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MICRO FEATURE ENHANCED SINTER BONDING OF METAL INJECTION MOLDED (MIM) PARTS TO A SOLID SUBSTRATE

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MICRO FEATURE ENHANCED SINTER BONDING OF METAL INJECTION
MOLDED (MIM) PARTS TO A SOLID SUBSTRATE

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Automotive Engineering

by
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May 2011

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ABSTRACT

In metal injection molding (MIM), fine metal powders are mixed with a binder and injected into molds, similar to plastic injection molding. After molding, the binder is removed from the part, and the compact is sintered to almost full density.

The obstacle to sinter bonding a MIM part to a conventional (solid) substrate lies in the sinter shrinkage of the MIM part, which can be up to 20%, meaning that the MIM part shrinks during sintering, while the conventional substrate maintains its dimensions. This behavior would typically inhibit bonding and/or cause cracking and deformation of the MIM part. It is also the reason, why sinter bonding MIM to solid substrates is not an industrially applied process and little to no prior research exists.

By applying a structure of micro features to the surface of the MIM part, this allows for shrinkage while bonding to the substrate. The micro features tolerate certain plastic deformation to permit the shrinkage and thermal expansion/contraction without causing cracks after the initial bonds are established. The bonding and deformation behavior of the powder compacts is analyzed and modeled. A new approach to simulate the deformation is developed. Finally, the samples are evaluated and compared with other joining processes.

DEDICATION

For my family, who offered me unconditional support throughout the course of this dissertation.

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It is a pleasure to thank the many people who made this thesis possible. I am heartily thankful to my advisor, Dr. Mears, whose encouragement, supervision and support from the preliminary to the concluding level enabled me to develop a deep understanding of the subject.

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1. INTRODUCTION

1.1. Metal Injection Molding

In Metal Injection Molding (MIM), fine metal powders are mixed with a binder and injected into molds, similar to plastic injection molding. Table 1 shows the particle sizes of MIM powders produced by typical powder production techniques, adapted from [1]. Table 2 lists some typical MIM materials and the properties that can typically be achieved, adapted from [2]. The binder is a temporary vehicle for homogeneously packing the powder into the desired shape and holding the particles in that shape until the beginning of sintering [3]. After molding, the binder is removed from the so called green part, and the now “brown” compact is sintered to almost full density. Figure 1 illustrates the process.

Table 1: Comparison of small particle production techniques [1]

Technique	Size [μm]	Shape	Cost
Gas atomization	5 – 40	Spherical	High
Water atomization	6 – 40	Rounded, ligamental	Moderate
Oxide reduction	1 – 10	Polygonal to rounded	Low
Carbonyl decomposition	0.2 – 10	Rounded to spiky	Moderate
Milling	1 – 40	Angular, irregular	Moderate

Table 2: Selected mechanical properties of MIM metals and alloys (HT=heat treated) [2]

Material	Composition [wt. %]	Density [%]	Yield [MPa]	Ultimate [MPa]	Elonga- tion [%]	Hardness
1020 steel	Fe-0.2C	96	185	380	23	-
4140 (HT)	Fe-1Cr-0.4C	93	1240	1380	2	40HRC
Iron nickel steel (HT)	Fe-2Ni-0.5C	94	1230	1230	1	45HRC
Inconel	Ni-19Cr- 18Fe-5Nb- 3Mo-1Ti- 0.4Al	100	1130	1330	14	-
Hastelloy	Ni-28Mo- 2Fe	97	350	800	40	30HRC
Stainless 17-4PH	Fe-16Cr- 4Ni-4Cu	96	750	900	10	25HRC
Stainless 304L	Fe-18Cr-8Ni	97	240	480	35	85HRB
Stainless 316L	Fe-17Cr- 12Ni-2Mo- 2Mn	96	220	510	45	75HRB
Ti-6-4	Ti-6Al-4V	98	800	880	12	35HRC
Titanium	Ti	95	1100	1300	16	-
Tungsten heavy alloy	W-5Ni-2Cu	98	900	1050	10	35HRC
Gold 18 ct	75Au- 12.5Ag- 12.5Cu	75	108	147	1	66HRB

Sintering is a high-temperature treatment that causes the particles to join, gradually reducing the volume of pore space between them, until the powder compacts are converted into dense monolithic components [4].

Figure 1: The MIM process [5]

The metal powder consists typically of equiaxed, rounded particles which are below 20 μm in size. The binder systems are typically mixtures of thermoplastic or thermosetting plastics and/or wax, water-based or gelation systems. Debinding is a delicate process step, since it is crucial that all binder is removed, while on the other hand a so-called back-bone needs to be conserved to allow for handling of the brown compact

from the debinding furnace to the sintering furnace and support the part between debinding and sintering. Depending on the binder system, there are different debinding processes: solvent-, thermal-, or catalytic-debinding or drying of the compact. Once the compacts are debound, they are sintered at a temperature which is typically above 0.5 of its absolute melting temperature. Depending on the material, there will be a vacuum, an oxidizing, a reducing or an inert atmosphere in the sintering furnace.

Figure 2: Economy of the MIM process (after [6]).

As complexity and production volumes increase, MIM becomes more preferred due to ease of complex geometry creation and high initial investment cost which must be amortized.

Figure 2 illustrates the typical application of the MIM process. Since the injection molds are usually big investments, MIM is used for the cost effective [7] production of large quantities of parts. Also, this process is used to manufacture complex parts. Simple

parts can be manufactured more economically by press and sinter powder metallurgy, die casting or machining.

Typical applications are small parts for the automotive, medical, electronics or power tool industry as can be seen in Figure 3.

Figure 3: Typical MIM applications [8].

Typical MIM applications are e.g. medical devices, (suturing jaws), power tools (hack saw blade clamp), or components of measuring devices.

Although the MIM industry is concerned about raw material costs, the MIM market is growing and the North American market is expected to count for \$200 million in component sales in 2011 [9].

While in North America only about 7% of the MIM market is dedicated to the automotive industry, medical applications and firearm components take the biggest share. In Europe the automotive industry is responsible for 50% of the total MIM market. Raw material fluctuations continue to impact metalworking processes, favoring MIM's netshape appeal [10].

1.2. Limitations

However, there are still size and shape limitations in the MIM process. Besides the cost of the feedstock these limitations are mainly imposed by the debinding and sintering operations. The general rule is that parts with a weight over 200g are usually more economically manufactured through other processes.

The feedstock cost exceeds the advantages of the MIM process at this weight. As stated by EPMA (European Powder Metallurgy Association) [11]: there is, theoretically, no limit to the maximum size of part that could be produced, but economic considerations restrict the sizes that are currently viable. The larger the part the greater is the proportion of the overall cost that is attributable to the raw material which is costly. The total cost of the powder is a linear function of the weight of the part, but in the case of parts produced by machining from solid bar stock, for example, the machining costs increase with increasing part size at a much lower rate. Also, tooling costs per part can be reduced by increasing the number of cavities per mold. But as the part size increases, the number of cavities for a given mold or machine size is limited.

Figure 4: Schematic of some limitations in MIM.

The binder needs to be safely extracted from the center of the component; unsupported areas may sag due to gravity.

Thick cross sections are difficult to debind (see Figure 4) or would take too much time to debind and make this process step too cost intensive. An upper limit for a wall thickness of 6mm is suggested from the binder removal operation [12]. Depending on the binder system, thicker cross sections can be achieved. Besides the cost of debinding time there is also the risk of binder not being removed at all. Excess residue binder will lead to cracks, pores and deformation during sintering. Also, uniform wall thickness is critical because non-uniform walls may cause distortion, internal stresses, voids, cracking and sink marks. Variations in wall thickness also cause variations in shrinkage during sintering, making dimensional control difficult [13].

The second aspect is that unsupported areas of the parts can deform during sintering. Figure 5 shows the effect of gravity. Here, an unsupported portion of the part, the hand piece of an arthroscopic instrument, sagged during sintering. This could be overcome by designing the part in such a manner that all features of the part are always supported through the part structure. Olevsky and German [14, 15] show that gravity causes anisotropic shrinkage and shape distortion even in fully supported parts, so that non-supported areas be of even greater concern. To design a part such that all portions

are always supported is sometimes difficult to realize or would lead to secondary operations, where portions of the part would need to be removed after sintering. Another way to prevent sintering deformation from sagging is to insert supports made of alumina or other heat resistant materials that do not interfere with the sintering process of the MIM part. These would have to be manufactured to match the shape that needs to be supported after sintering densification [16]. But this process would be very cost intensive, since the inserts would need to be manufactured, inserted before sintering and removed after sintering by a manual process.

Figure 5: Effect of gravity during sintering.

The pocket, where the second half of this arthroscopic handle would be inserted, deformed through sagging.

1.3. Motivation

The motivation of this research is to present a solution that can overcome the limitations of the MIM process. The here presented approach is to combine the MIM compact with a solid part in the critical areas. This will e.g. allow for a reduction of wall thicknesses of the MIM part by substituting it with a solid part, or place solid parts in areas that are in danger of sagging.

Figure 6: Comparison of manufacturing processes.

MIM components are weight limited, and bigger parts need to be manufactured in other manufacturing processes.

Figure 6 adds a third dimension to Figure 2: part weight. It is clear that MIM has a noticeable disadvantage against other manufacturing processes regarding the weight of the parts. But this disadvantage could be overcome by the solution presented in this research.

According to experts in the field of metal injection molding and powder metallurgy that have been contacted regarding sinter bonding a MIM compact to a solid substrate, this is very difficult to achieve, if not impossible, due to the shrinkage of the compact. Since the substrate would maintain its shape and dimensions, the powder compact is expected to crack and/or undergo distortion during sintering. This seems to be the reason, that there are no publications in relation to this topic available at this point.

This work could be the foundation to achieving sinter bonding powder compacts to solid substrates. Beginning with identical materials, as shown here, this can be extended to other material combinations metal-metal, or even metal-ceramics.

Sinter bonding powder compacts with solid substrates has several advantages over parts that are only made by powder injection molding or e.g. by machining only. Adapted from Tabata [17], who was working in the area of traditional powder metallurgy, that is press and sinter, the advantages of composite parts are:

1. Amount of powder used can be reduced with maintaining a merit of the MIM process, that is, parts of complex shape can be made easily.
2. Parts that are only difficult to make by MIM (for example limited by mold design, cost or size) can be fabricated, for example, by combining a MIM part with a long, thick or thin solid metal.

3. High mechanical strength or other properties can be acquired only at a necessary portion by using different materials, for example, an alloy steel feedstock and comparatively cheap steel. Achieve other properties like magnetic-non magnetic in one part.
4. Other joining processes like welding or brazing can be replaced. In this context, a study has been done by Parmigiani and Kosco [18], investigating several joining methods to join PM components. They investigated friction welding, high speed pulse welding, tungsten inert gas welding, brazing and fusion welding. The results show that there is room for improvements. Especially brazing and fusion welding showed to be problematic processes in joining PM components.
5. The above mentioned advantages (1), (2), (3) and (4) may lead to cost reduction.

1.4. Dissertation outline and organization

After having given an introduction to the metal injection molding process and its limitation, the motivation for this research was laid out in this chapter.

The structure of the remainder of this dissertation will be as follows:

Chapter Two is an in depth discussion on the background. First there is the literature review, which is divided into three blocks, a review on sintering in general along the historic timeline, followed by reviews of available literature on sinter bonding in traditional powder metallurgy, and sinter bonding in metal injection molding. The last block is a detailed review on sintering models and simulations with an emphasis on the Master sintering curve approach, as this is the model that will be used later in this research. The next section covers the previous work. These are some test and samples that were produced to get a better understanding of sinter bonding a MIM powder compact to a solid substrate. These samples led to the formulation of the here presented proposed solution to overcome the limitations of the MIM process.

Chapter Three presents the research methodology. The research goal, objectives, questions and tasks will be defined and explained. The basis for this research is a series of reference samples that have been produced at the CGEC's manufacturing lab as described in this chapter.

The research results will be presented in Chapter Four. Again, the chapter will be divided into sub sections: the first one on sinter bonding, the second on post bond and deformation, and the last one on the model and bonding and model evaluation. The

section on sinter bonding is an examination of the actual bonding process and its development through the sintering cycle. In the post bond and deformation section, the actual deformation of the micro features will be modeled and simulated with ANSYS. Finally, in the last section, the bonds will be evaluated for shear strength and the results will be compared with theoretical values and the limits will be explored.

In Chapter Five, a summary will be presented in the form of answering the previously stated research questions individually and thus fulfilling the research objectives and goal. The last section in this chapter will be an outlook on future work.

This will be followed by the appendices, in this case printouts of MATLAB code, and finally the references used throughout this dissertation.

2. BACKGROUND

2.1. Literature Review

The literature on sinter bonding refers primarily to traditional powder metallurgy. The first part of this literature review is on sintering basics, developing the theory of sintering along the historic timeline. This first part is followed by a review on sinter bonding in traditional powder metallurgy and a review of literature on sinter bonding in metal injection molding. The final part is a literature review on sintering models and simulations.

2.1.1. Sintering

“Sintering is a thermal treatment of particulate material or a porous body which remains predominantly solid and, with the formation and growth of particle contacts, becomes a more coherent mass of lower free enthalpy.” [19]

According to Ristic, “the first theory of sintering was established by Y. I. Frenkel in the paper “Viscous flow of crystalline bodies under action of surface tension” [20], in which the cause of sintering and its transferring force were defined as sufficient of Gibb’s surface energy” [21].

Figure 7: Frenkel's model [21].

Two particles join during sintering in the shape of two drops touching each other.

Frenkel stated that the first stage of sintering could be represented as the joining of two liquid drops touching each other in one point at the beginning. After some time τ , the drops would touch each other along a circle with a radius of $Y(t)$. He assumed that remaining parts of both drops retained their shape, Figure 7. The following publications still stated that density increase could not be explained by volume diffusion of vacant lattice sites or surface migration of atoms, but must involve macroscopic flow, with the driving force for this flow being surface tension [22]. Kuczynski [23], however, improved Frenkel's basic postulate. He discussed diffusion along grain boundaries and volume diffusion as possible densification mechanisms and concluded that volume diffusion was the mechanism that was more probable to cause shrinkage.

Ashby [24] defined four stages in the sintering process, during which six transport paths appear, all leading to neck growth, but only three leading to densification. The stages are (0), the instantaneous neck formation which interatomic forces cause when powder particles are placed in contact. Stage (0) is followed by stage (1), the early stage of neck growth. Next is the intermediate stage (2): the necks are quite large, and the

pores are roughly cylindrical. In the final stage, stage (3), the pores are isolated and spherical.

Table 3: Mass transport mechanisms [24]

Transport path	Source of matter	Sink of matter
Surface diffusion	Surface	Neck
Lattice diffusion	Surface	Neck
Vapor transport	Surface	Neck
Boundary diffusion	Grain boundary	Neck
Lattice diffusion	Grain boundary	Neck
Lattice diffusion	Dislocations	Neck

Table 3 lists the mass transport mechanisms defined by Ashby. Only the last three lead to densification. The rate at which the particle centers approach each other is non-zero only when matter is removed from the grain boundary which separates two particles or from dislocations within the neck region. Figure 8 from German [25] illustrates the sintering stages.

Figure 8: Sintering stages [25].

The powder particles approach each other, eliminating the pores between them, until finally only small individual isolated pores are left.

The mechanisms identified by Ashby were extended as Kang [26] illustrates in his book. His table (Table 4) on material transport in sintering also shows viscous flow as a transport mechanism, as had already been defined in the early publications.

Table 4: Material transport mechanisms during sintering [26]

Material transport mechanism	Material source	Material sink	Related parameter
1. Lattice diffusion	Grain boundary	Neck	Lattice diffusivity, D_l
2. Grain boundary diffusion	Grain boundary	Neck	Grain boundary diffusivity, D_b
3. Viscous flow	Bulk grain	Neck	Viscosity, η
4. Surface diffusion	Grain surface	Neck	Surface diffusivity, D_s
5. Lattice diffusion	Grain surface	Neck	Lattice diffusivity, D_l
6. Gas phase transport			
6.1. Evaporation/condensation	Grain surface	Neck	Vapour pressure difference, Δp
6.2. Gas diffusion	Grain surface	Neck	Gas diffusivity, D_g

Figure 9: Material transport paths during sintering [26].
 Diffusion and viscous flow contribute to mass flow and eventually densification.

Figure 9 illustrates the transport paths of the mechanisms listed in Table 4. Only lattice diffusion (D_l) and grain boundary diffusion (D_b) remove material from the grain boundary and thus, together with viscous flow (η), permit densification. The other transport mechanisms contribute only to neck growth by transporting mass to the neck.

Figure 10: Densification curve of a powder compact over four stages [26].
The highest rate of densification takes place during the heating up in the intermediate stage of sintering; elimination of isolated pores in the final stage takes long to achieve.

The densification curve as shown in Figure 10 demonstrates how a typical powder compact densifies over time, with stage (0) being at $t=0$, when initial contact between the powder particles is made. Processes during the initial stages of sintering, especially bond formation and densification have been investigated by Danninger and Gierl [27]. They found that the surface chemistry is changed during sintering within fairly narrow temperature intervals, the position of which depends on the composition of the powder particles and in part on pre-treatment. Densification in the final stages of sintering has been modeled and described by Riedel et al. [28, 29].

Schatt [30, 31] provided an in detail overview over the sintering process broken down into the different phases. He examined the processes step by step and concluded that densification only occurred as the sintering temperature rose. At constant temperatures almost no shrinkage could be observed.

The latest developments in sintering theory have been made with the use of continuum mechanics, which has been successfully applied to the analysis of compaction of porous bodies. The sintering kinetics of real porous bodies is determined not only by the properties of the powder particles and the nature of their interaction, but also by macroscopic factors. Among them are kinematic constraints (for example, adhesion of porous sample's end face and furnace surface), externally applied forces and, also, inhomogeneity of properties in volume under investigation [32].

2.1.2. Sinter bonding in traditional powder metallurgy

Bonding a metal powder compact to a solid substrate during sintering is well known in traditional powder metallurgy. Tabata [17, 33] did several experiments, where the powder and the substrates were brought into close contact by pressing the powder around a solid cylinder, pressing it inside a solid tube, or rolling it onto a flat strip.

Figure 11: Tabata's set-up for two types of composites [17].
 The metal powder is pressed around a massive cylinder (a), or inside a tube (b) to evaluate bonding.

Figure 11 illustrates Tabata's set-up. This configuration brings the metal powder and solid metal into very close contact that enhances the bond strengths. He achieved good bond strengths between the powder and the substrate, which could even be improved by repressing and resintering.

Figure 12: Relation between bond strength τ and relative density ρ [17].

The higher the density through pressing and/or re-pressing, the higher is the bond strength, which also depends on the surface roughness of the solid part. The higher the roughness, the higher is the bond strength.

The closer the contact between the powder and the substrate, the higher the bond strength will be. Figure 12 demonstrates this relation. The density is a function of the compaction pressure, the higher the pressure, the higher the density.

The process of joining traditionally pressed metal powder parts with a solid metal is also used in the automotive industry for example to manufacture camshafts [34]. In this case, the pressed lobes and journals are assembled with a tube and the whole assembly is sintered. This case is also reinforced by Asaka [35]. He studies diffusion bonding methods of green compacts with wrought steel parts during sintering. His result was that high bond strength can be achieved when the powder compact is located around

the wrought part, e.g. a tube or shaft. He concluded that this is because the wrought part expands more than the powder compact.

Figure 13: Dilatometric curves of three types of Fe-1C components and Fe green compacts during sintering in N₂ [35].

The dilatometric curve shows that certain material pairings almost eliminate differential movements; in this case, the expansion/contraction difference between wrought steel and the Fe-1C compact is less than 0.05%.

The small volumetric changes in traditional P/M can be appreciated in Figure 13. The wrought steel thermally expands slightly more than the powder compact which is also thermally expanding while it is densifying at the same time. This expansion-shrinkage differential creates a stress that promotes a better sinter bond.

The above mentioned papers demonstrate that it is possible to bond a powder compact to wrought metal. The advantage in traditional P/M is that the shrinkage during sintering of the powder compact is very low compared to metal injection molded

compacts. For die-compacted ferrous alloys, a common net change may be less than 0.1% [36].

2.1.3. Sinter bonding in metal injection molding

In the field of metal injection molding, so far there has only been work published regarding bonding of green components, either by assembling previously injected compacts or by injecting the components simultaneously or successively directly onto each other. A first paper was published by Miura [37], where he evaluated the influence of the debinding methods. He assembled previously injected compacts, and debound and sintered the assemblies. This work was the foundation to more research in the area of sinter joining MIM parts. In a later paper [38] he also evaluated the tensile strength of the bond.

Figure 14: Schematic illustration of the sample set-up [37].

Several pre-injected sections of different materials were assembled in the green state and joined by sintering.

Figure 15: The tensile strength of MIM compacts and various couples sintered at 1573K in H2 (after [38]).

The tensile strengths of the components which were assembled from two different materials were not much less than those consisting of just one material, indicating that the bonds were almost as strong as the bulk material.

Miura compared the strength of tube shaped injection molded compacts with those that were assembled from tube shaped injection molded compacts. These were either made of one type of steel (SUS420J/SUS420J) or two different steels (SUS304L/SUS420J), see the set-up in Figure 14. Miura showed that the bond strength of the compact assemblies was the almost the same as that of the parts that were injected as one, as can be seen in Figure 15.

Baumgartner and Tan [39, 40] went a step ahead at injecting two materials successively on one injection molding machine. He demonstrated that with careful attention to powder composition and physical characteristics well-bonded and high quality near-size components can be produced using a twin-barrel molding machine. Injection molding bimetal parts gives better dimensional control, as there can be no distortion from a secondary joining process as can be seen in Figure 16 and Figure 17.

Figure 16: Bi-metal part made by welding [39]

Figure 17: Bi-metal part produced by MIM [39]

The part on the right, two different materials injected sequentially to create one compact, could eventually replace a configuration as the welded assembly shown on the left.

Insert injection molding of a hard material (SUS420J) onto a stainless steel (SUS316L) was evaluated by Harikou [41]. This process would be especially helpful to manufacture machine tools. Harikou achieved high bond strength and hardness, which he improved through heat treatment.

Another method of manufacturing complex, composite parts (piston utilized in the aerospace industry) using sinter bonding of MIM compacts was described by Zhang [42].

Figure 18: Two different part designs: two cavities (a) and three cavities (b) [42]. By injecting and assembling three components, it was possible to save a considerable amount of weight. The components were assembled in the green state and sintered.

Here, several components of an assembly were injected (Figure 18), some of them machined to exact dimensions, pre-sintered and completed by shrink-fit or adhesive bonding; the adhesive was an iron powder cooking oil mixture.

A different approach to sinter joining powder injection molded parts was done by Potente and Wilke [43]. They investigated joining processes used in the plastics industry to join green powder compacts. The investigated processes were ultrasonic welding, vibration welding and heating element welding. In these processes, the joining was basically done through melting the binder, joining the components and cooling down the

part. They obtained good results, being able to create complex assemblies of green parts which were subsequently co-sintered.

Imgrund [44, 45] did another research on manufacturing multi material components by sequentially or simultaneously injecting feed stock into a mold and sinter bond the resulting part (Figure 19 and Figure 20). His conclusion was that manufacturing of 316L/17-5PH micro tensile specimens was successfully carried out for both processing routes investigated.

Figure 19: Micro tensile test specimens after molding, sintering and testing [45].

The tested sample (below) shows that the failure was not where the two different materials were joined, but rather in the bulk of one of them (on the left).

Figure 20: Illustration of (a) successive molding and (b) simultaneous molding [45].

The different shapes of the interface between two materials are clearly visible. For successive molding, a part of the mold cavity needs to be shut off during injection of the first material, thus making the mold more complicated.

While the sequential injection route led to straight interfaces that could be positioned precisely, better inter-diffusion of the materials was detected in the simultaneously injected samples.

Ruh et al. developed a so called two-component micro-injection molding and sinter joining process (2C-MicroPIM). The goal was to avoid separate mounting and assembly steps by creating fixed and loose junctions between at least two components during injection and sintering.

Figure 21: Ruh's composite part configuration [46].

In this case it was even possible to create a two material assembly where the toothed wheel was able to rotate on the rod after sintering.

When producing components consisting of different materials via PIM or MIM, sintering is a major barrier. Heaney et al. [47, 48] found that for successful sintering of two material PIM components require one material to mimic the densification behavior of the other material. In addition, the net shrinkage of the compacts after sintering should be equal. Mismatch in the sintering behavior, especially in the initial stage of sintering increases the susceptibility to form defects.

2.1.4. Sintering models and simulations

Computer simulations of sintering first emerged between 1955 and 1965, and the field has expanded rapidly [49]. Especially with wide availability of FE software packages, the number of models and approaches has grown substantially.

The problem in MIM is the shrinkage the part undergoes through sintering, which can be up to 20%. To be able to design the injection mold, it is important to model the

final shape of the part. Part and material properties are generally assumed to be isotropically [50]. This is in reality not the case [51] and gravity, friction or other constraints can introduce shape distortions during the sintering process.

Reiterer and Ewsuk [52] compare four different sintering models. The models compared by Reiterer and Ewsuk are:

- 1) Riedel and Svoboda (RS), a microstructure (in this case grain structure) based model for solid state sintering

The modeling concept, with regard to sintering mechanisms, takes into account the diffusive transport of matter and grain coarsening, and distinguishes between open and closed porosity. The constitutive equation is expressed as a relation between the macroscopic strain rate tensor and the stress tensor:

$$\dot{\varepsilon}_{ij} = \frac{\sigma_{ij}}{2G} + \delta_{ij} \frac{\sigma_m - \sigma_s + \Delta p}{3K} \quad (1)$$

where σ_{ij} is the stress deviator, σ_m is the hydrostatic stress, Δp is a gas pressure that can develop in closed pores, δ_{ij} is the Kronecker symbol, G and K are shear and bulk viscosity, respectively, and σ_s is the sintering stress. This version of the model contains a term for source-controlled diffusion, which modifies the viscous moduli G and K , as follows:

$$K = K_{lin} \left(1 + \frac{\alpha_{RS}}{\bar{\sigma} R^2} \right), \quad G = G_{lin} \left(1 + \frac{\alpha_{RS}}{\bar{\sigma} R^2} \right) \quad (2)$$

where the linear viscosities K_{lin} and G_{lin} are obtained from Riedel et al. [29] and from a term derived to consider interface reaction-controlled diffusion. α_{RS} is an adjustable parameter, $\bar{R}$ is the mean grain radius, and $\bar{\sigma}$ is the effective stress given by:

$$\bar{\sigma} = \frac{1}{2} |\sigma_m - \sigma_s + \Delta p| + \frac{1}{2} \sigma_e \quad (3)$$

where σ_e is the von Mises equivalent stress.

2) Skorohod, Olevsky viscous sintering (SOVS) model

The SOVS model derives from a rheological theory of sintering developed by Skorohod and advanced by Olevsky [32]. The SOVS model predicts the inelastic deformation of a porous body during sintering. In the SOVS model, the constitutive equation is expressed as the relation between the macroscopic strain rate tensor, $\dot{\varepsilon}_{ij}$, and the stress tensor, σ_{ij} :

$$\dot{\varepsilon}_{ij} = \frac{\sigma_{ij}}{2\tilde{G}} + \frac{\sigma_m - \sigma_s}{3\tilde{K}} \delta_{ij} \quad (4)$$

where δ_{ij} is the Kronecker delta, σ_m is the mean or hydrostatic stress, and σ_s is the effective sintering stress, which is approximated by the Laplace pressure. $\tilde{G}$ and $\tilde{K}$ are the effective shear and bulk viscosity, which are dependent on the normalized viscosities φ and ψ and on the temperature-dependent shear viscosity η_0 of the fully dense (solid) skeleton phase.

$$\tilde{G} = \eta_0 \varphi \quad (5)$$

$$\tilde{K} = 2\eta_0 \psi \quad (6)$$

$\tilde{G}$ and $\tilde{K}$, through φ and ψ , and σ_s , are also dependent on the relative density, ρ

$$\varphi = a_1 \rho^{b_1} \quad (7)$$

$$\psi = a_2 \frac{\rho^{b_2}}{(1 - \rho)^{c_2}} \quad (8)$$

$$\sigma_s = a_3 \rho^{b_3} \frac{3\alpha}{r} \quad (9)$$

where a , b , and c are adjustable parameters, α is the surface energy and r is the grain radius.

According to the SOVS model, the influence of porosity on the stiffness of the sintering body is covered by φ and ψ , and η_0 is a function of the temperature T only. A suitable function $\eta_0(T)$ has been derived from Coble's creep law, as follows [53]:

$$\eta_0(T) = A_1 T \exp\left(\frac{Q_{SOVS}}{RT}\right) \quad (10)$$

where A_1 is an adjustable parameter, Q_{SOVS} is the effective activation energy for material flow, and R is the gas constant. The influence of grain growth is lumped into the viscosity function, $\eta_0(T)$. Reiterer and Ewsuk [53] implemented a FE code for this model.

3) Kinetic Monte Carlo (KMC) model ([54-56])

The KMC model can simulate the coarsening of grains by short-range diffusion across grain boundaries, pore migration, and pore coarsening by surface diffusion, vacancy diffusion along grain boundaries, and vacancy annihilation. The model generates

a series of microstructure images as a function of simulation time that is linearly related to real time.

Figure 22 illustrates the elimination of a pore and evolution of the grain structure through the processes of short-range diffusion of atoms from one side of the grain boundary to the other; long-range diffusion of material to pores by grain boundary diffusion and along pore surfaces by surface diffusion; vacancy annihilation at grain boundaries.

Figure 22:KMC simulation results showing microstructural (grain) evolution during sintering of three particles [52].

The particles densify through vacancy annihilation at the grain boundaries, thus eliminating eventually the isolated pores.

The shrinkage y at time t in the KMC model according to Tikare [57] is:

$$y(t) = \left(\frac{\Delta A}{A_0} \right) (t) = \frac{N_{p,0} - N_p(t)}{N_g + N_{p,0}} \quad (11)$$

Where A_0 is the initial area; ΔA is the change in area; $N_{p,0}$ is the initial number of pore sites; $N_{p(t)}$ is the number of pore sites at time t ; and N_g is the total number of grain sites, which remains constant.

A two-component, two-phase system, with uniform and isotropic interfacial energies between grains, and with grains and pores, is generated by assigning each grain one of the Q energy states, whereas the pores are assigned one energy level. Hence, boundaries exist between grains, but not within pores. Next, the sum of all of the nearest neighbor interaction energies in the system is calculated. To perform a grain growth step, a grain site is selected at random. Then, a new state is temporarily assigned to the site, and the change in energy is evaluated. Densification can be described by vacancy annihilation at grain boundaries. In the implemented algorithm, pore annihilation is simulated by exchanging an isolated pore site with a grain site at the perimeter of the model. After the change, the new grain site assumes the state of the adjacent grain [58]. This algorithm gives realistic densification results, but leads to a slight distortion of the outer shape of the sintering structure.

4) Master sintering curve (MSC) model,

The basis of the MSC approach is that it is supposed that identical samples sintered to the same density, even with different time–temperature sintering profiles, will have the same microstructure, including the same average grain size. Since this approach will be used in this research, it will be reviewed in more depth below.

Reiterer and Ewsuk conclude that based on the extensive published literature on Monte Carlo simulations, the KMC seems to have the greatest potential for providing improved understanding and control of micro[grain]structure evolution as it relates to mesostructure. The RS and the MSC have the greatest potential to allow the user to quickly understand and control the effects of processing conditions with minimal testing. The SOVS and RS models, which are implemented as subroutines in finite element codes, can readily be used to predict final dimensions and density distributions, including those induced by green density variations or gravity, and in complex shape components.

2.1.5. The MSC model

With the Master-Sintering-Curve (MSC), originally defined by Su and Johnson [59], approach, the densification behavior of a powder compact can be predicted under arbitrary temperature-time excursions following a minimal set of preliminary experiments. Once obtained, the MSC can be used to predict sintering results. The advantage of the MSC approach is that it delivers results fast. Of course, the MSC can be applied only to powder compacts made from the same powder and by the same green-

body processing. Different powders and green-body processes result in differences in particle size, particle-size distribution, initial pore-size distribution, packing properties, and green density. These quantities affect densification behavior [60, 61].

The basic approach is to determine first the work of sintering with the time-temperature integral:

$$\theta = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (12)$$

With Q being the activation energy for sintering and R being the universal gas constant. The value for the activation energy can be taken from tables or determined for each specific case.

Based on the work of sintering, the relative density can be calculated for every step during the sintering process:

$$\rho = \rho_0 + \frac{1 - \rho_0}{1 + \exp\left(-\frac{\ln\theta + a}{b}\right)} \quad (13)$$

Once the values for Q , a , and b have been determined for a known sintering cycle, the equations can be applied for an unknown cycle.

The MSC concept has been expanded by the following references:

- 1) “Application of Work-of-Sintering Concepts in Powder Metals” D.C. Blaine, S.J. Park, P. Suri, R.M. German [62]: In this study, the master sintering curve concept is applied to several powder metal systems: 17 to 4PH stainless steel, 316L stainless steel, nickel, niobium, tungsten heavy alloys with two different compositions, and molybdenum.

Figure 23: MSC of 17-4PH [62].

The dashed line of the model shows a close fit with the experimental data (solid lines).

Figure 23 shows the result that Blaine et al. obtained. It shows the MSC of 17-4PH stainless steel as a function of relative density over the work of sintering Θ compared with the experimental sintering curve. A good agreement can be observed.

- 2) “A New Scheme of Finding the Master Sintering Curve”, S. Kiani, J. Pan, J.A. Yeomans [63]: This is a modification to the original master sintering curve approach, so that it is more suitable for finite-element analysis.

Figure 24: Piecewise approximation for a MSC [63].

The master sintering curve is divided into many small sections to determine the shape functions.

Figure 24 illustrates Kiani's approach which provides a general representation for the MSC. A varying activation energy can be used together with the piecewise approximation for the MSC, conferring extra flexibility to the approach. When the quadratic shape functions as described in this paper are used, only a few data points are required to represent a densification curve. The piecewise approximation therefore also reduces the total number of experimental data points required to obtain the master sintering curve. The modified master sintering curve, together with the approximate finite-element scheme [64], forms a powerful tool in predicting sintering deformation from a limited set of experimental data.

- 3) "Master Sintering Curve Formulated from Constitutive Models", S.J. Park, P. Suri, E. Olevsky, R.M. German [65]: Generalized formulations of several

constitutive equations including both grain growth and densification are developed using the concepts of MSC. The developed MSC models can be applied to obtain material properties for the finite-element method simulation and evaluate the effect of compaction pressure, phase change, grain growth, and composition on densification, to classify regions having different sintering mechanism, and to help engineer design, optimize, and monitor sintering cycles.

- 4) “Linearization of Master Sintering Curve”, D.C. Blaine, S.J. Park, R.M. German [66]: In this work, the sigmoid form of the MSC is linearized by relating the natural logarithm of the work of sintering to the densification parameter. Linearization of the MSC simplifies the characterization of the model parameters.
- 5) “Master Sintering Curve for a Two-Phase Material” D.C. Blaine, R.M. German [67]: A new two-phase master sintering curve model for sintering densification of gas-atomized 17-4PH stainless steel, with consideration of δ -ferrite content, is developed. A phase transition from α -austenite to δ -ferrite starts at 1200°C in 17-4PH stainless steel, changing the rate of densification during sintering from this point on.

Figure 25: Two-phase MSC showing crossover from low temperature region to high temperature region [67].

In this hypothetical case the value for the work of sintering, Θ , changes at 1200°C, and a new value is calculated based on the thermal history (ramp and holds).

Figure 25 illustrates the two phase concept. This concept is applicable e.g. for sintering a 17-4PH stainless steel in a H_2 atmosphere. Yunxin et al. [68] have shown that the formation of δ -ferrite promotes pore shrinkage and results in rapid densification, because of the increased number of pathways for mass transport and the higher atomic diffusivity in the bcc δ -ferrite lattice than in the fcc austenite lattice. Blaine concludes that the original MSC and the two-phase MSC both provide good prediction of the final density; however the two-phase MSC provides a more accurate prediction of the sinter density point by point over the thermal cycle.

2.2.Previous work

Based on the experiences in traditional P/M, as well as in metal injection molding, it seemed reasonable to conduct trials on the possibilities of sinter bonding MIM components to solid metal.

Figure 26: Multi cavity mold.

The upper left cavity of this three cavity mold was used to inject the test coupons.

Figure 26 shows the movable half of the multi cavity mold used to inject the first series of samples. The mold was manufactured at the CGEC. By rotating the sprue bushing, either one of the three cavities can be injected. In this case, the cavity on the upper left was used. The cavity dimension is 25mm x 25mm x 4mm.

A series of samples was prepared and injected. In the first group of parts (Table 5), the MIM compacts were injected directly onto the solid metal. Figure 27 shows a

MIM-compact (BASF Catamold 17-4PH-A feedstock) injected onto a flat coupon of rolled 17-4PH steel. The thickness of the coupon as well as that of the MIM compact is 2mm. The MIM compact shrunk 15.7%, as can be seen in Figure 28. The part showed no cracks or distortion.

Figure 27: Green MIM-solid composite part

Figure 28: Sintered MIM-solid composite part

Flat composite test part before (left) and after (right) sintering. The shrinkage is clearly visible, although the MIM compact did not deform or crack.

When the part was cut and polished, it could be observed that the MIM compact deformed in the center during sintering (Figure 29), but the edges were bonded to the solid substrate. The grains at the edges show the contact and bonds in Figure 32. Bordia and Scherer [69-71] worked on a series of papers treating the implications of constrained sintering. In this case the constraint was implied by the powder compact bonding to the substrate before reaching its full density.

Figure 29: Flat MIM-solid composite part.

The V-shape of the sintered powder compact indicated that the part was in compression at the interface with the substrate, which was an sign of differential movements.

The deformation experienced on the flat sample can be explained with thermal expansion/contraction. The two parts were heated up during the sintering cycle (2-5K/min) and the powder compact started densifying. As the temperature increased, the edges reached first the temperature which was necessary to establish the sinter bond. The edges bonded to the substrate and thus impeded further shrinkage. Comparing the dimension a in Figure 29 with the dimensions of the full MIM reference part, it showed that the sinter bonded part did not reach full density. The shrinkage of the reference part was 17.4% compared with 15.7% in the sinter bonded part. Also, porosity could be observed in the sinter bonded part, which confirmed that the part did not reach full density. Since the coefficient of thermal expansion (CTE) is a weak function of density, the two parts, powder compact and solid substrate, would behave differently during thermal expansion and contraction. An estimate of the CTE can be obtained by taking the cube root of the relative density of the powder compact and multiplying that value with the bulk CTE.

Figure 30: CTE as a function of density.

The coefficient of thermal expansion of a powder compact approaches that of a bulk material as the density increases.

Figure 30 illustrates the CTE's dependency on the relative density. For this case, the relative density of the powder compact bonded to the substrate was 0.902 which means that the CTE was 0.965 of the bulk material's, which in this case was the substrate, CTE. A bigger CTE means that the substrate contracts more than the powder compact during cooling. This is confirmed by the powder compact's shape. The red lines in Figure 29, illustrating the shape, indicate that the compact was in compression at the bottom, thus bending the powder compact in the center and breaking weaker bonds in that area. The actual difference in shrinkage was determined by measuring the distance between the bonds and the height of the arc.

Figure 31: geometry of deformed flat sample.

The height (b) in this graph represents the separation between the powder compact and the flat substrate after sintering as measured, in center of the not-bonded area.

The measured chord length l was 21.22mm, the measured height b 0.22mm. That gave a calculated arc length of 21.24mm and a difference in contraction of 0.02mm.

Taking the temperature at the point of bonding as determined in Section 4.5.2, 1267K, the thermal expansion of the substrate is:

$$\Delta l_{bulk} = l_1 * CTE_{bulk} * (T_b - T_{ref}) \quad (14)$$

$$\Delta l_{bulk} = 21.22mm * 1.06E - 5 \frac{mm}{mm K} * (1267K - 273K) = 0.219mm \quad (14a)$$

The thermal expansion a the powder compact with the relative density of 0.902 for the same temperature range is:

$$\Delta l_{compact} = l_1 * CTE_{compact} * (T_b - T_{ref}) \quad (15)$$

$$\Delta l_{compact} = 21.22mm * 9.97E - 6 \frac{mm}{mm K} * (1267K - 273K) = 0.198mm \quad (15a)$$

This calculation confirms the geometrical calculation of the difference in thermal contraction of 0.02mm.

This small difference could imply sufficient stress as to cause buckling of the powder compact and break any bonds in the center. Also, the Young's modulus decreases significantly with temperature. According to the software MPDB, just between 290K and 590K it decreases by approximately 20% [72].

The stresses, so called self-stresses, appearing in this configuration can be of considerable magnitude. As Green et al. state, "It is also important to understand that self-stresses arise in multi-component bodies during the cooling stage of the sintering process, usually in the form of residual stresses. These stresses usually result from mismatches in the thermal expansion behavior of the various components or from other types of strain mismatch and can be orders of magnitude greater than the stresses that occur during densification" [73].

Figure 32: Bonding area on flat MIM-solid composite part.

The MIM part (top) is bonded to the substrate (below), with grains connecting both components.

The problem with injecting onto a flat surface was that the green MIM compact did not adhere to the substrate. The two components came apart right after ejection from the injection molding machine. Additionally, different surface finishes were evaluated, from polished to EDM cut, open 0.3mm grooves. When the surface was rough enough to provide adhesion to the MIM compact, this would crack during sintering. On the parts with a sufficiently smooth surface, it was found that during sintering, the shrinkage could actually move the compact into any direction. This shift in location is dependent on friction, the surface condition of the substrate, or where the first bond was formed.

To avoid the problems encountered with the flat samples, some solid parts had features like slots or high surface roughness to allow for mechanical interlock between the MIM compact and the solid metal. Figure 33 shows a section of a composite part, where a V-slot had been cut into the substrate to allow for a mechanical interlock between powder compact and substrate. Again, contact and bonding was achieved at the

edges and, in this case, in the center, where the V-slot was. Figure 36 also shows how the V-slot was originally filled with feedstock, which then shrunk and left a gap. The filled V-slot avoided the larger deformation in the center as observed in the flat part. But there were still areas where no bonding took place or where the bonds had been broken apart (Figure 35 and Figure 36).

Figure 34 shows an interesting effect. Here the grain structure seems to continue between the substrate and the powder compact. Although there is a gap between both components, the grain structure seems to be aligned. This is a consequence of the sintering of the powder compact. Sintering of the powder compact begins at relatively low temperatures around 600°C when necks begin to form. When a neck is formed, the grain extends from one particle to the other or from one particle to the solid plate. At this stage there is no densification that has taken place. With increase in temperature, initially there is only neck growth and densification takes place at higher temperatures. As the powder mass densifies, it shrinks and creates stresses at the solid metal powder mass interface. Some of the vacancies, pores can be considered to be a mass of vacancies, migrate to heavily stressed areas to relieve stress. Also, while all this is happening in the powder portion of the structure, the only thing happening inside the solid substrate is grain growth [74].

Table 5: First series of samples

Feature	Two V-slots	One V-slot	One T-slot	Flat	Full MIM
Picture
Note	Strong deformation of powder compact due to constrained shrinkage	Bonding only at the edges and along V-slot	Strong deformation of powder compact due to constrained shrinkage	Bonding only at the edges	Reference part to measure unconstricted (ideal) shrinkage

Figure 33: V-slot in solid part

Figure 34: Grain structure continues over gap

The part with one V-slot after cutting (left). After polishing and etching, the grain structure is visible and seems to continue over the gap between the powder compact (top) and the substrate (below).

Figure 35: Point contact on V-slot composite part

Figure 36: Point contact on V-slot composite part

Magnifications of the V-slot sample. Sinter bonds were established at the edges and in the center, where filled slot held the two components in contact.

A second test series to evaluate the influence of the substrate surface was done by cutting small perpendicular grooves (0.3mm) with the wire EDM. Figure 37 shows how the shrinkage of the MIM compact was constrained and thus cracked and deformed. The powder bonded to the substrate “on top” of some grooves, filled others and left many open pores, as can be seen in Figure 38.

Figure 37: Composite part with rough surface structure on substrate

A rough surface prevents free sintering shrinkage and causes cracks and deformation in the powder compact.

Figure 38: Cross section of part with rough surface

To avoid cracks/deformation in the MIM compact or the substrate during sintering, the material must be able to follow the shrinkage movement, even once the initial bond with the substrate is made and sintering continues until the compact reaches the desired density. Figure 39 illustrates the effect of sintering on a substrate with too high a friction or a constrained powder compact. The powder will not be able to densify uniformly and cracks and large pores will be the result.

Figure 39: Sintering on a substrate with friction.

When the powder compact cannot densify unrestricted, cracks and large pores will appear.

2.3.Problem statement

The shrinkage of the powder compact, caused by the elimination of the open pores left after debinding during sintering is the main obstacle to sinter bonding a powder compact to a solid substrate, because the solid substrate will have the same dimensions after sintering as it had before. The binder, which is necessary for the metal injection molding process, leaves an open pore structure in the powder compact. After debinding, the compacts are up to 60% dense, meaning that 40% of the volume is open porosity [75]. In an ideal sintering process (Figure 40), the pores are reduced to a minimum, and the compact is sintered to near full density.

Figure 40: Ideal sintering shrinkage [76].

Only unrestricted densification allows the powder compact to reach near full density with only a minimum of isolated pores left.

There is a series of volumetric changes in the MIM compact and the substrate during debinding and sintering. First, while the parts are heated up during thermal debinding, pre-sintering and final sintering, the substrate expands continuously due to thermal expansion. The powder compact, on the other hand, expands at the beginning

due to thermal expansion, but as the sintering process starts and advances, it contracts as a result of sinter shrinkage. As has been shown above, even among same materials, the thermal expansion and contraction of the powder compact and the solid substrate are different and vary through the process depending on the powder compact's density. The two components, powder compact and substrate thus experience opposing movements. After the last, isothermal, sintering step, when the powder compact has reached its maximum density, the combined part is cooled down and shrinks due to thermal shrinkage. Furthermore, depending on the materials, there can be phase transformations during heating and cooling, which result in volumetric changes [77, 78]. This can be especially difficult in sinter bonding different materials as these might experience the phase transformations at different temperatures.

2.4. Proposed solution

To overcome the problems and limitations outlined above, an elastic or deformable interface between the powder compact and the solid substrate must be created. This interface must be able to absorb the differential movements between both components while assuring dimensional stability of the powder compact, so this does not deform or crack. At the same time, the interface must provide for a strong bond.

A microstructure applied to the powder compact, as shown in Figure 41, allows the powder compact to shrink and densify even after initial contact has been made and the pillars start to bond to the substrate. In the upper half of the Figure, we can see the green powder part located on the solid substrate below. Green means, that the part has

been injected and not yet debound. It is preferable to debind the powder compact before placing it on the solid part, so that the debinding agent (solvent, catalytic gas or heat) has unconstrained access to all surfaces. But some feedstock can be very delicate after debinding and it might not be able to handle them safely [79]. In this case the debinding has to be carefully performed after assembly.

The lower part of Figure 41 shows both components after sintering, the micro features are bonded to the substrate and deformed through the sintering shrinkage of the bulk of the powder compact.

Figure 41: Proposed solution, powder compact with microstructure.
The micro features on the surface of the powder compact allow for densification even after the initial bonds with the substrate have been established.

This set-up was expected to impart certain elasticity and permits differential movements between the powder compact and the solid substrate. Especially during the initial sintering stages, while the part is being heated up, the powder compact shows a high shrinkage rate. At the same time, the substrate expands due to thermal expansion.

This elasticity was estimated to prevent the part from cracking and deforming. At the same time the pillars would have to be able to deform sufficiently without reaching their deformation limits which would break the bonds.

Also, the structure provides a “gap” between both components which allows for a more uniform temperature distribution on the bonding surface, so that all pillars start bonding at the same time, thus theoretically preventing the deformation experienced in the initial, flat samples.

An understanding and a model of this configuration needed to be developed to be able to design a structure that could be optimized for bonding strength and to benefit from the possibilities that this new design offers.

3. RESEARCH METHODOLOGY

3.1. Outline

The overall goal of this research was to investigate, understand and model the proposed process of micro feature enhanced sinter bonding a MIM powder compact to a solid substrate. This comprised three objectives: model the time temperature dependent process of bonding a powder to a solid substrate, model the deformation of the micro features once the bond between powder compact and substrate has been established and finally model and evaluate the overall sinter bonding process.

Six research questions have been established to reach the objectives. Furthermore, to answer the six questions, eight tasks have been defined. The outcomes of the earlier tasks are the inputs for the later ones.

3.1.1. Objective 1: Sinter bonding

The first objective of this research was to develop a fundamental understanding of the process of sinter bonding a powder compact to a solid substrate and model this process and its time-temperature dependant development. It was fundamental to understand the difference between the bonding among the powder spheres and the bonding of powder spheres to the solid substrate. From the reference samples it was observed that the particles first bonded among themselves and then to the substrate. The research questions for this objective were:

1. How does the classical two-sphere sinter model apply to sinter bonding powder to a solid substrate?
2. How and when during the sinter cycle is the bond between the powder compact and the substrate established?
3. How can the process of sinter bonding a powder compact to a solid substrate be modeled?

3.1.2. Objective 2: Deformation

The second objective of this research was to model the “post-bonding” deformation and densification of the microstructure and bulk of the powder component.

The research questions for this objective were:

1. How will the structure deform and what are the deformation limits?
2. How does the microstructure behave after the initial bond is established?

3.1.3. Objective 3: Model and evaluation

The third objective of this research was to combine the results from objectives one and two into one model, evaluate the structure design for bond strength and prove the concept. To evaluate the strength of the sinter bonds, a shear test fixture was designed and built and the different samples were tested and compared with samples of traditional joining methods. The research question for this objective was:

1. How can the pre-bonding and post-bonding phases be combined, modeled and simulated?

3.2.Tasks

The seven tasks defined to answer the research questions, and thus the objectives and finally the research goal, were as follows:

Task 1: Produce samples for fundamental measurements and characterizations

As a foundation, it was necessary to produce a number of samples to gather data for the research objective 1.

Method: Three series of samples were injected and evaluated:

Evaluation:

- Measure bulk before and after sintering (characterize shrinkage and density)
- Shear test
- Cut
- Polish
- Etch
- Measure microstructure, optical or SEM (characterize microstructure shape and behavior)

Expected outcome and contingency plan:

The goal of this task is to obtain a set of fundamental data on the behavior of the powder compacts as to shrinkage, deformation, strength. If there would be problems with the parts (e.g. due to sintering problems), a second series could be injected and sintered

at a different toll sintering company. Also, there are still the samples from the preliminary tests which could be evaluated further.

Task 2: Literature research

Extensive literature regarding the basics of sintering was available. Most publications describe the bonding process between two or more sphere shaped particles.

Method: In this task it needed to be evaluated how far these models could be applied to bonding a particle to a solid (flat) substrate. The second part of this literature research was to obtain information on the conditions for the creation of sinter bonds in general.

Expected outcome and contingency plan:

The purpose of this task was to identify a model that applied to sinter bonding a sphere to a solid substrate and gather information on the requirements and conditions for establishing sinter bonds. If no directly applicable models could be identified, a model must be created.

Task 3: Evaluate samples; compare samples that were bonded to substrate with “MIM only” samples

This task was a continuation of Task 1. Comparing the samples that were bonded to a substrate with those that are not, it was possible to isolate the influence of the constraints during sintering. The evaluation was based on the same procedure as in Task 1:

Method:

- Measure bulk before and after sintering (characterize shrinkage and density)
- Shear test
- Cut
- Polish
- Etch
- Measure microstructure, optical or SEM (characterize microstructure shape and behavior)

Expected outcome and contingency plan:

This task was expected to provide data on the deformation and densification of the powder compacts, especially the difference between those that were bonded to the substrate, and thus constrained, and those that were not. If there would have been problems with the parts (e.g. due to sintering problems), a second series could be injected and sintered at a different toll sintering company. Also, there were still the samples from the preliminary tests which could be evaluated further.

Task 4: Identify the elements of the model, e.g. surface properties, powder size, material, sintering cycle, etc.

This was a fundamental task for the modeling of sinter bonding a powder compact to a solid substrate.

Method: Based on the literature research (Task 2) and sample evaluations (Task 3), the elements of such a model were identified.

Expected outcome and contingency plan:

This task should deliver a series of elements that would be joined to one model. The influence of each element would be weighted. Additionally, and also as contingency, the models in later tasks would be created on the bases of existing models with their elements.

Evaluation: The applicability of the identified elements was evaluated by testing their influence in the models, varying the identified elements. This could be done by comparing the results (dimensions and shape) of the models with the original samples.

Task 5: Create a model that describes the process of bonding between the powder compact and the substrate.

Method: With the input from Tasks 2-4, a model would be created

Expected outcome and contingency plan:

The model to be designed would describe the process of establishing the bond between the powder compact and the substrate. It should be able to predict when the bond is established, the mechanisms for creating the bond and its strength. There would be two approaches, a theoretical and an empirical which ideally complement each other. In case of problems with one of the approaches, the weight can be shifted towards the other.

Evaluation: The model and simulation were evaluated by comparing its results with SEM images and dimensions taken from samples.

Task 6: Model the microstructure deformation

Tasks 3 and 4 lead to model the deformation of the microstructure

Method: Based on Tasks 3 and 4, a model would be created that demonstrated and predicted the deformation of the microstructure during sintering.

Expected outcome and contingency plan:

Based on the deformation model, the “overall” model would be created. The deformation model would deliver data on the constraints acting on the bulk of the powder compact during

sintering. It was also important for geometric control of the compact. As in task 5, there would be two approaches, a theoretical and an empirical which ideally complement each other. In case of problems with one of the approaches, the weight could be shifted towards the other.

Evaluation: The model and simulation were to be evaluated by comparing its results with SEM images and dimensions taken from samples. The agreement between the physical samples and the simulation would be a measurement for the precision of the model.

Task 7: Integrate the results of above tasks into one model for sinter bonding a powder compact to a solid substrate.

The “final” model would represent the complete process, from the start of the sintering process, creation of the first sinter bonds, to the final sintering stage, where the compact reached nearly full density.

Method: Based on the results of Tasks 1 – 6, a model would be designed. This model would consider boundary conditions such as material, surface properties, sintering cycle, etc.

Expected outcome and contingency plan

The anticipated outcome of Task 7 was a model that allowed developing a microstructure to sinter bond a powder compact to a solid substrate and predict the properties of the part as to strength and final dimensions. If the model could not describe the complete

process, a divided model would be considered. This model would divide the process in stages and describe each one successively from start to finish.

Evaluation: The model and simulation were to be evaluated by comparing its results with SEM images and dimensions taken from samples. The agreement between the physical samples and the simulation would be a measurement for the precision of the model.

Error! Reference source not found. shows the structure of this research and how the goal, objectives, research questions and tasks are connected feed into one another.

The basis of this research was a series of reference samples which were evaluated and measured under the optical microscope and the SEM as described in task 1.

Figure 42: Structure of this research

Figure 43: Injection molding machine in CGEC manufacturing lab.
Injection molding machine with mold heater (left) and tool cart (right).

The samples consisted of 25mm x 43mm x 2mm injection molded coupons which had different sized micro features on one surface. The details are listed in Table 6.

Table 6: Micro feature characteristics

Pattern	Shape	Height	Pitch
005	10 μ m circles	25 μ m	20 μ m
002	50 μ m circles	70 μ m	100 μ m
009	100 μ m circles	170 μ m	200 μ m

The feedstock used was a BASF CATAMOLD 17-4PH A [80], which is a special grade for high surface definition.

The typical composition after sintering of this material is as follows:

Table 7: Typical composition of BSAF Catamold 17-4PH A after sintering

C%	Cr%	Ni%	Cu%	Nb%	Mn%	Si%	Fe%
≤0.07	15-17.5	3-5	3-5	0.15-0.45	≤1	≤1	balance

The characteristic properties:

Table 8: Characteristic properties of BSAF Catamold 17-4PH A

	as sintered	heat-treated
Density	≥7.6g/cm ³	
Yield strength R _{p0.2}	≥660MPa	≥950MPa
Ultimate tensile strength R _m	≥950MPa	≥1100MPa
Elongation A ₁₀	≥3%	≥5%
Hardness	320 HV 10 (32HRC)	370 HV 10 (38HRC)

Figure 44: Two cavity mold.

The two mold inserts are connected by the central sprue. The inserts can easily be exchanged.

Figure 44 shows the two-cavity mold used to inject the samples used to inject the second set of samples. This mold was also manufactured at the CGEC. It has exchangeable inserts, so differently shaped parts can be made by changing the inserts. For making these samples, the mold was installed with two cavities of the same geometry, so two samples could be injected at the same time. If necessary, one cavity could be shut off. The samples were injected onto RTV (room temperature vulcanizing) rubber inserts. These inserts were made by casting/embossing [81, 82] the rubber compound over the original micro feature shapes, which were produced by photo lithography.

Figure 45: RTV rubber insert for 100µm features

Figure 46: RTV rubber insert for 50µm features

The arrangement of the features can be observed, alternating in the 100µm pattern on the left and orthographic in the 50µm pattern on the right.

The surfaces of the RTV rubber inserts can be observed in Figure 45 and Figure 46. The 10µm insert was too small to be captured with an optical microscope.

These parts were either injected on the Milacron-Fanuc Roboshot injection molding machine in the CGEC manufacturing lab (Figure 43), or compression molded by

Hoowaki. The coupons were debound and located on 25mm x 40mm x 2mm 17-4PH rolled sheet and finally sintered.

Figure 47: MIM part injected onto RTV insert.

The wavy deformation at the edge of the part is a consequence of injecting onto a soft RTV rubber mold insert. The rubber deforms under the injection pressure.

Figure 47 shows a MIM part with the 100µm surface feature. Also, one of the problems of the RTV inserts can be seen. The edges are slightly wavy. Since the rubber compound is very soft, it is difficult to inject the material in such a way that the mold and all features are completely filled, and the insert would not deform at the same time. As a result, there was always a slight deformation in the parts. Better flatness has been obtained with the compression molded samples. That is because the molding pressure is distributed evenly over a larger area.

To determine the flatness of the samples, 9 measurements of 4 different 24mm x 43mm samples have been taken.

Figure 48: Layout of measurement points.

To measure the flatness of the samples, nine measurements from four samples were taken according to the layout in this figure.

According to ASME [83], “A flatness tolerance specifies a tolerance zone defined by two parallel planes within which the surface must lie”. The lowest value of the nine measurements was subtracted from the other values of the sample, and so the flatness could be evaluated by comparing the highest values of each sample, which in this case would indicate the location of the upper plane.

Table 9: Flatness measurements

Sample	Measurement									Max
	1	2	3	4	5	6	7	8	9	
50 IM	0.37	0.32	0	0.46	0.42	0.13	0.28	0.29	0.19	0.46
50 CM	0.07	0.08	0.03	0.04	0.05	0.1	0.04	0.03	0	0.10
100 IM	0	0.3	0.13	0.53	0.66	0.25	0.25	0.34	0.12	0.66
100 CM	0	0.02	0.01	0.1	0	0.09	0.1	0.11	0.08	0.11

Table 9 shows the flatness measurements. IM stands for injection molded, CM for compression molded; 10 and 50 for the feature sizes. The two compression molded samples have a much better flatness than the injection molded samples.

Also, compression molding, or hot embossing, is capable to achieve very low surface roughness with RTV rubber mold inserts [84]. Injection molding of polymers and metal or ceramic powders into micro features has gained a lot of attention during the last years and is in steady development [85-88].

The problem here is to fill the finer features (10 μ m) with the rather coarse powder (average particle size 4 μ m). Also, the smaller the features, the more difficult it gets to get any trapped air out.

Figure 49: Surface structure.

The 2:1 aspect ratio of the 100 μ m features is clearly visible

The side view in Figure 49 illustrates the surface features and their height to diameter ratio.

The feedstock used was BASF Catamold 17-4PHA. The solid substrate sheet was also 17-4PH. The BASF samples were processed by DSH Technologies, LLC.

Figure 50: DSH sintering cycle.

The sintering cycle employed by DSH to sinter the parts used in this research. During heating up, there are several holds to assure complete binder burn-off.

The BASF samples processed at DSH technologies were all sintered according to Figure 50, which shows the temperature over the sintering time. The sintering atmosphere was H_2 . The cycle was designed to sinter a variety of part sizes. Several holding steps were integrated to burn off any residual binder and thus guarantee distortion free and structurally sound parts. The maximum sintering temperature had a vital influence on the final part density [89, 90]. Sung et al. [91], investigating the effect of the sintering temperature on the microstructure and mechanical properties of a 17-4PH stainless steel, concluded that the pores of sintered specimens appeared to become more rounded and isolated in their distribution as the sintering temperature was increased. The

closure of pores enhanced elongation and strength of sintered specimen. The tensile strength of sintered specimens was found to increase almost linearly with the sintering temperature.

As explored by Yunxin et al. [68], using pure H_2 as the sintering atmosphere as opposed to a mix of H_2 and N_2 has the advantage, that this produces a higher shrinkage rate. The $H_2 + N_2$ atmosphere retards densification significantly at both the earlier (900°C to 1100°C) and later (above 1220°C) stages of sintering.

4. RESEARCH RESULTS

4.1. Introduction

Similar to the approach outlined in chapter three, *Research Methodology*, the research results will be presented according to the three research objectives: model the time temperature dependent process of bonding a powder to a solid substrate, model the deformation of the micro features once the bond between powder compact and substrate has been established and finally model and evaluate the overall sinter bonding process. The six posed research questions will be answered in the proper order to fulfill each objective.

4.2. Sinter bonding

The primary objective of this research was to develop a fundamental understanding of the process of sinter bonding a powder compact to a solid substrate and model this process and its time-temperature dependant development.

To determine the geometrical structure of the micro features and the contact area was the first step to be performed.

Figure 51: Basic MIM compact-substrate geometry.

The dashed line represents the center of the part, where the shrinkage would only be vertically. The blue arrows indicate where the powder compact and the substrate would bond.

Figure 51 shows the basic design of the sinter bonded samples in the green state. Only the tips of the micro features of the MIM compact are in contact with the substrate. To determine the shape of the micro features one of the samples was measured under the white light interferometer (Figure 52).

The radius on the feature tips is clearly visible. The feature diameter was $100\mu\text{m}$, with a tip radius of about $14\mu\text{m}$.

Figure 52: Zygo image of micro features.

The Zygo was used to determine the exact profile of the tips of the features.

The SEM images in Table 10 illustrate the arrangement of the powder spheres in the pillar shaped features. The powder compact was not a homogenous mass, but the individual spheres stood out of the binder. Also, a wide particle size distribution can be observed. The median particle size is $4\mu\text{m}$, but there are clearly visible much bigger and much smaller particles (particle size distribution [92]). Especially in the SEM picture of the $10\mu\text{m}$ features, the $10\mu\text{m}$ diameter pillars are highlighted by red circles, the actual particle sizes can be well estimated.

Table 10: MIM features dimensions

Wide particle size distributions have an advantage in providing a high content of small powders which have a high sintering activity; thus, early in sintering there is a benefit to a wide distribution [93, 94]. However, at long sintering times and high sintered densities the benefit is lost [95]. Also, it was found in a numerical study by Pan et al. that the shrinkage and shrinkage rate between two particles is not significantly affected by the size difference of the two particles as long as the difference is less than 50% [96].

In sinter bonding a MIM compact to a solid substrate, there are two scenarios: the sinter bonds “inside” the compact and the sinter bonds between the metal powder spheres and the substrate. In this research it is assumed that the curvature of the solid substrate is much larger than the curvature of the powder particles and will thus be represented as a flat surface.

Figure 53: Sphere distribution in pillar.

In an ideal case, where the substrate surface would have a large radius ($r \cong \infty$), only one powder particle would be in contact with the substrate.

Figure 53 illustrates how the spheres were located in the 100 μ m pillars. Only a few spheres were actually in contact with the substrate.

The larger the pillar diameter, the more regular was the sphere distribution. In the small pillars, only a few small spheres were located in the pillars, while the larger spheres were too big to enter the features in the mold. To be able to use efficiently the smaller features smaller powders would need to be employed, as for all feature sizes an appropriate powder should be used.

Table 11 shows the particle size distribution of three commercially available 17-4PH powders, extract from [97]. D10 is the particle size at 10% point on the cumulative particle size distribution, D50 is the median particle size and D90 is the particle size at 90% point on the cumulative particle size distribution.

Table 11: Particle size distribution of commercially available 17-4PH powders (after [97])

	D ₁₀	D ₅₀	D ₉₀
BASF	2.3	4.1	10.0
Ultrafine	4.6	11.0	18.0
Mitsubishi	4.8	20.7	50.9

The implication of the particle size on filling of the features is described in Figure 54. The two vertical lines represent the diameters of two of the features used in this research, the red one the 10 μ m feature, the black one the 50 μ m feature. Even of the finest represented powder not all particles will be able to enter the 10 μ m feature, 10% of the particles are larger than the feature diameter. Likewise, 10% of the particles of the coarsest powder are bigger than the 50 μ m feature.

Figure 54: Graphical representation of particle size distribution (after [97])
The two vertical lines represent the diameters of two of the features used in this research, the red line the 10μm feature, the black line the 50μm feature.

4.2.1. Initial contact

Once two bodies are brought into contact, the initial adherence occurs due to weak forces, including van der Waals forces [98]. After the initial adherence, the sintering mechanisms are surface-, grain boundary- and volume-diffusion, evaporation-condensation, vacancy climbs and plastic flow. Also, not all particles are in contact with all their neighbors at the beginning of the sintering cycle. Densification leads to the

delayed formation of new contacts that start sintering later relative to the primary contacts. The number of new contacts varies with the square of the neck size ratio [99].

Figure 55 shows the van der Waals forces as functions of sphere diameter, and distance, for the case of a sphere-sphere and a sphere-plate bonding. Assuming the ideal case, where $R_1=R_2$, and $R \gg l$, the van der Waals force between sphere and plate is twice that of the force between sphere and sphere [100].

Figure 55: Van der Waals forces sphere-sphere and sphere-plate.

The van der Waals forces between a sphere and a plate are twice as high as those between to spheres.

The interaction free energy G in the above figure is a function of the Hamaker coefficient A_{Ham} and the geometry. The Hamaker coefficient depends on the material. Since the bonding was between the same materials in the case of sphere-sphere and sphere-plate, the Hamaker coefficient is the same in both cases.

Figure 56: Relative van der Waals forces.

Depending on the size of the spheres, the van der Waals forces vary, but never reach the magnitude as those between a sphere and a plate.

The van der Waals forces as functions of the geometries is illustrated in Figure 56. The three lines represent the relative forces between two spheres of the same size (green), a sphere and a plate (red) and two spheres of different diameter, with one being $R=2.5$, the second one being given on the horizontal axis (blue). The forces are represented as relative forces and not absolute forces, because the materials are assumed to

be the same and thus all material properties and constants are the same. It can be seen that the force between sphere and plate is in all cases larger than the force between two spheres.

This result was at a first look basically contrary to the finding that the powder compact shrunk a certain percentage before bonding to the substrate.

Figure 57: Zones on bonded samples.

A MIM (top)-solid (below) compound part shows three zones, one where the powder compact shrunk and did not bond, the second, where the powder compact is above the substrate, but could not establish any bonds due to the deformation of the mold insert, and the third zone, where the parts are bonded and the features deformed to follow the sintering shrinkage.

In Figure 57, the surface of the solid substrate has been divided into three zones. Zone one is an area of “pre-shrinkage”, meaning that the powder compact, which was originally the same size of the substrate, shrunk over this area without bonding. Zone two is an area of deformation where bonding was not possible. The powder compact was deformed as a result of injecting onto the soft RTV rubber mold inserts. Only zone three

shows the expected bonding of the micro features to the substrate and the subsequent deformation of the features caused by shrinkage of the bulk of the compact. According to Figure 56, the powder compact should have bonded to the substrate from the start of the sintering cycle on. But there is no indication of this early bonding, meaning that the powder compact started to develop the “internal” bonds among the powder spheres first.

It can be seen in Figure 53 that, based on the assumption of a large substrate curvature, there can be only one contact point with the substrate per powder sphere, while it can have several contact points with other spheres. For monosized spheres in three dimensions, the initial coordination number at a green density of 64% of theoretical is about seven contacts per particle [99].

This explains that there was no trace of the pillars trying to bond to the substrate. The spheres in contact with the substrate had stronger bonds towards the powder compact. And only later on during the sintering cycle did the bonds with the substrate form.

Once the initial contacts were made, the compact started sintering and densifying through the sintering mechanisms of diffusion, evaporation-condensation and plastic flow as described in the literature review. The ideal sintering model of two spheres sintered for infinite time is illustrated in Figure 58.

Figure 58: Ideal sintering model for infinite time [3].

In ideal sintering of two spheres, these converge to one sphere after infinite time.

While this does apply to two spheres, it does not apply to a powder compact consisting of multiple spheres. When several spheres are placed in a chain-like order, they sinter to the shape of a cylinder with the ends being two hemispheres. A MIM powder compact shows an isotropic shrinkage of up to 20%, depending on the feedstock and sintering process. Figure 59 illustrates how two spheres would sinter in a chain like configuration, resulting in an isotropic shrinkage of 20%. The centers of the two spheres approach each other. The material of the segments filling up the neck, and at the same time material from the surfaces moves towards the neck region. The result is an overall reduction of the dimensions of up to 20%

Figure 59: Sintering of two spheres to 20% shrinkage.

Model of real sintering behavior, where the spheres shrink up to 20%, which means that the distance between the center of the two spheres is 80% of the original distance.

To illustrate this effect, a MATLAB program was written that calculated the final outer diameter and center distance of two spheres that sinter in such a manner that they ended up as a cylinder with two hemispheres and thus eliminating any pores between them. Figure 60 shows the relation of sphere diameter and center distance for the sintering of two spheres. For a linear reduction of the center distance of 18%, the sphere diameter shrunk about 4.3%. Translating this property to the three dimensional space explained why the compact maintained its overall shape.

Figure 60: Sphere diameter vs. center distance.

This graph shows that due to material moving from the surface to neck, the diameter of the sphere is reduced by about 4.3%.

This sintering behavior explains the details observed in Figure 61 and Figure 62. The tips of the pillars maintained their shapes. The overall dimensions shrunk, but the pillars did not notably flatten and lose their shapes.

Figure 61: Deformed surface feature

Figure 62: Deformed surface feature

The features deformed and followed shrinkage, but maintained the radius at the tips.

Only the tips bonded to the substrate and then followed the shrinkage of the bulk of the compact in a “rolling” motion, as illustrated in Figure 63. This motion brought additional surface area of the pillar into contact with the substrate which then increased the bonded area and thus the bond strength.

Figure 63: Pillar tips in rolling motion over substrate.

While following the shrinkage, the features deform and the “rolling” movement of the tips brings more surfaces into contact with the substrate, thus increasing the bond strength.

4.2.2. Bond strength

The in-situ strength of the powder compact is a function of the neck size. A MATLAB program has been written to illustrate the relationship between neck growth and shrinkage and to be able to calculate the in-situ strength during sintering

The approach in the MATLAB code is based on Figure 64 [101, 102]. It illustrates how the material is transported from the “disappearing” spherical section to the neck.

Figure 64: Schematic of solid state material transport [101].
Material is transported from the spherical sections to the neck, thus eliminating pores.

Figure 65: Material transport in sintering a sphere to a plate.

As in the sphere-sphere sintering process, material is transported from the sphere section to the neck while the compact is densifying.

Figure 65 shows how the material transport for a sphere plate sinter bond is calculated in the MATLAB approach. The material that would be in the sphere section at the bottom is transported to the neck.

Figure 66 shows the neck size of a sphere-flat bond at the beginning of the sintering cycle. The upper half of the sphere is plotted over the horizontal axis; the flat substrate is being represented by the left vertical axis. The initial contact has been made and the neck is growing. The neck is formed in such a way that it is tangent with the flat substrate and with the sphere. The volume of the neck equals to the volume of the segment of the sphere which is a result from the sphere moving towards the substrate. The diameter of the sphere is assumed to be $5\mu\text{m}$. The ration X/D indicates the ratio of the neck size (diameter) to the sphere diameter.

Figure 66: Neck size sphere-flat at cycle start.

At the beginning of the cycle, the neck is very small compared with the particle diameter.

An important observation can be made in Figure 67. To completely fill the porosity between the sphere and the substrate, i.e. a neck size ratio of 1, the sphere bonded to the substrate has to move closer to the substrate than the 20% necessary between two spheres, because in this case only one sphere is providing the material necessary to fill the pores.

Figure 67: Neck size sphere-flat at cycle end.

Once the neck size to particle diameter approaches a value of 1, the pores are closed.

In Figure 68 the neck formation between two spheres can be appreciated. Again, the upper half of one sphere is plotted over the horizontal axis; the left vertical axis is representing the center plane between the two spheres, with the second sphere being a mirror image of the first one.

Figure 68: Neck size sphere-sphere at cycle start.

The diameter of the neck between two spheres is very small at the beginning of the cycle, just after the initial contact has been established.

The diameter of the neck between two spheres is very small at the beginning of the cycle, just after the initial contact has been established. As the spheres approach each other, as the shrinkage reaches, depending on the feedstock, a maximum of 20%, the porosity will be eliminated and the neck size to diameter ratio approaches 1.

Figure 69: Neck size sphere-sphere at cycle end.

As the diameter of the neck approaches the diameter of the spheres, the porosity will be eliminated.

According to Xiaoping [103], the nominal strength of a porous material is a function of the fractional density.

4.2.3. Sub-conclusion

The sintering process in sinter bonding a MIM powder compact to a solid substrate is basically the same as the sintering process in the bulk powder compact. The difference found in this case is geometrically given in that the tips of the micro features have a spherical shape. This shape permits only a very few powder particles to come into contact with the substrate. On the other hand, these powder particles have multiple

contacts with other particles inside the powder compact. This configuration inhibits bonding of the MIM compact to the substrate at an early stage of the sintering cycle. Although van der Waals forces are stronger between a sphere and a plate than between two spheres, due to the number of contacts, initial contacts will be made inside the powder compact. Even if the tip of the feature was flat, there could still be only one point of contact between a powder particle and the substrate with multiple contacts between the same powder particle and other particles in the compact. Once the bonds are established, either between plate and sphere, or between two or more spheres, the sintering mechanisms are the same as in the classic sintering models. The mechanisms for neck growth and densification, surface diffusion, volume diffusion, grain boundary diffusion, lattice diffusion evaporation-condensation and plastic flow [104] are the same as has been shown in the literature review.

4.3. Post bond and deformation

After injection, debinding and sintering, the sinter bonded samples were cut, polished and some then etched for analysis as described in task 1:

Figure 70: MIM part with 10µm dia. surface features (top) bonded to a solid substrate (below).

The parts are bonded over a large area, connected by the micro features on the surface of the powder compact.

Figure 70 shows how the MIM compact with surface features was bonded to a solid substrate over large areas. Although there seems to be a gap between both components, both are connected and bonded by the micro features on the surface of the MIM compact. A very slight deformation can be observed. The features are tilted to the right. Towards the right of the image, there is one area that seems to be completely filled and bonded. This is very interesting, since it was not possible to realize such a bond over a larger area with the initial flat samples.

The next figure (Figure 71) illustrates in more detail how the surface features (here with 100 μ m dia. features) were bonded to the substrate.

Figure 71: Micro features bonded to substrate.

The features on the surface of the powder compact are bonded to the substrate and deformed by following the shrinkage of the bulk of the material (shrinkage direction right to left).

The next step was to analyze the bonded samples. In the previous section it was shown that the powder compacts create the initial bonds internally and densify considerably before the micro features bond to the substrate.

The inclination of the pillars of the high aspect ratio microstructure parts was evaluated. Since the mold inserts were, as mentioned before, made of RTV-rubber, the samples were not completely flat, and thus not the whole area was bonded. For the evaluation, a completely bonded area was identified and 10 pillars were measured (Figure

72) with ImageJ [105]. The first one (0) being at 90° was taken to be the center of shrinkage of the evaluated area.

Figure 72: Part of the evaluated area of sinter bonded part.

10 micro features were measured (only 9 are shown in this figure). The first one (0) being the center of shrinkage and the following features (1 – 9), showing successively more inclination.

Comparing the angles of the pillars with the measured shrinkage of the part, 17.4%, there was a mismatch. The inclination was too small for the shrinkage. This indicated, that the compact must have shrunk to a certain extend before the pillars bonded to the substrate, as has been shown in the previous section, and then deformed while following the shrinkage until the final value.

The point of bonding was determined by using the known dimensions (Figure 73). The assumption for the model was that the pillars were not bonded to the substrate at the moment the powder compact started to sinter and densify (brown state). The compact continued to shrink with the pillars still at 90° , sliding over the substrate to follow shrinkage. At a certain point, the bond between the pillars and the substrate was established. From this point on, the pillars had to deform, so the bulk of the powder compact could continue to shrink. If the deformation of the pillars was constrained, these, the bond itself, or the bulk of the compact would break.

Figure 73: Determining the point of bonding.

Geometric model developed to determine the point at which the powder compact bonded to the substrate. The compact (brown at the beginning of the cycle) starts densifying before it bonds to the substrate (blue outline). And finally shrinks to full density (grey outline).

$$\tan(\alpha) = \frac{a}{s_b - \Delta s_b} = \frac{a}{b(s - \Delta s)} \quad (16)$$

$$\Delta s = s - \frac{a}{b * \tan(\alpha)} \quad (17)$$

The results of the measurements and calculations are listed in Table 12.

Table 12: Measurements and results to determine the point of bonding

a	b	s	α	Δs
[mm]	[mm]	[%]	[°]	[%]
0.132			90.00	
0.132	0.165	17.40%	84.88	10.25%
0.132	0.331	17.40%	82.94	12.45%
0.132	0.496	17.40%	78.53	12.00%
0.132	0.662	17.40%	73.55	11.51%
0.132	0.827	17.40%	68.96	11.26%
0.132	0.992	17.40%	63.03	10.63%
0.132	1.158	17.40%	55.01	9.42%
0.132	1.323	17.40%	59.30	11.48%
0.132	1.489	17.40%	47.23	9.20%
				10.91%

The result gave a mean value for Δs , which was the shrinkage until the point of bonding, of 10.91% with a standard deviation of 0.1% among the measured pillars. This meant that the powder compact shrank 10.91% before the pillars bonded to the substrate, and then continued to shrink until it reached its final value of 17.4%.

4.4. Post bonding deformation and simulation

The Master Sintering Curve (MCS) approach had been chosen to calculate the densification over the sintering cycle. As described in the literature review, the MSC method can predict densification behavior under arbitrary temperature-time excursions following a minimal set of preliminary experiments [59]. In this case the advantage was that the preliminary experiments had been performed by BASF, the feedstock provider. However, the MSC as simple empirical approach to predict densification behavior has some limitations (i.e., a unique sintering path as function of density is prescribed) which constrains the flexibility of the modeling [106].

4.4.1. Calculating sintering shrinkage

Shrinkage is caused by elimination of the pores between the powder particles during the sintering cycle. Mass is transported by bulk transport processes as grain boundary diffusion, volume diffusion and plastic flow. Vacancies from the pores migrate through the lattice or along grain boundaries, giving a reverse flow of mass into the pores [3].

The driving force for mass flow is the sintering stress. The smaller the particles, the greater the driving force and sintering requires mass flow to respond to the inherent stress.

4.4.2. Model development

The basis for this model is the dilatometer curve of a known material. In this case, the final part was to be made from BASF CATAMOLD 17-4PH-A. The manufacturer provided the original dilatometer data over the sintering cycle corresponding at that particular feedstock, Figure 74.

Figure 74: BASF sintering cycle and dilatometer curve.

Dilatometer curve provided by BASF, showing the shrinkage (red line) and temperature (green line) over the sintering time. The highest densification rates are during the heating up sections.

Figure 75: Dilatometer curve from BASF data.

The data from the original dilatometer curve was transferred to a MATLAB database and plotted with the shrinkage represented as positive values.

Figure 75 shows the original data after reading out from the original graph and transferred to a MATLAB database. In this case, not the complete cycle is shown; the cooling part is missing since no densification takes place during that step. Also, the shrinkage has been represented positive.

The next step was to determine the constants of the master sintering curve. The conventional MSC links the time-temperature (t - T) integral, also called the work-of-sintering θ [107] to the relative sinter density, ρ at time t during the thermal cycle, starting at $t=0$ [67].

$$\theta = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (18)$$

And

$$\rho = \rho_0 + \frac{1 - \rho_0}{1 + \exp\left(-\frac{\ln\theta + a}{b}\right)} \quad (19)$$

The activation energy Q for the sintering system is either determined through minimizing the error between the experimental data and the model, or it is assigned a value based on known diffusional activation energy for the system [59]. ρ_0 is the relative density at the start of the sintering cycle, a and b are constants defining the curve. Here, the activation energy was determined to be $Q=290\text{kJ/mol}$, and the constants $a=10.03$ and $b=1.45$.

Figure 76: Sintering curve with MSC fit.

The master sintering curve fitted to the original dilatometer curve. The MSC starts at a lower value than the original curve and does not show the holds as explicit as the original, but as the temperature increases, the fit gets closer.

Figure 76 shows the original curve and the MSC fit. With the constants determined through the MSC approach, the densification curves of parts made of the same material and processed under the same conditions (basic heating rates, atmosphere, etc.) can be established. In this study, the method was necessary to calculate the sintering stress for a known sintering cycle (time and temperature), which was to be used to sinter the specific parts, because it was important to know the deformation during the cycle. The MSC approach was used to calculate the relative density of the powder compact through the cycle.

Figure 77: Calculated densification through known sintering cycle modeled with MSC.

The coefficients which were determined through the curve fit were applied to the time temperature data of the sintering cycle used in this research.

Figure 77 shows the results of that calculation. The predicted density of a powder compact was calculated over a known sintering cycle.

In the subsequent step, the sintering stress was determined. This stress or sintering potential is the driving force for densification and can be seen as an external pressure that compresses the part and causes it to shrink. The sintering potential in isotropic densification is equivalent to the hydrostatic stress that is sufficient to halt the densification process and hence reflects the driving force for sintering, i.e., the reduction of interfacial energy [73]. According to Kwon [108], the sintering stress (σ_s) can be calculated for three stages: first, for the case of open pores,

$$\sigma_{si} = \frac{6\gamma}{D} \rho^2 \left(\frac{2\rho - \rho_0}{1 - \rho_0} \right) \quad (20)$$

And, for the case of closed porosity

$$\sigma_{sf} = \frac{4\gamma}{d_p}, d_p = \frac{D}{2} \left(\frac{1 - \rho}{6\rho} \right)^3 \quad (21)$$

Where γ is the surface energy, d_p is the pore diameter, and D is the particle diameter. For the transition from open to closed pores, which is at relative density between $\rho_1=0.85$ and $\rho_2=0.95$, the sintering stress is

$$\sigma_{st} = \frac{(\rho_2 - \rho)}{(\rho_2 - \rho_1)} \sigma_{si} + \frac{(\rho - \rho_1)}{(\rho_2 - \rho_1)} \sigma_{sf} \quad (22)$$

With these equations, the sintering stress over the cycle is calculated with the material parameters of $\gamma=2\text{J/m}^2$ [68] for the steel used in this samples and $D=4\mu\text{m}$ [80] as the median particle diameter.

Figure 78: Sintering stress over sintering cycle.

With the densification values determined through the MSC approach, the sintering stress was calculated over the time-temperature profile of the sintering cycle.

The sintering stress over the sintering cycle is shown in Figure 78. The highest sintering stress of 120MPa appeared at the point of the maximum shrinkage of 19.33%.

4.4.3. Simulation

The simulation software used in this study was ANSYS Workbench. In ANSYS, first the geometry of the part is either generated in its own CAD application or loaded from any commercial CAD package.

The next step is to set up the material. In this case, a new, substitution material was inserted. As mentioned before, the shrinkage was assumed to be isotropic. The only property of the material was isotropic elasticity, which comprised Young's modulus and

Poisson's ratio. Young's modulus was determined through the bulk modulus K , which is the sintering stress divided by the shrinkage [109]:

$$K = \frac{\sigma_s}{s} \quad (23)$$

$$E = 3K(1 - \nu) \quad (24)$$

with ν being Poisson's ratio, in this case 0.31. The sintering stress could now be applied to the part as pressure acting on all surfaces of the part. This could be done either as one value, the maximum value through the cycle, which would lead to the total shrinkage/deformation at the end of the cycle, or as tabular data, over time (Figure 79). This way the deformation during the cycle can be observed.

Figure 79: Pressure profile in ANSYS

Figure 80: Simulation of sintering shrinkage.

Densification simulation applied to the geometry of the full-MIM reference part that was injected during the preliminary work. The colors represent the absolute deformation with red being the highest value.

To test the concept, the simulation was applied to a known part. Figure 80 shows the shrinkage of the reference full-MIM part. The wireframe of the undeformed part can be observed.

The next step was to apply this approach to the MIM compact with the surface features. The surface of the MIM part consisted of pillars with a diameter of 50 μ m, which had to be able to deform and follow the shrinkage of the bulk of the part while they themselves undergo shrinkage. Here, only the mid plane of the part was evaluated to show the deformation in more detail.

Figure 81: Undeformed pillar model.

The geometry of the powder compact with the micro features on the surface, after importing into ANSYS applying the standard mesh.

Figure 81 shows the undeformed pillar model with the mesh generated by ANSYS. The part is supported by a frictionless support on its left edge, which is representing the center of the part. Further supports are fixed supports at the bottoms of the pillars, where they are bonded to the substrate.

Figure 82: Deformed pillar model.

The model of the powder compact after bonding to the substrate and applying the sinter stress as a hydrostatic pressure. The sintering stress causes shrinkage and deformation, since the features are bonded to the substrate. The colors indicate the absolute deformation, with red being the highest value.

The deformation the part and especially the pillars experience is illustrated in Figure 82. The pillars are connected to the substrate and have to bend to follow the shrinkage of the part. The farther away from the center the pillars are, the stronger is the inclination.

The next illustration, Figure 83, shows an SEM image from the actual part. The only differences are slightly different dimensions of the pillars. The part was sintered with the sintering cycle similar to the one described in the MSC part.

Figure 83: SEM image of a MIM compact (top) sinter bonded to a solid substrate (below).

In this SEM image, the deformation of the real micro structure can be compared with the result of the simulation as shown in Figure 82.

The deformation of the pillars was as predicted by the ANSYS simulation. The pillars were inclined and showed the same curvature as the simulation. Furthermore, the

“flat”, horizontal sections between the pillars also showed a slight deformation, agreeing between the real part and the simulation.

To evaluate the precision of the model, the deformation of two different feature sizes was simulated and compared dimensionally with samples. Solid Works models of the micro features with the nominal geometry of the physical samples were created and imported into ANSYS. The sintering stress as illustrated in Figure 79 was applied as a load over the sintering cycle. The starting point for the simulation was the point, when the features are initially bonded to the substrate. A frictionless support was applied to the center of the parts, fixed supports to the feature tips, where these would be bonded to the substrate.

Screenshots of the simulations were imported in the ImageJ software [105] for dimensional analysis. For the 100 μm feature, a SEM image was taken as reference, for the larger 200 μm features, an optical microscope image.

Due to irregularities of the features in the samples, caused by the RTV rubber inserts and since the samples could not be cut and polished exactly through the feature centers, the inclination of the features was measured.

Figure 84: Comparison between samples and simulation, 100 μ m features.
The inclination of four features has been measured and compared between sample and simulation.

Table 13: Result of measurements, 100 μ m features

Feature	Sample	ANSYS
	[°]	[°]
1	106.9	103.3
2	109.2	110.0
3	111.5	113.2
4	114.5	116.8
Correlation coeff.:		0.97

Table 13 lists the results of the measurements of the 100 μ m features as measured in Figure 84. There is a good agreement between the simulation and the samples with a correlation coefficient of 0.97 [110]. The same is true for the 200 μ m features, where the correlation coefficient is 0.99, Figure 85 and Table 14.

Figure 85: Comparison between samples and simulation, 200 μ m features.
The inclination of four features has been measured and compared between sample and simulation.

Table 14: Result of measurements, 200 μ m features

Feature	Sample	ANSYS
	[°]	[°]
1	106.3	101.9
2	112.8	107.8
3	113.6	112.5
4	115.6	114.1
5	124.4	125.2
Correlation coeff.:		0.99

4.4.4. Limitations

The limitations of the approach described here can be divided into two parts, first there are the limitations of the MSC model, and then there are those from the simulation and its underlying assumptions itself.

The MSC can be applied only to powder compacts made from the same powder by the same green-body processing [59]. Also, Reiterer and Ewsuk have observed that

densification curves generated using heating rates slower than 5K/min often do not fall on the same MSC [52].

The validity of the simulation itself is basically limited by the assumptions made. In the example presented here, isotropic shrinkage was assumed, although it has been shown that this is not exactly the case [50, 51]. If the values of anisotropic shrinkage for a particular material are known, they can be modeled in the ANSYS' material database and thus overcome this limitation. Also, gravity can be applied to the powder compact as a load during sintering.

4.4.5. Sub-conclusion

In section 4.3 it has been shown that the bonds between the powder compact and the substrate are not established until later in the sintering process. The goal of this section was to determine the point in time when this bonding takes place and how the features deform, once the bonds are established.

Analyzing the SEM images of bonded samples, the point of bonding could be determined as taking place at a shrinkage of 10.91%. This means that the powder compact shrunk 10.91% before the bonds were established and then the compact continued to shrink until it reached its final value of 17.4%.

Based on the MSC approach, the shrinkage of the powder compact was calculated. Finally, the sinter stress was calculated and applied as an external pressure in ANSYS to simulate the shrinkage and deformation. The pressure was applied as a profile over the sintering cycle. To this end, a substitution material was created, consisting of

Young's modulus and Poisson's ratio. The Young's modulus was calculated based on a calculated bulk modulus.

The result of this simulation showed good accordance with the deformations, observed on the sample parts. The simulation results were dimensionally compared with sinter bonded samples with 100 μ m and samples with 200 μ m and correlation coefficients of 0.97 and 0.99 respectively were achieved. The correlation coefficients mean that there was a very agreement between the measurements taken from the simulations and those taken from the physical samples. The ANSYS software has the option to apply also different boundary conditions as gravity or anisotropic behavior.

The MSC approach has some limits, and the quality of the reference data and its generation is very important.

4.5. Model and evaluation

To evaluate the sinter bonding process and measure the strengths of the sinter bonds, a shear test fixture was designed and built. The design foundation of this fixture was to be able to shear the samples on the CGEC's INSTRON tensile test machine. The fixture was build from steel and case hardened.

Figure 86: Shear test fixture.

The shear test fixture consists of six components, an upper yoke (1), a lower T-shaped support (3), two inserts to hold the test part in place (2) and (6), and a front and back plate, which are not visible in this view. The test part, is fixed with its bonding surface in the shear plane, (4) and (5) being its two components.

The cross section in Figure 86 shows the fixture design. A yoke (1) and an inverted “T” shaped lower part (3) constitute the main structure of the fixture. Both have 15mm x 20mm rectangular openings to install the sample to be tested. The sample, comprised of the solid substrate (4), together with the MIM part (5) which it is bonded to, was held and clamped by two blocks (2 and 6), which were secured by setscrews, in the shear plane of the fixture.

Figure 87: Shear test fixture placed in INSTRON.

The test fixture is located on the closed jaws of the tensile test machine, and loaded in compression.

The upper half of the INSTRON (Figure 87) was pushed down while the lower half remained fixed. To evaluate the bond strengths of the sinter bonded parts, a series of samples was prepared:

- MIM compact with 100 μ m diameter surface feature bonded to a solid substrate (3 samples)
- MIM compact with 50 μ m diameter surface feature bonded to a solid substrate (3 samples)
- MIM compact with 10 μ m diameter surface feature bonded to a solid substrate (3 samples)
- Two coupons of rolled sheet joined by a 2-K adhesive bond (JB Weld) (1 sample)
- Two coupons of rolled sheet joined by brazing (1 sample)
- Two coupons of rolled sheet joined by a resistance weld spot (1 sample)

All samples were EDM cut to a dimension of 15mm x 15mm. As mentioned before, due to the properties of the soft prototype molds (RTV) used in these tests, the parts were not completely flat, as measured after injecting, and thus the samples were not bonded over the entire area. That is why the effectively bonded areas were measured after the shear tests to calculate the actual shear stresses (Table 15).

Table 15: Shear strength results

Sample	Force	Bonding area	Shear stress	Average shear stress
	[kN]	[mm^2]	[MPa]	[MPa]
Braze_1	15.16	252.00	60.16	
Braze_2	3.58	80.00	44.75	
Spot weld	1.00	1.77	565.88	
JB Weld	5.02	290.00	17.31	
10_1	25.56	48.00	532.50	452.84
10_2	24.41	crushed after break loose		
10_3	33.96	91.00	373.19	
50_1	22.93	80.00	286.63	242.16
50_2	23.50	77.00	305.19	
50_3	10.10	75.00	134.67	
100_1	9.53	54.00	176.48	183.52
100_2	damaged during set up			
100_3	10.29	54.00	190.56	

Evaluating the bonding surfaces after the test under a SEM, it was found that one part of the features, in this case circular shaped pillars, were sheared off at the bottom, while the other part was sheared off at the top. This indicated that the bonding must have been equally strong on the MIM sides as well as on the substrate side. Otherwise all features would have failed on the same side. Figure 88 shows a bonding surface, where the different areas are clearly distinguishable. In the center area some pillars are still in place, while others failed and were found on the opposite part. The areas further to the left and right did not bond at all due to lack of flatness of the MIM part.

Figure 88: Shear test failure area.

This part was bonded in the center. The areas on the left and right did not bond due to lack of flatness and following deformation of the RTV rubber mold inserts.

Figure 89 is a magnification of the two different failures. Some pillars were sheared off at the bottom, slightly above the surface, others at the top. This indicates that the bonding with the substrate is as strong as the bulk strength of the powder compact itself. Otherwise the micro features would all fail on the same side. Here, one can see the small shear deformation the pillars experienced before failure during the shear test.

Figure 89: Shear test failure pattern.

In the bonded areas, the micro features on the side of the powder compact as well as on the side of the solid substrate, indicating that the bonds with the substrate were as strong as the bulk material.

Failing on both sides meant that the bond itself was as good as the strength of the bulk of the MIM compact.

Figure 90 illustrates in more detail the shear failures. Especially the pillar in the center of the image shows how it was going to fail at the bottom, but finally failed at the top. It can be observed how the pillars deformed from right to left following the shear movement, then started to shear off (semi circle of the right hand side of the features, top

and bottom) and finally failed and left a rough fracture on the left hand side of the pillar tops.

Figure 90: Detail of shear failure.

The feature tips show typical shear deformation (semi-circles on the right of the tips) followed by failure through fracture.

The sinter bonds have shown shear strengths of up to 80% of that of welded joints, as illustrated in Figure 91. The resistances of the braze joint and the adhesive bond were much lower. The strength of the joints depended on the size of the micro features, the smaller features showing higher strengths.

Figure 91: Shear test results.

Comparing the micro feature enhanced sinter bonds, it was determined that the 10μm diameter features achieved bond strengths of up to 80% of that of a resistance weld. Even the samples joined with the bigger features were stronger than those joined with braze bonds or 2K adhesive bonds.

4.5.1. Evaluation of bond strength

To be able to correlate the bond strength to the micro feature geometry, the configurations have been measured and evaluated with respect to shear strength. This was also necessary to be able to design more efficient micro feature layouts in the future.

Figure 92 and Figure 93 show how the ratio between features in contact with the substrate to entire bonding area was measured. It was not possible to do this measurement for the 10μm features, because most of the features were deformed and the feature “tips” did not form a regular pattern. The bonding area in Table 15 comprises the entire area, features and “free” space in between.

Figure 92: Area/feature ratio 50μm feature.

The apparent net bonding to entire surface area was determined by calculating the area of a square with the side length a , and dividing this by the area of one surface feature of diameter d .

Figure 93: Area/feature ratio 100μm feature.

The apparent net bonding to entire surface area was determined by calculating the area of a isosceles triangle with the side length a , and dividing this by one half of the area of a surface feature of diameter d .

The dimensions measured and results were as follows (Table 16):

Table 16: Feature to area ratio 50 μ m and 100 μ m features

Feature	Dimension a	Dimension d	Feature to area ratio
50 μ m	90 μ m	56 μ m	0.304
100 μ m	210 μ m	100 μ m	0.247

Comparing the results listed in Table 16, shows how good the bonding was. The Ultimate tensile strength (UTS) of the 17-4PH feedstock was 950MPa [80]. According to Deutschman [111], the ultimate shear strength (USS) of an alloy steel is 0.75 of the UTS.

Table 17: Shear strength

Feature	UTS [MPa]	USS [MPa]	Measured shear strength [MPa]	% of USS	Feature to area ratio
10 μ m	950	712.50	452.84	63.60	n/a
50 μ m	950	712.50	242.16	34.00	0.304
100 μ m	950	712.50	183.52	25.80	0.247

Table 17 summarizes the shear test results. For the 100 μ m feature, the measured shear strength was 183.52MPa, which is 25.80% of the material's bulk USS. This was achieved with a feature to area ratio of 0.247, meaning that 24.7% of the apparent total bonding area was actually bonded features. The same for the 50 μ m feature, the measured shear strength was 242.16MPa, which is 34.00% of the material's bulk USS. This was achieved with a feature to area ratio of 0.304, meaning that 30.4% of the entire bonding area was actually bonded features.

Taking into account that it was very difficult to determine the exact entire bonding area due to the shape irregularities, a good agreement can be observed between the % of shear strength and the feature to area ratio. Figure 94 to Figure 96 show the actually bonded areas of some typical samples marked in red.

Figure 94: Bonded areas on 10 μ m sample.

The areas outlined in red are the areas that were effectively bonded to the substrate; the remaining area was not bonded due to lack of flatness of the powder compact caused by the soft RTV rubber inserts during injection.

Figure 95: Bonded area on 50µm sample.

The area outlined in red in the center, is the area that was effectively bonded to the substrate; the remaining area was not bonded due to lack of flatness of the powder compact caused by the soft RTV rubber inserts during injection.

Figure 96: Bonded area on 100µm sample.

The area outlined in red in the center-left, is the area that was effectively bonded to the substrate; the remaining area was not bonded due to lack of flatness of the powder compact caused by the soft RTV rubber inserts during injection.

This means that all features located in the bonding area bonded to the substrate and formed a bond with a strength equal to that of the material's USS.

Another factor is the actual area of bonding per micro feature. It has been show above that the micro features used in this research have a radius on the tip opposed to a flat surface. After bonding, densifying and deforming, in many cases not the entire cross sectional area of the feature was bonded.

Figure 97: bonding area per feature.

Due to the radius on the tips of the features, not the entire diameter of the features can always be taken to calculate the net bonding area. Variations between 70% and 100% of the gross area have been measured.

Figure 97 illustrates the difference in the effectively bonded area per feature. Features a, b and c were bonded with 100%, 70% and 87% respectively of the total cross section of the features.

4.5.2. Maximum deformation

Figure 98 and Figure 99 represent the feature deformation. From the ANSYS simulation and the SEM images it could be deduced that the features deformed in the way illustrated here.

Figure 98: Figurative representation of feature deformation

Representations of the bending movement of the micro features. On the right the figurative representation, and on the left the free body diagram.

Figure 99: Free body diagram

The features are fixed on the powder compact side and are free to rotate on the substrate side as can be seen in Figure 100.

Figure 100: Shape of deformed feature

In the comparison of the micro feature deformation between the simulation and a SEM image the typical shape caused by bending can be identified.

The figure shows the characteristic curvature of a cantilever beam in bending. Due to the geometry of the features in this research with this relative small aspect ratio, ($l/d < 2$), a comparison stress might be calculated. For long beams, ($l \geq 4 \dots 5d$), only the normal stresses are important, for short beams, ($l \leq d$), only the shear stresses are important [112]. This means that the part would fail rather through shear than through bending stress.

Figure 101 confirms that statement: although the micro features are loaded as bending beams, the characteristic failure is through shear, as can be observed here and has been show in the previous sub-section.

Figure 101: Shear failure of micro feature.

The typical deformation of a shear failure can be seen on the surface of the failed bond.

This leads to the finding that there are basically two load scenarios, the first one during sintering, after the features have established bonds with the substrate and the powder compact continues to densify, and the second one with applied external loads, as e.g. during the shear strength testing. For the second scenario, the material's ultimate shear strength is the limit for failure. For the first case, the problem is to determine the material properties, i.e. the ultimate shear strength at elevated temperatures.

As has been found in the chapter "*Post bond and deformation*", the bonding of the features with the substrate takes place when the shrinkage is 10.91%. Xiaoping et al. [113] developed a method how to determine the in-situ strength of a powder compact during sintering:

Due to a reduced load bearing area, the nominal strength of a porous material can be approximated as $\sigma_0 V_s$, where σ_0 is the strength of a wrought material and V_s is

fractional density. Therefore, the strength of a sintered compact can be estimated as the product of the nominal strength and the ratio of total effective bond area to the projected particle area [114].

$$\sigma = \sigma_0 V_s \frac{N_c}{K\pi} \left(\frac{X}{D} \right)^2 \quad (25)$$

Where σ_0 is the strength of the wrought material, V_s is the fractional density, N_c is the average particle packing coordination number, K is the stress concentration factor associated with the interparticle neck, which reduces the apparent bond strength, and X/D is the neck size to particle diameter ratio, as discussed before. The stress concentration factor can be determined from a data base like e.g. Peterson's Stress Concentration Factors [115].

Figure 102: The schematic diagram showing the geometric profile of the neck, which is approximated as two circular cylinders, and in the lower drawing this approximation is overlaid on the two particle sintering geometry [113].

With the value of the neck size ratio, 0.35, which was determined by calculating the sintered density, 5.28g/cm³, at a shrinkage of 10.91%, the stress concentration factor was determined as being 0.459 from the graph in Figure 103.

Figure 103: Stress concentration factor.

The stress concentration factor decreases as the neck-size to particle diameter ratio increases, because the neck diameter increases and thus the shape impact is less severe.

The solid coordination number is linked to the density for monosized spherical particle compacts as follows:

$$N_c = 14 - 10.3(1 - V_s)^2 \quad (26)$$

The *in situ* strength in sintering can be approximated by adding a thermal softening factor f_T which represents the remaining strength fraction. The softening factor can be modeled [116], or as in this case obtained from readily available data.

According to our sintering diagram, the temperature at 10.91% shrinkage is 1267K. The thermal softening data according to the material properties data base [72], can be extracted from Figure 104.

Figure 104: Thermal softening of 17-4PH [72].

As the temperature increases, the tensile strength of stainless steel 17-4PH decreases considerably.

Since the data only cover the tensile strength up to a temperature of 813K, the data was extrapolated using the Arrhenius equation, which calculates the temperature effect on a reaction rate. The rate of change can be calculated from the activation energy, which was determined by Blaine to be 321kJ/mol [67], the universal gas constant and absolute temperature.

$$k = Ae^{-\frac{E}{RT}} \quad (27)$$

To test the Arrhenius equation, logs are taken on both sides of the equation, and if the law applies, a plot of $\ln(k)$ against $1/T$ will be a straight line.

Figure 105: Testing the applicability of the Arrhenius equation

If the Arrhenius equation applies, a plot of $\ln(k)$ against $1/T$ will be a straight line which is the case in this graph.

As can be seen in Figure 105, a plot of $\ln(k)$ against $1/T$ is a straight line, indicating that the Arrhenius equation applies to this case. The UTS at higher temperatures can thus be determined using the calculated rate of change k . Figure 106 shows how the UTS approaches 0MPa at about 940K.

Figure 106: Extrapolation of tensile strength over temperature.

Extrapolation of the UTS using the Arrhenius equation, leads to an UTS of about 0MPa at 940K.

The general form of in-situ strength during sintering is as follows:

$$\sigma_{in situ} = f_T \sigma_0 V_s \left(\frac{14 - 10.3(1 - V_s)^{0.38}}{K\pi} \right) \left(\frac{X}{D} \right)^2 \quad (28)$$

This model predicts both the *in situ* strength and room temperature strength of a sintered structure, depending on the test temperature T up to a temperature of 1000K in the case of 17-4PH. This can also be derived from Figure 106, where the strength approaches 0 at high temperatures. The neck size ratio X/D and solid fractional density V_s can be determined by the sintering cycle and be based on computer simulations.

The other limiting aspect of deformation during sintering is elongation. As has been shown, bending of the features is not a problem. At the same time, once the bond with the substrate is established, the features are stretched.

Figure 107 illustrates how the features are increasingly stretched, the farther away from the center of shrinkage they are. In this case, the shrinkage after bonding was 6.49%.

Figure 107: Elongation of features.

Elongation is the second load besides shear experienced by the micro features. The farther away from the center of shrinkage they are, the larger is the elongation.

Elongation is a function of temperature as can be seen in Figure 108. After a minimum at 593K, the elongation increases, but there are not values available for temperatures above 813K.

Figure 108: Elongation as a function of temperature of stainless steel 17-4PH [72].
The elongation as a function of temperature is u-shaped; after a minimum at 593K, it increases.

The farther away from the center, the more elongation a feature will experience, Figure 109. Typically, a material will undergo elongation under a tensile load, deform elastically, then plastically, and when reaching the ultimate tensile strength, it will fail. The problem in this case is to determine the maximum elongation and strength at the bonding temperature. Analyzing approximately 20 samples, in no case has an inclination below 40° been observed, which corresponds to 55.6% elongation. Also, no ruptured features have been observed. A possible explanation is that the sintering stress as an internal force maintains the geometry of the powder compact and is stronger than the initial bonds the features would create with the substrate. This would mean that a feature would eventually bond to the substrate, deform while following the sintering shrinkage of

the powder compact, until a certain deformation is reached and then brake lose. The deformation limit is independent of the ultimate or yield strength of the material.

Figure 109: Elongation of features as a function of distance

The farther away from the center a feature is located, the more elongation it experiences while following the shrinkage of the bulk of the powder compact.

The final bonding would then only take place during the last of these bonding-deformation-brake lose intervals towards the end of the sintering cycle, when the powder compact is finalizing the densification process.

To determine the exact mechanisms of this deformation would be part of subsequent research.

4.5.3. Sub-conclusion

In this section, the strength of the bonds has been evaluated and compared with the theoretical values. For this purpose, a shear test fixture has been designed and built. The sinter bonded samples were tested with the test fixture on an INSTRON tensile test machine and compared with reference samples, joined by welding, brazing and adhesive bonding. The sinter bonded samples achieved bond strengths of up to 80% of the strength of the welded sample.

This strength was confirmed by calculating the theoretically possible shear strength of the bulk material. It was shown that the features are only loaded in shear and not in bending

Knowing the powder compact's relative density and temperature, it is possible to calculate its in-situ strength. It was not possible to calculate the strength of the powder compact at the determined point of bonding due to the temperature of 1276K. No values for the ultimate strength nor elongation are available for that temperature range. This limited also the calculations of the deformation limits. It was expected that there was a limit to the deformation of the micro features, but on the samples no broken or failed micro features were found, which leads to the assumption that the initial bonds between the features and the substrate are broken when a certain deformation is reached, and thus the final bonds will only be established towards the end of the sintering cycle.

5. DISCUSSION AND CONCLUSION

5.1. Introduction

In this chapter, the information and data obtained and collected during this research will be referred to the relevant research questions. That information will then be summed up to reach the research objectives and answer the overall goal of this research, where limitations and validity will be discussed. This chapter will close with a discussion of the results and provide an outlook and further directions.

5.2. Research questions

1. How does the classical two-sphere sinter model apply to sinter bonding powder to a solid substrate?

The sintering process in sinter bonding a MIM powder compact to a solid substrate is basically the same as the sintering process in the bulk powder compact. The difference found in this case is geometrically given in that the micro features bond to a substrate. This solid substrate is assumed to have a large radius. This permits only a very few powder particles to come into contact with the substrate. On the other hand, these powder particles have multiple contacts with particles in the bulk of the material. Although the van der Waals forces, which create the initial contacts, are bigger in a sphere-plate combination, than in a sphere-sphere combination, the powder compact will

not bond to the substrate initially, because of the multiple contacts inside the bulk. The initial sintering takes place in the bulk of the material.

Once the initial bonds are established, either sphere-sphere or sphere-plate, the sintering process occurs according to current sintering models with neck growth and densification mechanisms through diffusion and viscous flow.

2. How and when during the sinter cycle is the bond between the powder compact and the substrate established?

A geometric model was developed that determined the point at which the micro features of a sample bonded to the substrate. Based on the micro feature deformation, and with the densification over the sintering cycle modeled, based on the Master Sintering Curve approach, it was determined that the features of the sample bonded after a shrinkage of 10.91%, after which the sample shrunk an additional 6.49% to its final density.

This point of bonding seems to depend on several factors:

- a) Contamination: in this study, the surfaces of the solid substrates have been cleaned before assembly, some irregularities have been observed. It is very possible that contamination or oxide layers can impede or delay the bonding of the micro features to the substrate.
- b) Material: it is expected, that different materials bond at different points during the sintering cycles. This would depend on their fundamental material properties, particularly thermal strength and diffusivity. Also, bonding different materials would certainly move the point of bonding.

c) Powder: the powder size could influence the bonding process, since smaller powders are sintering earlier. Also, the alloying process could be influential. Alloys in powder metallurgy can be processes as so called master alloys, where powders of the components are blended, or as prealloys, where the powder is made from a material that was alloyed in the liquid phase. In the first case it might be possible that alloying elements are first in contact with the substrate and show a different bonding behavior than the base material or final alloy would show.

3. How can the process of sinter bonding a powder compact to a solid substrate be modeled?

The sinter bonding process can be modeled with current sintering models.

The analysis of the samples and the literature review showed that for the sinter bonding process currently available models (e.g. [103, 113, 117]) can be applied. These models calculate neck growth, grain growth and strength evolution and their validity has been widely discussed in the literature. One important task that fed into this question was that of identifying elements of the model and their influences. It was found that part flatness was very important to assure good bonding. Measurements have shown that samples made by compression molding achieved much better flatness than injection molded parts when using RTV rubber mold inserts. As a consequence, samples of compression molded powder compacts were sinter bonded to

substrates. Figure 110 shows how the compression molded powder compact bonded to a substrate over a large area, the entire part is 35mm wide.

Figure 110: Compression molded MIM part (top) sinter bonded to solid substrate
The compression molded part bonded to the substrate over a large area.

Another important finding in this task was the influence of the particle size distribution. Even if the median particle size is much smaller than the micro feature diameter, there can still be a considerable amount of particles that are larger than the feature diameter. To effectively fill the features, the particle size must be clearly smaller than the feature diameter, otherwise there is the risk that the larger particles impede smaller particles entering the feature and thus create voids and/or irregular bonding surfaces.

4. How will the structure deform and what are the deformation limits?

From an analysis of SEM images and based on the ANSYS simulation it has been determined that the micro features are deforming in bending. They show the characteristic bending shape, but due to the relatively low aspect ratio the calculation of the load limit can be reduced to a pure shear load.

The problem in finding the deformation limits during the sintering process is the temperature at which the deformation occurs. It was found that the micro features bond at a temperature of 1276°C and the shrinkage continues to the maximum sintering temperature of 1360°C. For that temperature there is no data available for the tensile strength and elongation of the material. It would be supposed that the micro features bond to the substrate and are elongated following the sinter shrinkage of the powder compact. This would lead to a very large elongation of the features and eventually to distinctive necking and finally failure. On the analyzed samples, no such necking or failure was observed. Moreover, no feature deformation over 40° was observed, leading to the assumption, that the bonding process might take place in several intervals. The features could bond to the surface and these bond could be broken loose when a certain maximum deformation is reached. The powder compact continues to shrink and the features starts to bond again until the maximum deformation is reached. This process would then be repeated until the final density is reached and the features stay bonded to the substrate. The sintering stress is assumed to be the force maintaining the shape of the features.

To analyze this exact behavior, it would be necessary to do a series of sinter runs which could be stopped at certain points to evaluate the parts. This process would be very costly due to high equipment, energy and process gas cost.

5. How does the micro structure behave after the initial bond is established?

This question has basically been answered together with question 4. Once the initial bond is established, the micro feature will deform under a bending load as has been observed on the samples in the ANSYS simulation. The question raised above is, if there might be a sequence of bonding processes or bonding “intents”. The deformation could take place during the first or initial bonding and the deformed feature will maintain this shape until the final bonding process.

Another part of the structure behavior is the bond strength. That part will be discussed in question 6.

6. How can the pre-bonding and post-bonding phases be combined, modeled and simulated?

It has been shown that there are models, either currently available, or developed in this research, that comprise the pre and post bonding phases.

The key point to this question is to know the point of bonding. Current bonding and shrinkage models apply up to this point, once the feature has bonded to the substrate, the developed deformation model applies. The broader implication of this question is how to model or, even better; predict the strength of the bonds. Bond strengths of up to 80% of that of resistance welds have been achieved with the available micro feature design. The bond strength is a function of the apparent net bonded area. This area depends on the feature size, spacing and tip shape. The smaller the tip radius is, the

smaller the bonded area will be. Although a certain “rolling” motion which brings more material into contact with the substrate has been observed, the basic shape will have a larger influence.

Even though the micro features deform in bending while sintering and following the shrinkage of the powder compact, the load at failure is pure shear because of the low aspect ratio. This has also been confirmed by analyzing the failures through SEM images.

5.3. Research objectives

Objective 1: Sinter bonding

This objective has been achieved. The bonding and sintering processes have been analyzed and modeled where not available. The sintering mechanisms are the same as in currently available models, with the singularity of the sphere-plate interface. The point at which a feature of certain shape and size bonds to a substrate during a sintering cycle has been determined. Elements of the models and their influences have been established.

Objective 2: Deformation

The deformation which the micro features undergo after bonding to the substrate has been analyzed, modeled and simulated with the FE software ANSYS. To this end, a new approach for the FE simulation, which shows good agreement with the physical samples, has been developed. Evaluating the deformation limits of the features

during sintering and densification, it seems as if the “final” bonding location might be reached only after several bonding “intents”. Under the SEM there have no traces of these bonding intents been found, but the lack of necking and failure after extended elongation indicate that there might be previous bonding intents which fail before the powder compact reaches its final density. Although it would be interesting to analyze this phenomenon in detail, it has no effect on the final bond strength.

Objective 3: Model and evaluation

The model of sinter bonding of micro features to a solid substrate, the process is divided on two parts, the pre bonding and the post bonding part. The pre bonding part can be modeled with currently available models; the post bonding part has been show in this research.

The evaluation of samples showed shear strengths of up to 80% of that of resistant weld joints. A limitation of the absolute shear strength of the sinter bonded samples in this research was the lack of flatness of the injection molded powder compacts, due to the soft RTV rubber mold inserts. Compression molded compacts showed much better flatness and bonded over larger areas, which increases the absolute strength of the bonds.

5.4. Research goal

The overall goal of this research was to investigate, understand and model the proposed process of micro feature enhanced sinter bonding a MIM powder compact to a

solid substrate. This comprised three objectives: model the time temperature dependent process of bonding a powder to a solid substrate, model the deformation of the micro features once the bond between powder compact and substrate has been established and finally model and evaluate the overall sinter bonding process.

“Micro feature enhanced sinter bonding of MIM compacts to solid substrates” – this is a process to overcome the problems encountered in sinter bonding ‘traditional’ MIM compacts to solid substrates. The obstacle to sinter bonding was the sinter shrinkage of the powder compact and other differential movements as for example different thermal expansion and contraction between both components. Applying micro features to the surface of the powder compact can overcome these obstacles. This research has shown the effectiveness of this new process. High bonding strengths, compared with traditional joining processes, have been achieved, while avoiding cracks or deformation of the powder compact. The sintering and bonding mechanisms have been analyzed and modeled. A new approach to simulate the sinter shrinkage has been shown. Of course, there are some limitations to the findings in this research. First, the material; all samples were stainless steel 17-4PH. The applicability to other materials needs to be evaluated and is part of the future work. Also, the size of the samples needs to be taken into consideration. Industrial applications might require much larger bonding areas. To realize these large areas, differently shaped and sized features might be necessary. The features analyzed in this research were limited to mold inserts that were readily available.

5.5. Broader impacts

This research is the basis for future research, especially with regards to applications in industry. So far, no literature, research or applications on sinter bonding a MIM part to a solid substrate have been found. There are a variety of advantages to this process, as described in the section on the motivation of this research.

The possibility to combine different materials to one component and thus be able to specifically design the component's physical or chemical properties could make this process very attractive to many industries as for example electric/electronics, where magnetic-non magnetic or conductive-non conductive behavior could be easily combined into one component. Another application would be in the area of lightweight design, where high strength-low strength and/or high density-low density materials could be combined to reduce weight and increase component strength.

5.6. Outlook and further directions

Having finished this basic research on sinter bonding a metal injection molded part to a solid substrate, the door is open to a wide space for further research.

There are basically two areas that need to be pursued:

- a) Modeling and optimization: the ultimate goal would be to be able to design the optimum structure for a given application. In this research some important conditions of achieving strong bonds have been analyzed

and determined, as there is e.g. the feasible feature size as a function of the powder size distribution.

- b) Materials: in this research, only components of similar material, stainless steel 17-4PH have been sinter joined. Further research is necessary for joining others materials, and, ultimately, joining two or more different materials. How can different materials be combined and bonded? Do the same models apply to different materials? There is a great potential in joining different materials.

Another important step is to identify an application for this process and prove the concept in an industrial environment.

APPENDICES

MATLAB program to calculate van der Waals forces (vanderWaals.m):

```
clear;

% Calculation of van der Waals forces
%
%

R1=2.5;
R2=(1/2):(20/2);

for n=1:10;
    Fss1(1,n)=(2*(pi)*R1*R2(1,n))/(R1+R2(1,n));
end;

for o=1:10;
    Fss2(1,o)=(2*(pi)*R2(1,o)*R2(1,o))/(2*R2(1,o));
end;

for m=1:10;
    Fsp(1,m)=2*(pi)*R2(1,m);
end;

plot(R2,Fss1,R2,Fss2,R2,Fsp);
xlabel('R2 [mu]');
ylabel('Relative van der Waals force');
legend('Sphere-spere, R1=2.5','Sphere-sphere, R1=R2','Sphere-plate',...
    'Location','NorthWest');
```

MATLAB program to calculate the neck size between two spheres
during sintering (necksizecalculation_einfach.m):

```
clear;

% Program to calculate the neck size during the sintering of
% two spheres
%
%

D=1; % Original sphere diameter
Vg=4.21; % Green density
Vs=7.75; % Sintered (final) density
V0=pi()/3*D^3; % Original volume of two spheres
Sf=(Vg/Vs)^(1/3); % Final of 1 - shrinkage

% 1. Calculate neck size at end of sintering Xf (2 half spheres +
% cylinder) with final center distance Af=Sf*D.

syms R1;
S=2*R1^3-(3/2*Sf)*R1-1;
R1=solve(S,R1); % R1=D/X
R2=double(R1(1,1)); % convert symbolic R1 into number
Xf=D/R2; % final neck size

% Delta radius
dr=(D/2-Xf/2)/40;

% Delta Abstand

dA=(D-Sf*D)/40;

r=D/2;
L=D/2;

for n=1:40;
    D(1,n+1)=D(1,n)-dA;
    L(1,n)=D(1,n)/2;
    r(1,n+1)=r(1,n)-dr;
end;

for n1=1:40;
    % Volume Kugelkalotte
    a(1,n1)=sqrt(r(1,n1)^2-L(1,n1)^2);
    h(1,n1)=r(1,n1)-sqrt(r(1,n1)^2-a(1,n1)^2);
    Vks(1,n1)=(h(1,n1)^2*pi()/3)*(3*r(1,n1)-h(1,n1));

    % Volumen der beiden Kugeln minus Kalotten
    Vk(1,n1)=2*(pi()/6*(2*r(1,n1))^3-Vks(1,n1));
```

```

dx(1,n1)=a(1,n1)+0.1;
syms x;
V(1,n1)=int((2*pi()*x*(L(1,n1)-sqrt(r(1,n1)^2-
x^2))),a(1,n1),dx(1,n1));
Vr(1,n1)=double(V(1,n1));
%Gesamter Ring:
Vrg(1,n1)=2*Vr(1,n1);

while (Vrg(1,n1)<(V0-Vk(1,n1)));
dx(1,n1)=dx(1,n1)+0.1;
syms x;
V(1,n1)=int((2*pi()*x*(L(1,n1)-
sqrt(r(1,n1)^2-x^2))),a(1,n1),dx(1,n1));
Vr(1,n1)=double(V(1,n1));
%Gesamter Ring:
Vrg(1,n1)=2*Vr(1,n1);
X(1,n1)=2*dx(1,n1);
if X(1,n1)>Xf;
X(1,n1)=Xf;
end;
end;

end;

for n2=1:40;
Ds(1,n2)=D(1,n2)/D(1,1);
end;

plot(Ds(1:40),X(1:40));
xlabel('Relative center distance');
ylabel('Relative sphere diameter');

```

MATLAB program to determine the coefficients to fit the MSC curve
to the BASF shrinkage data (Determ_BASF_curve_coeff_1.m):

```
clear;
%
%Master Sintering Curve - Blaine Paper

% Constants:
Q=290000; %Original Blaine 350000
R=8.314472;
a=10.03; %Original Blaine 29.93
b=1.45; %Original Blaine 1.521
load Orig_BASF_data_ext.mat temp_K_1;
temp=temp_K_1;
load Orig_BASF_data_ext.mat time_sec_1;
time=time_sec_1;
load Orig_BASF_data_ext.mat shrink_pos_1;

rho0=4.21/7.74;

% Work of Sintering:

for n=1:20
Theta(1,n)=(exp(-Q/(R*temp(1,n)))*time(1,n))/temp(1,n);
end

% Relative Density

for m=1:20
rho(1,m)=rho0+(1-rho0)/(1+exp(-(log10(Theta(1,m))+a)/b));
end

% Absolut Density calculated
rhoabs=rho*7.74;

% Shrinkage calculated

shrink_calc_1=((rhoabs/4.21).^(1/3)-1)*100;

[AX,H1,H2]=plotyy(time,shrink_pos_1,time,temp_K_1);
set(AX,'FontSize',16);
ylim([0 20]);

set(get(AX(1),'Ylabel'),'String','Shrinkage [%]');
set(get(AX(2),'Ylabel'),'String','Temperature [K]');
```

MATLAB program to apply the MSC data

(MSC_application_onephase_1.m):

```
clear;

% Application of MSC to our sinter curve with constants from
% BASF curve
% fit
% Constants:
Q=290000; %determined in "Determ_BASF_curve_coeff_1.m"
R=8.314472;
a=10.03; %determined in "Determ_BASF_curve_coeff_1.m"
b=1.45; %determined in "Determ_BASF_curve_coeff_1.m"
load sintercurve_data_1.mat temp_K_1;
temp=temp_K_1;
load sintercurve_data_1.mat time_sec_1;
time=time_sec_1;
%load Orig_BASF_data_ext.mat shrink_pos_1;

rho0=4.21/7.74;

% Work of Sintering:

for n=1:20
Theta(1,n)=(exp(-Q/(R*temp(1,n)))*time(1,n))/temp(1,n);
end

% Relative Density

for m=1:20
rho(1,m)=rho0+(1-rho0)/(1+exp(-(log10(Theta(1,m))+a)/b));
end

% Absolut Density calculated
rhoabs=rho*7.74;

% Shrinkage calculated

shrink_calc_1=((rhoabs/4.21).^(1/3)-1)*100;

[AX,H1,H2]=plotyy(time,shrink_calc_1,time,temp_K_1);
set(AX,'FontSize',16);

set(get(AX(1),'Ylabel'),'String','Shrinkage [%]');
set(get(AX(2),'Ylabel'),'String','Temperature [K]');
xlabel('Time [sec]');
```


MATLAB program to calculate sintering stress (sintstress_1.m):

```
clear;

%   Sintering stress
%   Based on Kwon, et al paper...
%
%   Calculate density (from MSC_application_1.m)

%   Constants:
Q=290000;    %Original 350000, test 337000
R=8.314472;
a=10.03;     %Original 29.93, test 25.53
b=1.45;      %Original 1.521, test 4.721
load sintercurve_data_1.mat temp_K_1;
temp=temp_K_1;
load sintercurve_data_1.mat time_sec_1;
time=time_sec_1;
rho0=4.21/7.74;
D=0.000005;
Gamma=2;

%   Work of Sintering:

for n=1:20
Theta(1,n)=(exp(-Q/(R*temp(1,n)))*time(1,n))/temp(1,n);
end

%   Relative Density

for m=1:20
rho(1,m)=rho0+(1-rho0)/(1+exp(-(log10(Theta(1,m))+a)/b));
end

%   Sintering stress

for o=1:20
sigmasi(1,o)=((6*Gamma)/D)*(rho(1,o)^2)*((2*rho(1,o)-
rho0)/(1-rho0));
end;

for p=1:20
sigmasf(1,p)=(4*Gamma)/((D/2)*((1-
rho(1,p))/6*rho(1,p))^(1/3)));
end;

for q=1:20;
if (rho(1,q)<0.85);
sigmas(1,q)=sigmasi(1,q);
elseif (rho(1,q)>0.95);
sigmas(1,q)=sigmasf(1,q);
else
sigmas(1,q)=(0.95-rho(1,q))/(0.95-0.85)*sigmasi(1,q)+...
```

```

        (rho(1,q)-0.85)/(0.95-.85)*sigmasf(1,q);
    end;
end;

% Thermal softening

t=temp_K_1;

for r=1:20;
    if (t(1,r)>=293.0) && (t(1,r) <= 698.0);
        ft(1,r) = -1.222995e-005*t(1,r)^3+1.945933e-
002*t(1,r)^2-...
        1.050015e+001*t(1,r) +3.122457e+003;
    elseif (t(1,r) >= 698.0) && (t(1,r) <= 813.0);
        ft(1,r) = -5.217250e-005*t(1,r)^3 +...
        1.026377e-001*t(1,r)^2 -6.814111e+001*t(1,r)
+1.641424e+004;
    else
        ft(1,r) = 1;
    end;
end;

ftpa=ft*1000;

[AX,H1,H2]=plotyy(time,sigmas,time,temp_K_1);
set(AX,'FontSize',16);
hold on;

set(AX(1),'nextplot','add');

set(get(AX(1),'Ylabel'),'String','Sintering stress [Pa]');
set(get(AX(2),'Ylabel'),'String','Temperature [K]');
xlabel('Time [sec]');
hold off;

```

MATLAB program to calculate neck size between two spheres

(necksizecalculation_radius.m):

```
clear;
%
% Calculation of neck between two spheres
%
% Given values:
r1=2.5;
r2=0.01;
h=0.23*r1;

Vks=(1/3)*h^2*pi()*(3*r1-h);
x1=0:((2*r1-h)/20):(2*r1-h);

% Points circle 1 upper half

for n1=1:21
    y1(1,n1)=sqrt(r1^2-(x1(1,n1)-(r1-h))^2);
end

% circle 2 lower half

ym2=(sqrt((r1+r2)^2-(r1-h)^2));

% Touching point

alpha=acos(ym2/(r1+r2));
tx=sin(alpha)*r2;

% Neck volume

syms x;
V1=int(((pi()*(ym2-sqrt(r2^2-(x-r2)^2))^2)-(pi()*(sqrt(r1^2-(x-(r1-h))^2)^2))),0,tx);
Vn1=double(V1);

while (Vn1<Vks);
    r2=r2+0.01;
    ym2=(sqrt((r1+r2)^2-(r1-h)^2));
    alpha=acos(ym2/(r1+r2));
    tx=sin(alpha)*r2;
    syms x;
    V1=int(((pi()*(ym2-sqrt(r2^2-(x)^2))^2)-(pi()*(sqrt(r1^2-(x-(r1-h))^2)^2))),0,tx);
    Vn1=double(V1);
end;

% Circle 2 lower half
```

```

x2=0:(r2/20):(r2);

for n2=1:21;
    y2(1,n2)=ym2-sqrt(r2^2-(x2(1,n2))^2);
end

nd=2*(ym2-r2); % Neck diameter
xd=nd/(2*r1); % Neck size ratio

% Plot

plot(x1,y1,x2,y2);
axis([0 (2*r1) 0 (2*r1)]);
text(r2,ym2,['neck diam.',num2str(nd), ' X/D=',num2str(xd)]);
xlabel('D1');
ylabel('Center distance');
title('Neck size sphere-sphere');

```

MATLAB program to calculate neck size between two spheres

(test_sphere_flat_neu.m):

```
clear;

% Gegeben:
r1=2.5;
r2=0.01;
h=0.46*r1;

Vks=(1/3)*h^2*pi()*(3*r1-h);
x1=0:((2*r1-h)/20):(2*r1-h);

% Punkte Kreis 1 obere Haelfte

for n1=1:21
    y1(1,n1)=sqrt(r1^2-(x1(1,n1)-(r1-h))^2);
end

% Kreis 2 untere Haelfte

b=r1-h-r2;
ym2=(sqrt((r1+r2)^2-b^2));

% Beruehrungspunkt

alpha=acos(ym2/(r1+r2));
tx=r2+sin(alpha)*r2;

% Neck volume

syms x;
V1=int(((pi()*(ym2-sqrt(r2^2-(x-r2)^2))^2)-(pi()*(sqrt(r1^2-(x-(r1-h))^2)^2))),0,tx);
Vn1=double(V1);

while (Vn1<Vks);
    r2=r2+0.01;
    b=r1-h-r2;
    ym2=(sqrt((r1+r2)^2-b^2));
    alpha=acos(ym2/(r1+r2));
    tx=r2+sin(alpha)*r2;
    syms x;
    V1=int(((pi()*(ym2-sqrt(r2^2-(x-r2)^2))^2)-(pi()*(sqrt(r1^2-(x-(r1-h))^2)^2))),0,tx);
    Vn1=double(V1);
end;

% Punkte Kreis 2 untere Haelfte

x2=0:(2*r2/20):(2*r2);
```

```

for n2=1:21;
    y2(1,n2)=ym2-sqrt(r2^2-(x2(1,n2)-r2)^2);
end

nd=2*(ym2-r2); % Neck diameter
xd=nd/(2*r1); % Neck size ratio

% Plot

plot(x1,y1,x2,y2);
axis([0 (2*r1) 0 (2*r1)]);
text(r2,ym2,['neck diam.',num2str(nd), '      X/D=',num2str(xd)]);
xlabel('D1');
ylabel('Center distance');
title('Neck size sphere-flat');

```

REFERENCES

1. German, R.M., *Injection Molding of Metals and Ceramics*. 1997, Princeton, NJ: Metal Powder Industries Federation. p. 67.
2. German, R.M., *Injection Molding of Metals and Ceramics*. 1997, Princeton, NJ: Metal Powder Industries Federation. p. 294.
3. German, R.M., *Sintering Theory and Practice*. 1 ed. 1996, New York, NY: John Wiley & Sons, Inc.
4. Askeland, D.R. and P.P. Phulé, *The science and engineering of materials*. 5 ed. 2006: Thomson.
5. IFAM, F., *The MIM process*. 2010: Bremen, Germany.
6. AZoM. *Metal Injection Molding*. 2001 [cited 2010; Available from: <http://www.azom.com/Details.asp?ArticleID=742>.
7. Bhatkal, R. and T. Hannibal, *The technical cost modeling of near-net-shape P/M manufacturing*. JOM Journal of the Minerals, Metals and Materials Society, 1999. **51**(7): p. 26-27.
8. MPIF. *PICK PM*. 2010 [cited 2010; Available from: http://www.pickpm.com/designcenter/MIM_overview.asp?locarr=2|1|2|3.
9. Bulger, M., *North American MIM Status*, in *2011 International Conference on Injection Molding of Metals, Ceramics and Carbides*. 2011, Metal Powder Industries Federation (MPIF): Orlando, FL, USA.
10. Blömacher, M., *State of the European MIM industry*, in *2011 International Conference on Injection Molding of Metals, Ceramics and Carbides*. 2011, Metal Powder Industries Federation (MPIF): Orlando, FL, USA.
11. Dr. Georg Schlieper, D.G.D., Bernard Williams, Dr. Frank Petzoldt, *Metal Injection Moulding*. 2009, European Powder Metallurgy Association (EPMA): Shrewsbury. p. 13.
12. Li, Y., et al., *Critical thickness in binder removal process for injection molded compacts*. Materials Science and Engineering A, 2003. **362**(1-2): p. 292-299.
13. Heaney, D.F. and R. Spina, *Shrinkage prediction of MIM parts by finite element simulation*. International Journal of Computational Materials Science and Surface Engineering, 2007. **1**(1): p. 57-72.

14. Olevsky, E.A. and R.M. German, *Effect of gravity on dimensional change during sintering--I. Shrinkage anisotropy*. Acta Materialia, 2000. **48**(5): p. 1153-1166.
15. Olevsky, E.A., R.M. German, and A. Upadhyaya, *Effect of gravity on dimensional change during sintering--II. Shape distortion*. Acta Materialia, 2000. **48**(5): p. 1167-1180.
16. Kinetics, *MIM Design Guide*. 2004, Kinetics Inc.: Wilsonville, Or.
17. Tabata, T. and S. Masaki. *How to produce P/M composite parts from metal powder and solid metal by sinter bonding*. 1985. Toronto, Ont, Can: Metal Powder Industries Federation.
18. J. P. Parmigiani, J.C.K., *Joining of P/M components*, in *SAE International Congress and Exposition*. 1999, SAE International, Warrendale, Pennsylvania, USA: Detroit, Michigan, USA.
19. Mohan, A., N.C. Soni, and V.K. Moorthy, '*Definition of the term sintering*'. Science of Sintering, 1983. **15**(3): p. 139-40.
20. Frenkel, Y.I., *Viscous flow of crystalline bodies under the action of surface tension*. Science of Sintering, 1980. **12**(1): p. 7-18.
21. Ristic, M.M., *Frenkel's theory of sintering*. Science of Sintering, 1996. **28**(Special Issu): p. 1-1.
22. Mackenzie, J.K. and R. Shuttleworth, *Phenomenological theory of sintering*. Physical Society -- Proceedings, 1949. **62**(360B): p. 833-852.
23. Kuczynski, G.C., *Mechanism of densification during sintering of metallic particles*. Acta Metallurgica, 1956. **4**(1): p. 58-61.
24. Ashby, M.F., *A first report on sintering diagrams*. Acta Metallurgica, 1974. **22**(3): p. 275-289.
25. German, R.M., *Injection Molding of Metals and Ceramics*. 1997, Princeton, NJ: Metal Powder Industries Federation. p. 226.
26. Kang, S.-J.L., *Sintering: densification, grain growth, and microstructure* 2005, Oxford: Elsevier Butterworth-Heinemann.
27. Danninger, H. and C. Gierl, *Processes in PM steel compacts during the initial stages of sintering*. Materials Chemistry and Physics, 2001. **67**(1-3): p. 49-55.
28. Riedel, H., V. Kozák, and J. Svoboda, *Densification and creep in the final stage of sintering*. Acta Metallurgica et Materialia, 1994. **42**(9): p. 3093-3103.

29. Riedel, H., H. Zipse, and J. Svoboda, *Equilibrium pore surfaces, sintering stresses and constitutive equations for the intermediate and late stages of sintering - II. Diffusional densification and creep*. Acta metallurgica et materialia, 1994. **42**(2): p. 445-452.
30. Schatt, W., *Sintervorgänge*. 1992, Düsseldorf: VDI-Verlag GmbH. p. 77 ff.
31. Schatt, W., *Werkstoffwissenschaft*. 8 ed. 1996, Stuttgart: Deutscher Verlag für Grundstoffindustrie. 286.
32. Olevsky, E.A., *Theory of sintering: from discrete to continuum*. Materials Science & Engineering R: Reports, 1998. **23**(2): p. 41-99.
33. Tabata, T., et al., *Fabrication of composite parts by sinter bonding*. International Journal of Powder Metallurgy (Princeton, New Jersey), 1991. **27**(3): p. 265-273.
34. Genkichi Umeha, S.U., Saturo Kato, *Method for Manufacturing Camshaft*, U.S.P. Office, Editor. 1985, Nippon Piston Ring Co., Ltd., Tokyo, Japan: USA. p. 5.
35. Asaka, K. *Diffusion Bonding methods of Green Compacts with Wrought Steel Parts During Sintering*. in *2000 Advances in Powder Metallurgy & Particulate Materials*. 2000. New York, N.Y.
36. German, R.M., *Sintering Theory and Practice*. 1 ed. 1996, New York, NY: John Wiley & Sons, Inc. p. 453.
37. Miura, H., et al., *Joining for more functional and complicated parts in MIM process*. Funtai Oyobi Fummatsu Yakin/Journal of the Japan Society of Powder and Powder Metallurgy, 1997. **44**(5): p. 437-442.
38. Miura, H., T. Yano, and M. Matsuda, *MIM In-process joining of thin and hollow parts*. Funtai Oyobi Fummatsu Yakin/Journal of the Japan Society of Powder and Powder Metallurgy, 2001. **48**(11): p. 1097-1101.
39. Baumgartner, R. and L.K. Tan, *MIM 'marries' metals*. Metal Powder Report, 2002. **57**(3): p. 38-42.
40. Tan, L.-K., R. Baumgartner, and R.M. German. *Powder Injection Molding of Bi-Metal Components*. 2001. New Orleans, LA, United states: Metal Powder Industries Federation.
41. Harikou, T., et al., *Joining of stainless steels (SUS316L) and hard materials by insert injection molding*. Funtai Oyobi Fummatsu Yakin/Journal of the Japan Society of Powder and Powder Metallurgy, 2004. **51**(1): p. 31-36.
42. Zhang, S.X., et al., *Sinter bonding sticks MIM ahead again*. Metal Powder Report, 2003. **58**(12): p. 20-23.

43. Potente, H. and L. Wilke, *Joining injection moulded sintered parts in the green compact phase, Fuegen spritzgegossener Sinterteile in der Gruenlingsphase*. Kunststoffe Plast Europe, 2004. **94**(11): p. 58-61.
44. Imgrund, P., et al., *Manufacturing of multi-functional micro parts by two-component metal injection moulding*. The International Journal of Advanced Manufacturing Technology, 2007. **33**(1): p. 176-186.
45. Imgrund, P., A. Rota, and M. Wiegmann, *Getting better bonding at tiny interfaces*. Metal Powder Report, 2007. **62**(3): p. 31-34.
46. Ruh, A., et al., *Production of two-material micro-assemblies by two-component powder injection molding and sinter-joining*. Microsystem Technologies, 2008. **14**(12): p. 1805-1811.
47. Heaney, D.F., P. Suri, and R.M. German, *Defect-free sintering of two material powder injection molded components Part I experimental investigations*. Journal of Materials Science, 2003. **38**(24): p. 4869-74.
48. Suri, P., D.F. Heaney, and R.M. German, *Defect-free sintering of two material powder injection molded components Part II model*. Journal of Materials Science, 2003. **38**(24): p. 4875-81.
49. German, R.M., *Computer modeling of sintering processes*. International Journal of Powder Metallurgy (Princeton, New Jersey), 2002. **38**(2): p. 48-66.
50. Heaney, D.F. and R. Spina, *Numerical analysis of debinding and sintering of MIM parts*. Journal of Materials Processing Technology, 2007. **191**(1-3): p. 385-389.
51. Zavaliangos, A., J.M. Missiaen, and D. Bouvard, *Anisotropy in shrinkage during sintering*. Science of Sintering, 2006. **38**(1): p. 13-25.
52. Reiterer, M.W. and K.G. Ewsuk, *An Analysis of Four Different Approaches to Predict and Control Sintering*. Journal of the American Ceramic Society, 2009. **92**(7): p. 1419-1427.
53. Reiterer, M.W., K.G. Ewsuk, and J.G. Arguello, *An Arrhenius-type viscosity function to model sintering using the Skorohod-Olevsky viscous sintering model within a finite-element code*. Journal of the American Ceramic Society, 2006. **89**(6): p. 1930-5.
54. Bordère, S., *Original Monte Carlo Methodology Devoted to the Study of Sintering Processes*. Journal of the American Ceramic Society, 2002. **85**(7): p. 1845-1852.

55. Bordere, S. and D. Bernard, *Full resolution of the Monte Carlo time scale demonstrated through the modelling of two-amorphous-particles sintering*. Computational Materials Science, 2008. **43**(4): p. 1074-80.
56. Bordère, S., et al., *Monte Carlo Prediction of Non-Newtonian Viscous Sintering: Experimental Validation for the Two-Glass-Cylinder System*. Journal of the American Ceramic Society, 2005. **88**(8): p. 2071-2078.
57. Tikare, V., M. Braginsky, and E.A. Olevsky, *Numerical simulation of solid-state sintering. I. Sintering of three particles*. Journal of the American Ceramic Society, 2003. **86**(1): p. 49-53.
58. Braginsky, M., V. Tikare, and E. Olevsky. *Numerical simulation of solid state sintering*. 2005: Elsevier Ltd.
59. Hunghai, S. and D.L. Johnson, *Master sintering curve: a practical approach to sintering*. Journal of the American Ceramic Society, 1996. **79**(12): p. 3211-17.
60. Rahaman, M.N., L.C. De Jonghe, and M.-Y. Chu, *Effect of green density on densification and creep during sintering*. Journal of the American Ceramic Society, 1991. **74**(3): p. 514-519.
61. Yeh, T.-s. and M.D. Sacks, *Effect of particle size distribution on the sintering of alumina*. Journal of the American Ceramic Society, 1988. **71**(12): p. 484-487.
62. Blaine, D.C., et al., *Application of work-of-sintering concepts in powder metals*. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 2006. **37**(9): p. 2827-2835.
63. Kiani, S., J. Pan, and J.A. Yeomans, *A New Scheme of Finding the Master Sintering Curve*. Journal of the American Ceramic Society, 2006. **89**(11): p. 3393-3396.
64. Kiani, S., et al., *Finite element analysis of sintering deformation using densification data instead of a constitutive law*. Journal of the European Ceramic Society, 2007. **27**(6): p. 2377-2383.
65. Park, S.J., et al. *Master sintering curve formulated from constitutive models*. 2009. 350 Main Street, Malden, MA 02148, United States: Blackwell Publishing Inc.
66. Blaine, D.C., S.-J. Park, and R.M. German. *Linearization of master sintering curve*. 2009. 350 Main Street, Malden, MA 02148, United States: Blackwell Publishing Inc.

67. Blaine, D.C., Garg, P. & German, R. *Master Sintering Curve for a Two-Phase Material*. in *4th International Conference on Science Technology and Applications of Sintering*. 2005.
68. Yunxin, W., et al., *Sintering densification and microstructural evolution of injection molding grade 17-4 PH stainless steel powder*. Metallurgical and Materials Transactions A (Physical Metallurgy and Materials Science), 2002. **33A**(7): p. 2185-94.
69. Bordia, R.K. and G.W. Scherer, *On constrained sintering. I. Constitutive model for a sintering body*. Acta Metallurgica, 1988. **36**(9): p. 2393-7.
70. Bordia, R.K. and G.W. Scherer, *On constrained sintering. II. Comparison of constitutive models*. Acta Metallurgica, 1988. **36**(9): p. 2399-409.
71. Bordia, R.K. and G.W. Scherer, *On constrained sintering. III. Rigid inclusions*. Acta Metallurgica, 1988. **36**(9): p. 2411-6.
72. JAHM Software, I., *MPDB*. 2011: North Reading, Ma. p. Materials properties database.
73. Green, D.J., O. Guillon, and J. Rodel, *Constrained sintering: A delicate balance of scales*. Journal of the European Ceramic Society, 2008. **28**(7): p. 1451-1466.
74. Satyajit Banerjee, P.D., T. Martens, Editor. 2011: Cedar Grove.
75. German, R.M., *Injection Molding of Metals and Ceramics*. 1997, Princeton, NJ: Metal Powder Industries Federation. p. 200.
76. German, R.M., *Sintering Theory and Practice*. 1 ed. 1996, New York, NY: John Wiley & Sons, Inc. p. 190.
77. Jonsson, M.T.a.S. *A Material Model for Simulating Volume Changes during Phase Transformations*. in *COMSOL Users Conference*. 2007. Grenoble, France: COMSOL.
78. Porter, D.A. and K.E. Easterling, *Phase transformations in metals and alloys*. 1992: Nelson Thornes.
79. Liu, X.-q., et al., *Deformation behavior and strength evolution of MIM compacts during thermal debinding*. Transactions of Nonferrous Metals Society of China, 2008. **18**(2): p. 278-284.
80. BASF, *Data Sheet Catamold 17-4PH*. 2006, BASF Aktiengesellschaft: Ludwigshafen, Germany.

81. Cannon, A.H. and W.P. King, *Microstructured metal molds fabricated via investment casting*. Journal of Micromechanics and Microengineering. **20**(2): p. 025025 (7 pp.).
82. Rowland, H.D., et al., *Simulations of nonuniform embossing: The effect of asymmetric neighbor cavities on polymer flow during nanoimprint lithography*. Journal of Vacuum Science and Technology B: Microelectronics and Nanometer Structures, 2005. **23**(6): p. 2958-2962.
83. ASME, *Y14.5 - 2009*, D.a. Tolerancing, Editor. 2009, ASME.
84. J.C. Gelin, T.B., M. Sahli, *Experimental Charakterization and Manufacturing of Micro-Structured Die Mold Replications using Hot Embossing Process*, in *2011 International Conference on Injection Molding of Metals, Ceramics and Carbides*. 2011, Metal Powder Industries Federation (MPIF): Orlando, FL, USA.
85. Liou, A.C. and R.H. Chen, *Injection molding of polymer micro- and sub-micron structures with high-aspect ratios*. International Journal of Advanced Manufacturing Technology, 2006. **28**(11-12): p. 1097-1103.
86. Liu, Z.Y., et al., *Sintering activation energy of powder injection molded 316L stainless steel*. Scripta Materialia, 2001. **44**(7): p. 1131-7.
87. Piottter, V., et al., *Performance and simulation of thermoplastic micro injection molding*. Microsystem Technologies, 2002. **8**(6): p. 387-90.
88. Zhang, K.F. and Z. Lu. *Surface features of polymer and ceramic microstructured parts manufactured by micro injection molding*. 2008. Nice, France: Inst. of Elec. and Elec. Eng. Computer Society.
89. Bose, A., et al., *Faster sintering and lower costs with ultra-fine MIM powders [metal injection moulding powder]*. Metal Powder Report, 2008. **63**(5): p. 25-30.
90. Ye, H., X.Y. Liu, and H. Hong, *Sintering of 17-4PH stainless steel feedstock for metal injection molding*. Materials Letters, 2008. **62**(19): p. 3334-3336.
91. Sung, H.-J., et al., *Powder injection molding of a 17-4 PH stainless steel and the effect of sintering temperature on its microstructure and mechanical properties*. Journal of Materials Processing Technology, 2002. **130-131**: p. 321-327.
92. Masuda, H., K. Higashitani, and H. Yoshida, *Powder technology handbook*. 3 ed. 2006: Taylor & Francis.
93. German, R.M., *Sintering densification for powder mixtures of varying distribution widths*. Acta Metallurgica et Materialia, 1992. **40**(9): p. 2085-2089.

94. Patterson, B.R. and L.A. Benson. *Effect of powder size distribution on sintering*. 1984. New Orleans, LA, USA: Metal Powder Industries Federation.
95. German, R.M., *Sintering Theory and Practice*. 1 ed. 1996, New York, NY: John Wiley & Sons, Inc. p. 147.
96. Pan, J., et al., *A model for the sintering of spherical particles of different sizes by solid state diffusion*. *Acta Materialia*, 1998. **46**(13): p. 4671-4690.
97. German, R.M., *Injection Molding of Metals and Ceramics*. 1997, Princeton, NJ: Metal Powder Industries Federation. p. 77.
98. German, R.M., *Sintering Theory and Practice*. 1 ed. 1996, New York, NY: John Wiley & Sons, Inc. p. 96.
99. German, R.M., *Sintering Theory and Practice*. 1 ed. 1996, New York, NY: John Wiley & Sons, Inc. p. 97.
100. Parsegian, V.A., *Van der Waals forces*. 1 ed. 2006, New York: Cambridge University Press.
101. Richerson, D.W., *Modern ceramic engineering: properties, processing, and use in design*. 2006: CRC Taylor & Francis.
102. German, R.M. and S.J. Park, *Mathematical relations in particulate materials processing: ceramics, powder metals, cermets, carbides, hard materials, and minerals*. 2008: Wiley.
103. Xiaoping, X., Y. Wuwen, and R.M. German, *Densification and strength evolution in solid-state sintering. I. Experimental investigation*. *Journal of Materials Science*, 2002. **37**(3): p. 567-75.
104. German, R.M., *Injection Molding of Metals and Ceramics*. 1997, Princeton, NJ: Metal Powder Industries Federation. p. 225.
105. Rasband, W., *ImageJ 1.42q*. 2011, National Institutes of Health: Bethesda, Md.
106. Guillon, O. and J. Langer, *Master sintering curve applied to the Field-Assisted Sintering Technique*. *Journal of Materials Science*, 2010. **45**(19): p. 5191-5195.
107. Blaine, D.C., et al., *Master sintering curve concepts as applied to the sintering of molybdenum*. *Metallurgical and Materials Transactions A (Physical Metallurgy and Materials Science)*, 2006. **37A**(3): p. 715-20.

108. Young-Sam, K., et al., *Simulation of the sintering densification and shrinkage behavior of powder-injection-molded 17-4 PH stainless steel*. Metallurgical and Materials Transactions A (Physical Metallurgy and Materials Science), 2004. **35A**(1): p. 257-63.
109. Ryder, P., *Classical Mechanics*. 2007: Shaker.
110. Comrey, A.L. and H.B. Lee, *Elementary Statistics: A Problem Solving Approach 4th Edition*. 2009: Lulu.com. 111.
111. Deutschman, A.D., W.J. Michels, and C.E. Wilson, *Machine design; theory and practice*. 1975: Macmillan.
112. Grote, K.-H. and J. Feldhusen, *Dubbel-Taschenbuch für den Maschinenbau*. 22 ed. 2007, Berlin, Heidelberg, New York: Springer - Verlag 143.
113. Xiaoping, X., L. Peizen, and R.M. German, *Densification and strength evolution in solid-state sintering. II. Strength model*. Journal of Materials Science, 2002. **37**(1): p. 117-26.
114. German, R.M., *Manipulation of strength during sintering as a basis for obtaining rapid densification without distortion*. Materials Transactions, 2001. **42**(7): p. 1400-10.
115. Pilkey, W.D., *Peterson's Stress Concentration Factors (2nd Edition)*. 1997, John Wiley & Sons. p. 99.
116. Shoales, G.A. and R.M. German, *In situ strength evolution during the sintering of bronze powders*. Metallurgical and Materials Transactions A (Physical Metallurgy and Materials Science), 1998. **29A**(4): p. 1257-63.
117. Wakai, F., *Modeling and Simulation of Elementary Processes in Ideal Sintering*. Journal of the American Ceramic Society, 2006. **89**(5): p. 1471-1484.