test the effect of the size distribution since there is in practice no grade with only one size.

It would be useful if one could develop a model of the micro structure in order to simulate how it reacts to an applied pressure. This could be used to find the constitutive equation and see how it depends on parameters such as grain size and amount of cobalt. One would probably have to find some expression for the binding energy between grains, yet the difficult part would be to account for the shape and orientation of the grains relative to each other. In general it is a difficult problem to find the macroscopic properties of solids based on the micro structure [6] and this material is probably no exception. To complicate things further, grains tend to grow and thus change shape during sintering [8]. Therefore, experimental results will be used instead to determine the constitutive equation.

5.2 The constitutive equation

One of the interesting results in this study was that sufficiently thick samples show no deflection at all as seen in Fig. 9a. This is contrary to the theory which predicts the deflection to be inversely proportional to $T^2$ according to Eq. 10. The reason for the theoretical $T$ dependence is a result of the stress field in the beam. In a thinner beam the stresses are higher which results in a larger strain and deflection. To show this the longitudinal stress can be calculated from Eq. 3 and 8,

$$\sigma = \frac{6\rho g L^2 z}{T^2} \left( \frac{x^2}{L^2} - \frac{1}{4} \right). \tag{13}$$

The largest stresses are in the middle of the beam at at the top and bottom i.e. $x=0$ and $z=\pm T/2$ and this gives,

$$\sigma_{max} = \pm \frac{3\rho g L^2}{4T}. \tag{14}$$
This shows that the maximum stress is inversely proportional to the thickness, and the idea is now that the maximum stress needs to be greater than some threshold value for deformation to take place. By considering the micro structure, it is also reasonable that a minimum stress is required to overcome the binding energy between grains to make them slide. In the 0.5 mm thick samples the maximum stress is \( \sigma_{\text{max}} = 10 \text{ MPa} \) and in a 2 mm thick sample it is 2.5 MPa, so the threshold value must be somewhere in between these values for this grade. For applications this behaviour is very practical, since deformation should only occur in bodies where the stresses induced by gravity are larger than about 3 MPa. The stress field in bodies with complex geometries can then be calculated using FEM simulations, to see if the stress exceeds this value. However, a rule of thumb can be that the stress exceeds 3 MPa in bodies higher than about 2 cm. The reason is that the stress at the bottom of a pillar of height \( H \) is,

\[
\sigma = F/A = mg/A = \rho V g/A = \rho H g
\]  

and \( \sigma = 3 \text{ MPa} \) for \( H = 2 \text{ cm} \). It would be interesting to see if this hypothesis holds for the entire sintering cycle, since mainly pre sintered material has been used in this study.

Investigation of deformation during the initial stages of sintering has been carried out by Liu et al [4], and they also observed such a threshold value. Although, in that study a copper powder was used.

When the stress is higher than this threshold value the deformation is however very difficult to predict. One reason is that the rate of deflection decreases with time as seen in Fig. 9b. There are a few possible explanations for this time dependence, and one is that the material actually becomes stronger the longer it is sintered due to the micro structural evolution during sintering. This is the explanation given by Lee et al [7] who also observed similar behaviour in their bending tests, although they did as mentioned use a ceramic material. This hypothesis was however refuted by the fact that both samples of grade four were deflected almost as much, despite sample 4a had been sintered on a flat surface for six hours at 1500 °C before it was tested.

Another explanation could be that the results are interpreted in the wrong way. In the derivation of the deflection the stress fields were assumed to be constant, though perhaps the stresses become smaller when the beam changes into a bent shape. This could also explain the decrease of the deflection rate, yet the deflections in our experiments should be small enough to be neglected. The maximum deflection is no more than 0.3 mm, compared to the 10 mm length of the beam. It can also be shown that the strain in the beam is small by calculating \( \epsilon_{\text{max}} \) from Eq. 2, 8 and 11,

\[
\epsilon = \frac{192ZW_{\text{max}}}{5L^2} \left( \frac{x^2}{L^2} - \frac{1}{4} \right).
\]  

As the maximum stress, the maximum strain is also found at \( x = 0 \) and \( z = \pm T/2 \),

\[
\epsilon_{\text{max}} = \pm \frac{24TW_{\text{max}}}{5L^2}.
\]
In a 0.5 mm thick sample a deflection of 0.3 mm implies a maximum strain of no more than 0.7 %. This motivates that the deflections can be considered small and that the decrease in deflection rate is not a geometrical artefact.

The most probable reason for the decaying deflection rate is thus that the material becomes stronger in the direction it has been strained. This is what happens in an elastic material, yet it is strange for a viscous materials to behave like this since a purely viscous material has no memory. The explanation is that the material is both viscous and elastic as discussed in the introduction. The deflection in Fig. 9b in fact strongly resembles the initial stages of the typical creep curve in Fig. 3. In order to account for this time dependence a more detailed model must be used. The creep curve shows the general behaviour of the strain but there is no standard function that describes the entire curve. It is most interested to describe what happens in the initial stages since the liquid phase of sintering is usually no longer than about an hour. Different models can be used to describe the strain at short times and the Kelvin model has been chosen in this case. The constitutive equation of the Kelvin model is given by [6],

\[
\sigma = E\epsilon + \eta\dot{\epsilon},
\]  

which is essentially the equation of a spring and damper in parallel, and indeed illustrates the viscous and elastic properties of the material. If again, the stress is assumed to be constant this can be integrated to,

\[
\epsilon = \frac{\sigma}{E} \left(1 - e^{-Et/\eta}\right).
\]  

This model was fitted to the curve in Fig. 3 and it can be seen that it describes the deflection well during the first two hours. (The last measurement at six hours was not included in this curve fit since including it resulted in a bad fit.)

It thus seems like a constitutive equation has been found, that well describes the deformation during sintering. However, this is not entirely true as the threshold value discussed earlier has not been accounted for. If the stress must be larger than some threshold value before any deformation occurs, there can not be a purely linear relation between stress and strain in the constitutive equation. Although the model worked well in describing the deflection of our beam, it is not guaranteed that it will do so in samples with other geometries. Many metals at high temperature show some power law relation, which means replacing \(\sigma\) by \(\sigma^r\) in the constitutive equation, where \(r\) is some constant. There could also be a more complicated relation, and further studies are needed to investigate this in order to find an adequate constitutive equation.

6 Conclusion

This study has shown that when stresses induced by gravity are smaller than about 3 MPa there is no deformation during sintering. This is the case for most inserts used at SECO since most of them have no complex geometries with parts hanging free and most are no higher than 5 mm. Further investigation of this threshold value is however
necessary to see if there are large variations between different grades. It would also 
be interesting to see if the threshold value is lower in the initial stages of sintering, as 
mainly pre sintered hard metal has been considered in this study.

Another important result is that gravity is not responsible for the edge deformation 
seen in positive inserts. The RPKT 1605 M 0T-M18 insert has been investigated, and 
put to the extreme test of six hours of liquid phase sintering, after which it was hardly 
deformed at all. Edge deformation is thus more likely caused by anisotropic shrinkage, 
due to density variations in the green body after pressing.

This study has also shown that the strain of hard metal follows a creep behaviour, 
which is common for metals at high temperatures. For short times the Kelvin model 
well describes the deformation in our experiments. The goal of finding the constitutive 
equation is eventually to use it in FEM simulations in order to predict deformation, 
but we are not quite there yet. In order to verify the Kelvin model and perhaps find 
an even more precise constitutive equation, one would need to conduct tensile tests. 
Some thermo mechanical analysis equipment is probably best suited for this, and can 
be used to see in more detail how the material responds to a constant load. Even if 
the Kelvin model is shown to adequately describe hard metal, one must first map the 
parameters $\eta$ and $E$, in Eq. 18, in more detail before it can be used in any practical 
applications. It must be investigated how they depend on temperature and this must 
also be investigated for different grades, especially grades with small and large amounts 
of cobalt since it has the most influence on deformation. Only then can the model be 
used in simulations to predict the deformation of hard metal during sintering.
References


