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**NANYANG
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UNIVERSITY**

TITLE OF RESEARCH

**SINTERING STUDY AND CONSTITUTIVE MODELING
OF 316L STAINLESS STEEL MICROSTRUCTURED
PARTS FABRICATED BY PIM**

NAME
(if insufficient space, use abbreviations
eg. KANG K.)

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**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

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SINTERING STUDY AND CONSTITUTIVE MODELING OF 316L STAINLESS STEEL MICROSTRUCTURED PARTS FABRICATED BY μ PIM

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Abstract

Powder injection molding (PIM) of parts having structures in the sub-millimeter range, also known as micro powder injection molding (μ PIM), is a technology of potential for mass production of these parts due to the unique combination of properties obtainable from PIM. μ PIM comprises four processing steps: mixing, injection molding, debinding and sintering. Considering the dimensional regime of the microsize structures, control of sintering is important for microstructured parts in μ PIM. Hence, the effects of size of microstructured parts on the grain growth and densification are studied in this research. In addition, a constitutive model is developed to depict the densification of microstructured parts.

A circular disc of $\phi 16$ mm and 1.5 mm thick (sub-structure), with an array of 24×24 microsize structures with three different sizes, $\phi 100 \mu\text{m} \times \text{height } 200 \mu\text{m}$, $\phi 80 \mu\text{m} \times \text{height } 196 \mu\text{m}$ or $\phi 60 \mu\text{m} \times \text{height } 191 \mu\text{m}$, were molded using the in-house feedstock for the study. To investigate the effects of size of microstructured parts on the grain growth and densification, the debound microstructured parts were sintered at various time and temperatures after which the grain size and density of the sub-structure and three different microsize structures were characterized. It shows that the size reduction into micrometer regime increased densification. All the microsize structures were at the final sintering stage while the sub-structure was at the intermediate sintering stage within the temperatures studied. As compared to the microsize structures of $\phi 100 \mu\text{m}$

and $\phi 80 \mu\text{m}$, the microsize structures of $\phi 60 \mu\text{m}$ yielded the highest density within the temperatures studied. Analysis based on Brook, Coble and Herring's models shows that the controlling mechanism for grain growth and densification varied for the sub-structure and various microsize structures, the result of which is useful for modeling sintering behavior of the microstructured parts.

Since the grain number varies with sintering at the final sintering stage due to grain growth, a new sintering stress expression taking into account the variation in grain number was developed. A constitutive model was established to compute densification of the sub-structure and various microsize structures on the microstructured parts. In the model, Besson and Abouaf's constitutive equation and Brook's model for grain growth were used. The contribution of lattice diffusion, which was not included in Besson and Abouaf's work, was considered here. The effects of pore location and boundary energy on the densification of the various microsize structures were discussed during modeling. The theoretical calculations using the model were compared with the experimental results of the sub-structure and various microsize structures. As the computed densities based on the simplified assumption that all the pores were located at four-grain junctions were similar to that computed where pores on two-grain interface and separated pores were included, the treatment of all pores located at four-grain junctions can be used in the model. Including the work done by grain boundary energy gave higher densities for all the microsize structures which were generally closer to the experimental results. The model approximately agreed with the experimental results.

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Nomenclature

A	represents a constant
A_b	grain boundary area (m ²)
A_c	total pore surface area per polyhedron for the intermediate sintering stage (m ²)
A_s	total pore surface area per polyhedron for the final sintering stage (m ²)
B	represents a constant
c	a function of ρ
C_1	a material constant for strain rate (s ⁻¹ N ⁻¹ m ⁴ K)
C_2	a material constant for strain rate (s ⁻¹ N ⁻¹ m ⁵ K)
C_3	a material constant for strain rate (s ⁻¹ N ⁻¹ m ⁴ K)
D	particle diameter (m)
D_0	a temperature independent preexponential
D_B	boundary diffusion coefficient (m ² s ⁻¹)
D_L	lattice diffusion coefficient (m ² s ⁻¹)
$e = \cos \theta$	
$E = \frac{4}{3} \left(\frac{3}{2} - 2e^2 \right)^{1/2} - \frac{2}{3}e$	
f	a function of ρ
f_p	a fraction of pores on boundaries
G	grain size (m)
$\overline{G}$	grain size at the beginning of the final stage (m)
G_o	initial grain size (m)
H	an item representing $\frac{P_{cl}(1-\rho_{cl})}{T_{cl}\rho_{cl}}$ (Nm ⁻² K ⁻¹)
k	Boltzmann's constant (1.38 x 10 ⁻²³ JK ⁻¹)
k'	a proportionality factor (m)

Nomenclature

K'	a constant related to the temperature and grain growth mechanism
K''	a constant related to the temperature and densification mechanism
K_1	a material constant for grain growth under surface diffusion controlled pore drag (m^4Ks^{-1})
K_2	a material constant for grain growth under lattice diffusion controlled pore drag (m^3Ks^{-1})
K_3	a material constant for boundary diffusion controlled grain growth (m^2Ks^{-1})
l'	mean lineal intercept length during grain size measurement (m)
l_p	edge length of the tetrakaidecahedron (m)
m	an exponent related to the mechanism of densification
n	an exponent related to the mechanism of grain growth
N_g	number of grains per 1g of porous component
P_{cl}	gas pressure at the time of pore closure (Nm^{-2})
P_{eff}	effective pressure (Nm^{-2})
P_i	instantaneous internal gas pressure (Nm^{-2})
P_s	porosity
Q	activation energy
Q_B	activation energy of boundary diffusion (kJmol^{-1})
Q_L	activation energy of lattice diffusion (kJmol^{-1})
Q_S	activation energy of surface diffusion and (kJmol^{-1})
r	radius of curvature of a pore (m)
R	gas constant ($8.31 \text{ Jmol}^{-1}\text{K}^{-1}$)
r_c	radius of curvature of a cylindrical pore (m)
r_s	radius of curvature of a spherical pore (m)
S_G	surface area of a grain (m^2)
S_s	grain boundary area reduction due to the pores per polyhedron (m^2)
t	time (s)
T	absolute temperature (K)
T_{cl}	temperature at the time of pore closure (K)

Nomenclature

V	volume (m^3)
$\dot{V}$	volume change rate (m^3s^{-1})
V_c	total pore volume per polyhedron for intermediate sintering stage (m^3)
V_{cl}	pore volume at the time of pore closure for the porous component (m^3)
V_G	volume of a grain (m^3)
V_i	instantaneous pore volume for the porous component (m^3)
V_m	volume of a grain bulk (m^3)
V_s	total pore volume per polyhedron for final sintering stage (m^3)
W	effective shear viscosity of porous powder component
Y	effective bulk viscosity of porous powder component
z	a constant in the correction factor (m)
α, β, λ	coefficients depending on the dihedral angle of the pores
γ_b	grain boundary energy (Jm^{-2})
γ_s	surface energy (Jm^{-2})
Γ	related to driving force, mean diffusion distance and other geometric features of the microstructure during sintering
Γ_B	related to driving force, mean diffusion distance and other geometric features of the microstructure for grain boundary diffusion
Γ_L	related to driving force, mean diffusion distance and other geometric features of the microstructure for lattice diffusion
δ	diffusion thickness of grain-boundary diffusion (m)
$\delta' = \arccos \frac{\sqrt{2} - e(3 - E^2)^{1/2}}{E(1 - e^2)^{1/2}}$	
δ_{ij}	Kronecker symbol (when $i=j$, $\delta_{ij} = 1$ and when $i \neq j$, $\delta_{ij} = 0$)
$\dot{\epsilon}_{eff}$	effective strain rate for a porous powder component (s^{-1})
$\dot{\epsilon}_{ij}$	strain rate (s^{-1})
$\dot{\epsilon}_v$	volumetric strain rate (s^{-1})

Nomenclature

θ	dihedral angle
ρ	relative density
$\dot{\rho}$	densification rate (s^{-1})
ρ_o	initial relative density
ρ_T	theoretical density (kgm^{-3})
σ'_{ij}	deviatoric stress (Nm^{-2})
σ_m	hydrostatic stress (Nm^{-2})
σ_s	sintering stress (Nm^{-2})
τ_{eff}	effective pseudo-stress for a porous powder component (Nm^{-2})
$\phi = \arcsin \frac{E}{2(1-e^2)^{1/2}}$	
Ω	volume occupied by a vacancy (m^3)

Chapter 1 Introduction

1.1 Background

Powder injection molding (PIM) is a cost-effective, near net-shape forming process for the mass production of small, complex and precise parts. It combines the design flexibility of plastic injection molding and material variety of powder metallurgy. Due to the unique combination of properties obtainable from PIM, micro powder injection molding (μ PIM), which is adapted from PIM, is a process for mass production of microcomponents where miniaturization gives better results in terms of performance or cost [1-4]. In general, microcomponents can be categorized as microparts, microstructured parts and microprecision parts [5]. Microparts represent single or separate parts of outer dimensions of a few millimeters, which mostly have details in the sub-millimeter range. Microstructured parts are parts with outer dimensions ranging from several millimeters to a few centimeters with three-dimensional microsize structures located on one or several surface areas. Microprecision parts typically are high-precision products with outer dimensional tolerances or details of a few micrometers while dimensional accuracy is far smaller than 1%. As microstructured parts are frequently desired due to the combination of functions and easy handling [5], microstructured parts fabricated by μ PIM are studied in this research.

μ PIM comprises four similar processing steps as PIM: mixing, injection molding, debinding and sintering. The process begins by mixing powder (metallic or ceramic)

and a binder system in appropriate proportions to form the feedstock. The binder system is a temporary vehicle for the powder at molding during which the feedstock is forced into the mold cavity to form the required shape. After molding, the binder system is removed from the part at debinding. The debound part is then sintered to a temperature for bonding of the particles to take place, giving densification and the required properties.

1.2 Research motivation

Sintering is a challenge in μ PIM. In μ PIM, the use of small powder is necessary to reproduce the small structures from the mold [6]. The use of small powder, however, leads to high sintering stresses during densification [7]. Besides, the sintering shrinkage shows a dependence on the structure size when the size reduces from millimeter to micrometer [8]. As the post-finishing cost of microcomponents is rather high [8-9], control of sintering parameters such as time and temperature are highly important to achieve microsize structures of acceptable dimensions [10]. Grain size after sintering is also a concern for μ PIM as anisotropy effects which were previously neglected in macroscopic part can no longer be omitted at the micro level considering the dimensional regime of the microsize structures [11-14].

From the literature review discussed in chapter 2, only a few authors have embarked on research work in μ PIM. Most of the work at this stage focuses on exploring the applicability of μ PIM in fabricating desired metal and ceramic microcomponents [15-

19]. No research has been reported on sintering kinetics of microstructured parts. In addition, no model has been established to predict densification for the microstructured parts. Thus, sintering behavior of the microstructured parts fabricated by μ PIM is to be studied in this research. The effects of size of the microstructured parts on the grain growth and densification are to be investigated. A constitutive model is to be established to predict densification for the microstructured parts. As compared to particle level sintering model, the constitutive model has the potential for predicting macroscopic characteristics due to shrinkage during the sintering of complex porous parts. A new sintering stress expression is to be developed to take into account the influence of variation in grain number on sintering stress for final sintering stage. During final sintering stage, grain growth cannot be neglected and accordingly the grain number varies. When the contribution of grain boundary energy on sintering stress is included, the variation in grain number is taken into account due to their influence on the grain boundary area.

1.3 Objectives

- 1) To investigate the effects of size of microstructured parts on the grain growth and densification
- 2) To establish a constitutive model for the densification of microstructured parts

1.4 Scope of work

The molded microstructured part under study was a circular disc of $\phi 16$ mm and 1.5

mm thick, with an array of 24×24 (i.e., a total of 576) microsize structures as shown in Figure 1.1. Silicon mold inserts were used to replicate three different sizes of microsize structures. The dimensions of the microcavity in the silicon mold insert were $\phi 100 \mu\text{m}$ and $200 \mu\text{m}$ in height, $\phi 80 \mu\text{m}$ and $196 \mu\text{m}$ in height and $\phi 60 \mu\text{m}$ and $191 \mu\text{m}$ in height.

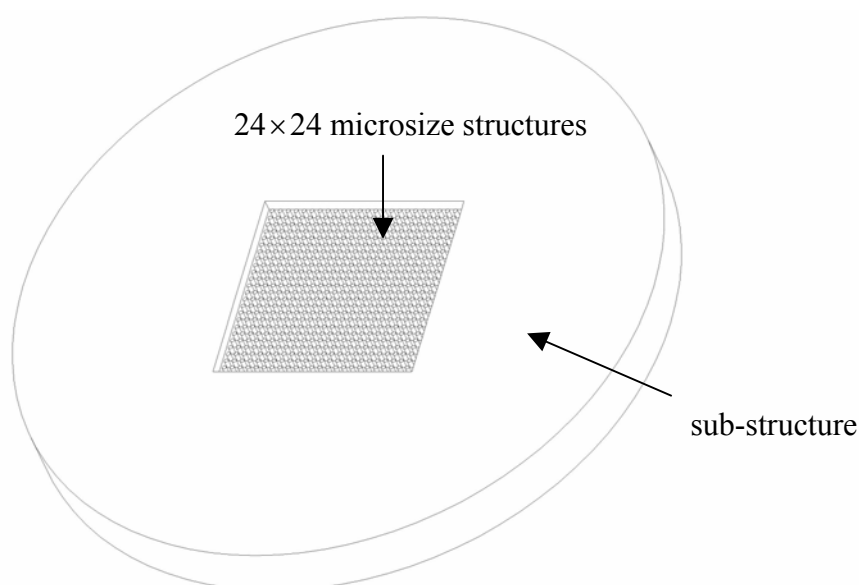


Figure 1.1 Molded circular disc with microsize structures on sub-structure

An in-house feedstock was prepared as commercial feedstock had some limitations in producing microsize structures [20]. 316L stainless steel powder was used because of its good overall mechanical properties and corrosion resistance. Characterization of the raw materials was conducted to enable the selection of suitable processing conditions for mixing, injection molding and debinding.

Experiments were conducted to investigate the effects of sintering temperature and time on the grain growth and densification of the sub-structure (in the millimeter regime) and various microsize structures on the microstructured parts. The effects of size on the sintering kinetics of the microstructured parts were investigated based on Coble and Herring's models [21-23]. A new sintering stress expression for the final sintering stage was developed where the variation in grain number was taken into account. Based on Besson and Abouaf's constitutive equation [24] and Brook's model for grain growth [25], a constitutive model was established to predict the densification of the sintered microstructured parts. The contribution of lattice diffusion (Nabarro-Herring creep), which was not incorporated in Besson and Abouaf's work [24], was considered here. Internal gas pressure was also included for sintering under gas atmosphere. The predictive capability of the model was verified by comparing the theoretical calculations with the experimental results of 316L stainless steel sub-structure and various microsize structures fabricated by μ PIM. The influences of pore location and grain boundary energy on the densification of various microsize structures were discussed. The model approximately agreed with the experimental results.

1.5 Contributions

1) The effects of size of microstructured parts on the grain growth and the densification were studied. The sintering behavior of various microsize structures was compared to that of the sub-structure in the millimeter regime and explanations were given to account for the difference caused by size.

2) A new sintering stress expression for the final sintering stage was established by taking into account the variation in grain number.

3) A constitutive model was established to predict densification for the microstructured parts, from the sub-structure to various microsize structures. The predictive capability of the model was verified based on 316L stainless steel microstructured parts.

Chapter 2 Literature Review

2.1 Powder injection molding (PIM)

2.1.1 Overview

PIM is a technology that combines the benefits of plastic injection molding of complex shapes and high productivity with the advantages of powder metallurgy (P/M) of nearly unlimited choice in alloy-composition and isotropic properties [26]. According to the materials used, PIM can be specifically classified into ceramic injection molding (CIM), developed first in 1920s, and metal injection molding (MIM), later in 1970s due to binder system innovation [27]. PIM technology has been around for several decades, but widespread commercialization only started in the 1980s.

Typically PIM comprises four main processing steps:

- i) mixing - to prepare a homogeneous feedstock comprising of selected powder and a binder system,
- ii) injection molding - to force the feedstock into the mold cavity to form a molded part (green part) with the desired shape,
- iii) debinding - to remove the binder system to form the debound part without inducing part deformation and
- iv) sintering - to impart final part properties, for example, density and strength.

The main technological features of PIM are as follows [28]:

- i) complicated three-dimensional parts is easy to process,
- ii) composite parts assembled using several parts can be produced by integration,
- iii) parts can be given custom-designed specification functions and
- iv) processing of hard-to-machine materials is easy.

PIM also has its own limitations [27]:

- i) it is costly for low-volume applications,
- ii) it is uneconomical for large, heavy parts (exceeding 50g in weight) because of material costs, debinding constraint and difficulty to maintain tight dimensional precision over large dimensions and
- iii) it is not competitive economically for the production of parts of simple or axial symmetry geometry, or parts that can be screw machined or stamped.

In summary, PIM has three main attributes for mass fabrication: shape complexity, high performance and low cost [29]. Additionally, PIM produces parts from alloys that are difficult or expensive to machine, stamp or cast. As such, the growth potential for PIM largely lies in seeking small, complex and high volume parts fabricated from difficult to machine or expensive materials.

2.1.2 Mixing

During mixing, elemental and/or prealloyed powders are incorporated into a binder system to form the feedstock whose behavior has a critical influence on the physical and mechanical properties of the final parts [30]. Ideally, the feedstock design should adequately consider ease of molding and the need to attain control over final dimensions. There are four factors that determine the attributes of the feedstock—powder characteristics, binder composition, powder loading (powder to binder ratio) and mixing method [31].

a) Powder characteristics

The selection of powder affects the properties of the final parts. Some effects of powder characteristics are listed in Table 2.1.

Table 2.1 Effects of powder characteristics on PIM [27, 30, 32]

Powder characteristics	Advantages	Disadvantages
Smaller mean particle size	Smaller molding defects. Better shape retention. Faster sintering. Low tendency for binder separation.	Propensity for agglomeration and lower packing density. Higher feedstock viscosity. Slower debinding. Higher sintering shrinkage. More contamination. Costly.
Wide particle size distribution	Higher packing density. Less sintering shrinkage. Maximize powder content. Reduced feedstock viscosity at a given solid loading.	More prone to size segregation. Inhomogeneous microstructure. Slower debinding. More quality problems.
Spherical shape	Higher packing density. Lower feedstock viscosity. Improved flow.	Lower strength. Slumping during debinding. Higher cost. Increased likelihood of powder-binder separation.

b) Binder system

The binder system is a temporary vehicle for homogeneously packing the powder into the desired shape and then holding the particles in shape until the beginning of sintering. It affects the properties of the feedstock primarily as follows [33]:

- i) aids the flow and packing of powder into the mold cavity,
- ii) wets the powder surface to assist mixing and molding,
- iii) imparts low viscosity to the high solid content in the binder-powder mixture and

iv) inhibits separation or agglomeration of the powder.

An appropriate formulation of the binder system should take into account both molding and debinding. A multiple-component binder system, comprising of low molecular weight components and backbone polymers in an appropriate ratio, is normally used to meet the need of molding and debinding because no single binder can meet all the requirements [34].

c) Powder loading

When a molten binder wets the surface of a particle during mixing, the binder forms a curved surface enclosing the particle. Critical powder loading refers to the solid loading of a feedstock in which the packing of the powder approaches theoretical close packing and all the particles are coated with binder and the spaces between the particles are filled with binder [35]. During mixing, the critical powder loading corresponds to the concentration of powder for which the measured mixing torque becomes unstable. It is generally accepted that the maximum powder loading, without sacrificing its ease for molding, would enhance sintering and minimize shrinkage.

d) Mixing

To obtain homogeneous feedstock, proper mixing is necessary [31]. Care must be given to temperature controls and mixing speed [36]. Temperature affects dispersion of the powder in the binder because of its effect on rheology. Too low a mixing temperature

may lead to poor wettability of the binder, resulting in inhomogeneous feedstock while too high a temperature will give rise to binder degradation or powder-binder separation due to the low viscosity of the binder. As for the mixing speed, too high a speed will induce micro-bubble formation in the feedstock that is difficult to remove although it is effective in breaking agglomeration. Lower speed helps to prevent air entrapment, however, contributes little to break down the agglomerates.

2.1.3 Injection molding

Injection molding involves heating the granulated or pelletized feedstock to a sufficiently high temperature such that it melts, followed by forcing this melt into a cavity where it cools and assumes the shape of the mold cavity. The molding cycle can be divided into five stages: plasticating (metering), filling, packing, holding and cooling. Figure 2.1 shows an example of a typical timing chart in one molding cycle [37]. The effects of important molding parameters on the part are listed in Table 2.2.

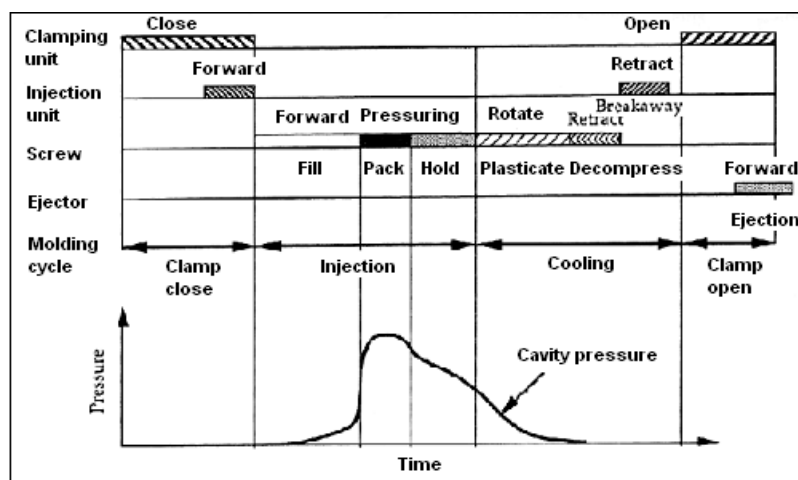


Figure 2.1 Timing chart and cavity pressure variation of an injection molding cycle [37]

Table 2.2 Main molding parameters and their effects on molding [27]

Molding parameters	Effects of parameter on molding
Melt temperature	• High melt temperature contributes to low feedstock viscosity. • Too high a melt temperature induces powder-binder separation, binder degradation and strong influence on the pressure profile.
Injection speed	• High injection speeds aids mold filling by prevent feedstock from cooling. • Too high an injection speed induces jetting as well as voids.
Follow-up pressure	• High pressure favors addition of the melt to compensate for part shrinkage and thus results in a denser part. • Too high a pressure induces flash, overpacking and high residual stress which may cause distortion in subsequent processing.
Follow-up time	• Long follow-up time contributes to preventing shrinkage. • Too long a follow-up time prolongs the cycling time and bring forth overpacking and residual stress.
Mold temperature	• Low mold temperature favors low surface roughness as well as large part shrinkage which ease demolding. • Too low a mold temperature reduces feedstock viscosity by heat transfer and induces filling problems.

2.1.4 Debinding

After molding, the binder system must be removed prior to sintering. Among various techniques, categorized mainly as solvent and thermal processes, thermal debinding appears to be the most viable method for mass production of parts due to the simplicity of the method and equipment used. In thermal debinding, time, temperature and atmosphere are three main factors [38]. For multi-component binder system, debinding is best achieved in multiple steps, an intricate combination of liquid and gas migration, pyrolysis of the binder, evaporation and heat transfer in porous media [39]. According

to Angermann, the burnt out of the low molecular-weight components is the most critical step in thermal debinding [40-41].

2.1.5 Sintering

Molding provides the basic shape but the resulting properties of the molded part do not have sufficient strength for application. Sintering provides thermal energy to initiate interparticle welds and improve the properties. By sintering, the porous debound parts are converted into a solid and imparted with the desired properties such as strength. The effects of various sintering parameters are discussed below:

a) Sintering temperature and time

Higher sintering temperatures are expected to shorten the sintering time and contribute to more efficient processing because a higher temperature induces more and faster atomic motion. For low green density ferrous parts formed from small powder by process such as injection molding, high-temperature sintering is common [42]. Along with higher densification, high-temperature sintering gives improved mechanical and corrosion resistance properties. An increase in density gives higher toughness and ductility for sintered metals. However, low-temperature sintering results in better dimensional control due to less severe shrinkage. Stainless steel parts are generally sintered at temperatures ranging from 1100 °C to 1500 °C [43]. During sintering, the process cycle time varies from one to several hours in a suitable atmosphere. Generally,

too long a sintering time favors grain growth rather than densification and the strength is lowered.

b) Sintering atmosphere

Atmosphere control is important during sintering of stainless steel because the material is sensitive to the oxidation potential of the sintering atmosphere [42]. Chromium in 316L stainless steel strongly contributes to the oxide formation and small particles aggravate such propensity while the generated oxide will reduce the sintered density. The sintering atmospheres recommended for stainless steel powder are: hydrogen, vacuum, dissociated ammonia and nitrogen [43]. Among them, hydrogen is the most reducing atmosphere and thus more effective in oxide removal.

2.2 μ PIM

Miniaturization, together with batch processing and replication techniques, is a promising technological trend when it comes to microtechnology like microelectronics, micromechanics, microfluidics and micro-optics [5, 15]. The economic, technical and ecological advantages of microsystem engineering enable the fabrication of better and novel products, such as airbag, electronic gear control, micro heat exchangers, DVD, microtiter plates, etc which are already used commercially. It has been predicted that microengineering would become as significant for innovative products as microelectronics is today [5]. The worldwide market for complete micro systems is expected to grow from about US\$ 50 billion in 2003 to more than US\$ 200 billion in

2010 [44]. However, it is regarded that microtechnology will only be successful in the future if the cost-effective utilization processing of a broad range of polymeric, metallic and ceramic materials could be established.

μ PIM is adapted from PIM and is developed for fabricating metallic and ceramic microcomponents since 1990's [45]. Since then, there is a growing interest in the process. μ PIM comprises the same basic processing steps in PIM: mixing, molding, debinding and sintering. As in PIM, μ PIM can be specifically classified into micro metal injection molding and micro ceramics injection molding, depending on the material used. The technology combines the possibility of large-scale serial production with a wide range of materials. Thus, it has great economic potential for fabricating microcomponents [46].

2.2.1 Applications of μ PIM

Figures 2.2 to 2.11 show some applications of μ PIM. Typical examples of metal or ceramic microstructured parts include micromechanical applications such as nozzle structures and steeped gear wheel. Specimens for micromechanical tests, like bending bars and tensile test bars, have been manufactured [47]. Microfluidic and biochemical devices are also potential applications of microcomponents. A recent development of high market potential is the manufacturing of micro annular gear pumps shown in Figure 2.4 [48]. Use of metal or ceramic materials makes these pumps suitable for the processing of hazardous fluids which cannot be handled by polymer-made devices. The

micro channels created by using sintering to bond two microstructured parts in Figure 2.5 can form new designs applicable as reactors, heat-exchangers or mixers [49]. A new type of titania ceramic scaffold for controlling hepatocyte distribution in cell culture is shown in Figure 2.7 [50]. Figure 2.8 shows an aluminium tooth crown to mount the dental implants.

As for microoptical applications produced previously by plastics, ceramic materials are under consideration with their low thermal expansion coefficient. An example is microoptical bench for outdoor applications as shown in Figure 2.9 [2].

Wear resistance tools are another application field for μ PIM as shown in Figures 2.10 and 2.11. LIGA mold inserts made of galvanic Ni or FeNi are used normally. However, these mold inserts not only are expensive but also show a reduced lifetime for processing temperature greater than 200 °C [51]. Moreover, suitable tool steels or hard metal cannot be processed galvanically or by machining, and to structure them by laser ablation or spark erosion often leads to restrictions in design and surface quality [8]. As such, μ PIM is developed for metal and ceramic microcomponents subject to wear, such as micro molds [5, 8, 52]. Initial work shows that with μ PIM, the surface roughness of parts made of 316L steel and small iron powder cannot be compared with advanced silicon etching (ASE) or LIGA parts, but are comparable with parts fabricated by other microfabrication methods such as micro laser ablation and micro cutting [8].

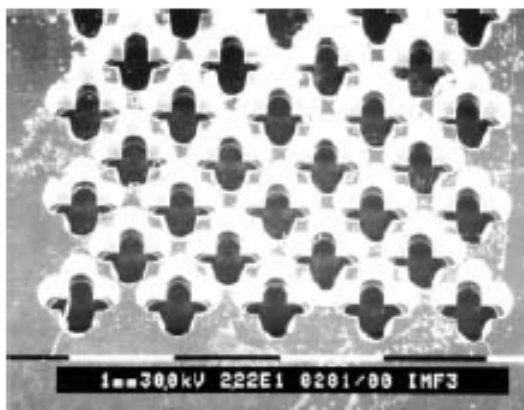


Figure 2.2 Nozzle test structures made of zirconia [5]

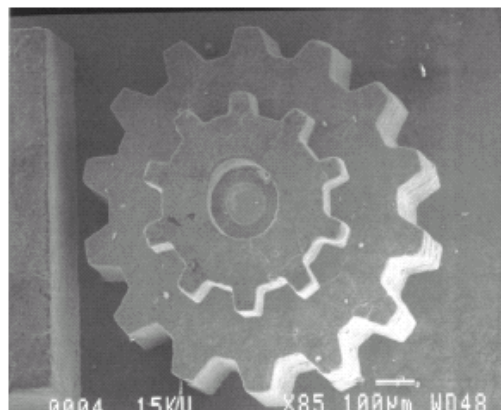


Figure 2.3 Stepped gear wheel made of 316L stainless steel [5]

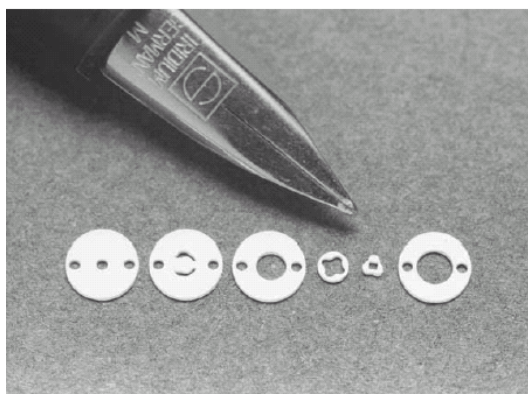


Figure 2.4 Isolated microcomponents of a micro annular gear pump [48]

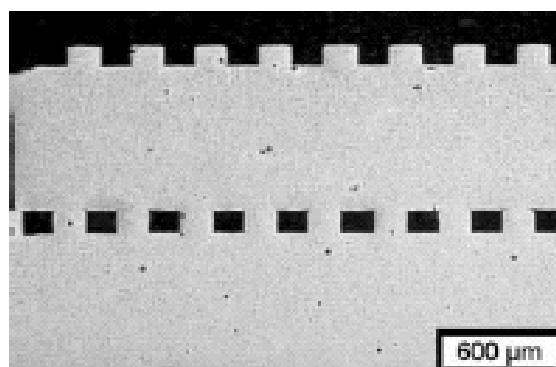


Figure 2.5 Micro channels bonded during sintering [6]

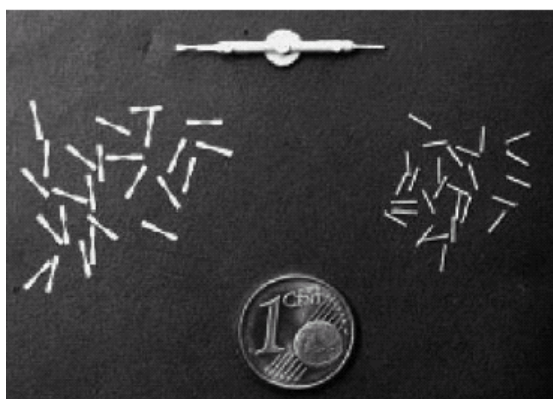


Figure 2.6 Zirconia bending test specimen [47]

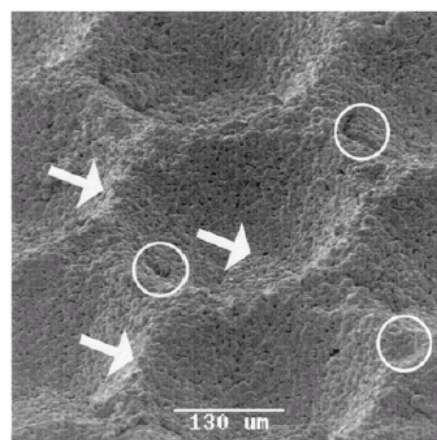


Figure 2.7 Titania ceramic scaffold [50]

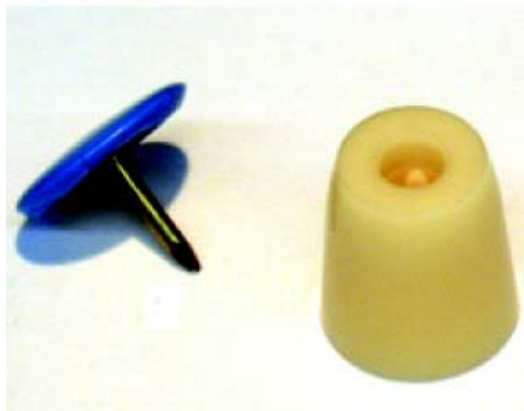


Figure 2.8 Aluminium tooth crown for mounting dental implants [53]



Figure 2.9 Alumina micro optical bench [2]

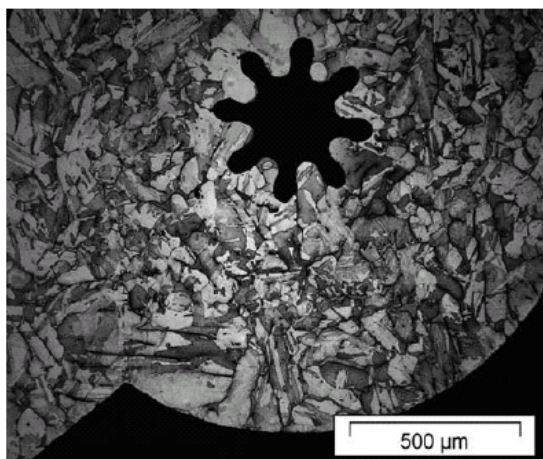


Figure 2.10 Micro steel mold [47]

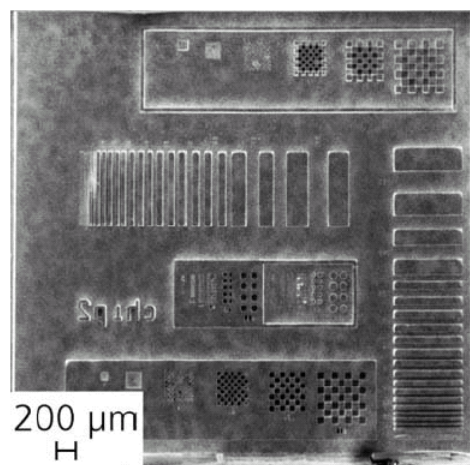


Figure 2.11 Hardmetal tool [8]

2.2.2 Developments in μ PIM

2.2.2.1 Feedstock

At the infancy of its development, the suitability of μ PIM for the production of microcomponents is first assessed without the development of a micro-specific feedstock [54]. A commercial feedstock with polyacetal binder that is used in

conventional PIM is employed [5]. However, work has shown that commercially available feedstocks are limited in their viscosities to produce microcomponents, especially when these microcomponents contain details with high aspect ratios [5, 20]. Besides, the real potential of microsystem technology can only be realized if powder with far smaller diameters are used [55]. Today, new feedstock suitable for μ PIM is under development, especially for the fabrication of metal microcomponents.

a) Powder

Particle size

Metal powder of mean particle size less than 3 μm , which is much smaller than the powder normally used in PIM, has been employed for molding and sintering [5, 56]. Smaller powder is favored in μ PIM due to various reasons. Firstly, the potential of molding minimum structural details and producible aspect ratio is defined by the particle size of the initial powder [5, 15]. For complete filling of especially small and complex detailed microsize structures, powder with a small particle size has to be used for good shape retention [20]. Secondly, particle size at least one magnitude smaller than the minimum features to be fabricated is believed to give better isotropic property of the final parts [57]. Thirdly, smaller powder contributes to faster sintering behavior. Finally, the mean particle size has a significant influence on the accuracy and surface quality of the replicated structures, which is very important for μ PIM [5, 8, 46].

Types of powder

Powders used in μ PIM include carbonyl iron (Fe), 316L stainless steel, alloyed, hardenable steel (17-4PH), hardmetal (WC-Co), aluminum oxide (Al_2O_3), zirconium oxide (ZrO_2), zirconium oxide-reinforced Al_2O_3 , aluminum nitride (AlN), silicon nitride Si_3N_4 and lead zirconate titanate (PZT) etc. [2, 5, 8, 20, 58-59]. Currently, many researchers are interested in exploring the possibility of utilizing stainless steel in μ PIM [5, 47].

b) Binder system

Binder system with sufficiently low viscosity is desired for complete filling of the microcavities during μ PIM. Compare with PIM, a relatively high mechanical stability of the binder system is also required in μ PIM to ensure safe demolding when the molded part is ejected from the mold cavity [2-3]. When a conventional PIM binder system or a binder system with low ratio of ethylene vinyl-acetate (EVA) is used, the microsize structures break during demolding [45]. Suitable amount of polymer is critical in this case because if there is too much polymer, it increases the feedstock viscosity that may hinder the filling of microcavities even though it improves the feedstock strength. In μ PIM, the binder system has to allow pressure free, complete debinding and sintering without deformation in the submillimeter range [20].

Except for commercial feedstocks, other binder systems reported in μ PIM include mainly: paraffin wax (PW) and EVA [45, 60], PAN250 (a patented binder)+ EVA+ high-density polyethylene (HDPE) [58], polyvinyl alcohol (PVA) + H₂O [58], polyethylene and PVA [5] and polypropylene (PP), low-density polyethylene (LDPE), PW and a surfactant with an ester function group [59].

c) Mixing

Small spaces or interstices between small particles, where the binder must flow, make mixing in μ PIM more difficult [34]. During mixing, the kneading stress should be large enough to break down the powder agglomerates consisting of ultra-small powder. Otherwise, the agglomerates are retained until sintering and become origin of fracture if the effective size of the defects is too large to withstand the fracture stress [59].

2.2.2.2 Mold insert, tooling and injection molding machine

Mold insert

A mold insert containing micro feature details is used in μ PIM to replicate desired microcomponents. The design of the mold insert as well as its surface roughness influences the quality of the molded part, both of which are dictated by the method used to produce the mold insert [5, 61]. The materials used for various mold inserts exhibit different wear resistance during injection molding, depending on their microstructures [44]. Currently, silicon mold insert is used as it is easy to process and it has other desired properties such as high modulus of elasticity, no mechanical hysteresis, good

thermal conductivity and low thermal expansion coefficient [62]. Plasma etching of silicon is normally used to fabricate the mold insert.

Tooling and machine

To replicate precisely the microsize structure of the mold insert onto the molded part, μ PIM requires a number of equipment modifications (as compared to PIM) and they are listed in Table 2.3. One reason for these modifications is because the edges of the curvature or the top portions of the microsize structures are usually difficult to be filled completely [3]. Some of them have been realized in micro plastic injection molding but are still being developed for μ PIM.

Table 2.3 Tooling and machine modifications for μ PIM [5, 9, 55, 61, 63-65]

Modifications	Functions
Variotherm mold heating/cooling System	• To facilitate complete filling of high-aspect-ratio microsize structures and improve dimensional accuracy of the parts in filling. • Lower melt temperature and slower filling rate can be used.
Cavity vacuum System	• To evacuate the cavity for complete microsize structure filling as the microsize structures in the mold insert represent “blind holes”.
Minimized runner system	• To reduce shot weight as well as heat transfer and control the accuracy of injection rate. • To facilitate opening and closing of the tool without misalignment by shorter flow distances, which is important to protect the microsize structures of the molded part from deformation.
Separate and smaller plastification unit	• To prevent binders from degradation and reduce cycling time as smaller volume of melt is needed for producing microcomponents.
Separation unit	• To eject the microcomponents without lateral offset and separate microsize structures from the mold insert.
High-performance control system	• To fulfill a high standard of parameters control and thus realize good reproducibility of the part geometry in the micron or even sub-micron range.

2.2.2.3 Injection molding

In the fabrication of microcomponents, some problems exist in molding. For instance, as the aspect ratio increases and the microsize structure becomes smaller, the filling of the melt into the microcavity becomes more difficult due to the longer flow path and steep pressure gradient associated with the flow through microcavity [5, 66]. The surface tension effect, which is considered insignificant for conventional injection molding due to high viscosity, can no longer be neglected when the dimension of the cavity decreases to several hundreds of micrometers [67]. This is because generally low

viscosity obtained at high temperature is used to fill the entire microcavity and in this case the surface tension is not negligible compared with the viscous stress. Due to the negative effect of surface tension on the pressure-driven flow during filling, flow difficulties as well as blockage has been observed on microchannels. Furthermore, demolding becomes a problem because the smaller and higher the microsize structures, the lower the mechanical stability of the microsize structures during demolding [61]. Hence, the molding conditions for μ PIM are different in some aspects as compared to PIM and they are shown in Table 2.4. Usually, powder loading in the PIM process ranges within 50-60 vol.% [20]. In μ PIM, powder loadings of 50 vol.% and 58 vol.% are reported in the work by Ruprecht [5] and Shimizu [45, 60] respectively.

Table 2.4 Molding conditions for μ PIM compared with PIM [5, 20, 46, 55, 61, 63, 65]

Molding condition for μPIM	Functions
Higher melt temperature	To provide lower melt viscosity by which the microsize structures can be better filled.
Higher mold temperature	To keep lower melt viscosity during filling because the rapid heat exchange between melt and mold insert, caused by high surface area/volume ratio, affects the viscosity melt.
Longer cycle time	To cool down to a certain temperature which is determined by the feedstock strength and the specific microsize structure to enable successful demolding.
Tighter control of process Parameters	To achieve the required reproducibility.

2.2.2.4 Debinding

In μ PIM, smaller particles and higher polymer content in binder systems add difficulty to binder removal as compared with PIM [27, 45]. The temperature profile during debinding has to be controlled very accurately to avoid distortion, formation of cracks and bubbles, and contamination [20].

Normally, debinding methods depend on the binder system used. So far, three different debinding methods have been reported in μ PIM [68-69]:

- i) debinding by thermal elimination of organic components,
- ii) catalytic debinding process e.g. for polyacetal binder system and
- iii) supercritical debinding.

For the binder systems developed for μ PIM, thermal debinding and supercritical debinding have been investigated [5, 45, 58, 60]. Although supercritical CO₂ debinding produces satisfactory results for microsize structures, further modifications would be required to obtain an economically viable process [5]. Thermal debinding of microcomponents using polyolefin and wax feedstock shows good results [5]. The limitation of thermal debinding is that it is not so suitable in the case where the backbone polymer ratio in the binder system is too high [45].

2.2.2.5 Sintering

Having formed into the required shape by injection molding, the transitory binder system is removed during debinding. The part is then densified during sintering where high shrinkage can be experienced. As the post-finishing cost of microcomponents is rather high [8-9], it is important to know the shrinkage of the microstructured parts fabricated by μ PIM as it concerns the contact and fitting of different microstructured parts in the micrometer regime. The sintering shrinkage shows a dependence on the structure size according to the study of Rota et al. [8]. A structure of 100 μm results in an increase in shrinkage as compared with larger structures of 500, 1000 and 10000 μm .

Depending on the powder, sintering is conducted in an oxidizing, inert or reducing atmosphere. Reducing atmosphere is often used for metal parts such as stainless steel to prevent oxidation as the particle size becomes smaller [45, 70]. In μ PIM, the use of small particle size leads to very high sintering stresses during densification [7]. According to Laplace equation, the sintering stress increases with the inverse of the particle size. Therefore, to achieve a microsize structure appropriate for microcomponents, sintering parameters such as time and temperatures are highly significant [10]. It is proposed that sintering cycles should contain sufficient time at critical densification temperatures to accommodate the induced stresses and to give them time to relax before the temperature is ramped up again and new stresses are induced [7].

The number of grains per cross-section, grain size as well as grain size distribution within the microsize structures are also crucial in the design of microcomponents due to their impact on mechanical properties [11-14]. For example, anisotropy effects in microsize structures which were previously neglected in macroscopic specimen, can no longer be omitted at the micro level. Isotropic material properties can be obtained if there are at least 10 grains within the smallest dimension of the microsize structure [10]. Besides, grain growth during sintering may deteriorate surface quality.

To determine the mechanical properties of the sintered microcomponents, special devices are necessary [12, 71]. To date, testing of the mechanical properties of microcomponents is still limited due to experimental restrictions. Micro-bending tests results show that the edge radius and the surface quality of the specimen have influence on the bending strength [14, 71]. The mechanical properties of micro-molded metals and ceramics after sintering are comparable to those of the same materials processed conventionally. The mechanical properties can be controlled by the parameters used in sintering [11].

Knowledge into effects of size on the grain growth and densification of microstructured parts is important for μ PIM. So far, to the author's knowledge, no research has been reported on the sintering kinetics of microstructured parts although Rota [8] reported a dependence of densification on sizes. Neither has any model been established to predict the grain growth and densification of microstructured parts.

2.3 Various fabricating techniques for microcomponents

Besides μ PIM, some other methods for fabricating metal and ceramics microcomponents are: micromachining, micro precision casting and hot embossing [54-55, 65, 72-74].

Micromachining

Micromachining can realize structures of high aspect ratios with accuracy in the micron or even submicron range. Table 2.5 lists the characteristics of some micromachining techniques. These techniques, however, are somewhat inflexible due to limited process materials, costly or intricate masks and strict control of complex processing steps [65].

Table 2.5 Characteristics of some micromachining techniques [75-76]

Technique	Feature size	Aspect ratio	Materials
Micro milling or micro turning	Min. 25 μm	10-50	PMMA, aluminum, brass, mild steel
Micro EDM	Typical Structure dimensions 100-1000 μm	100	Hard, brittle, conductive materials
Excimer laser	Min. 6 μm	Typical <10	Polymers, ceramics and metals to a lesser degree
LIGA	Submicron	>100	Electroformable: copper, nickel, permalloy

Micro precision casting

Micro precision casting using lost molds is used to fabricate metal microcomponents. In this technique, the investment material is burnt to form a hollow ceramic mold. Then the heated hollow ceramic mold whose inner walls carrying the image of the plastic microsize structures is filled with molten metal. Complete filling of the mold with molten metal is achieved either by centrifugal casting or by vacuum pressure casting [55]. After the metal has solidified and the ceramic mold has cooled down, the investment material is removed by chemical dissolution. The advantages and disadvantages of micro precision casting for fabricating microsize structures are summarized in Table 2.6.

Table 2.6 Advantages and disadvantages of micro precision casting [53, 73]

Advantages	Disadvantages
a) High surface quality of parts. b) Suitable for production of high aspect ratio metallic microsize structures where maximum aspect ratio reaches up to 90.	a) High cost of mold. b) Inhomogeneous properties of microstructure due to a higher cooling rate in thin areas as well as influence of chemical reactions on the surface. c) Removing a mold can be difficult which possibly result in a damaged product. d) Time consuming, tedious and more suitable for small/medium-scale production.

Hot embossing

Hot embossing is another shaping method for fabricating microcomponents. The embossing tool consists of two plates. The top plate usually process the negative image of the microsize structure or equipped with a mold insert while the bottom plate is non-structured. After the material has been inserted, the machine is closed and evacuated. The contact force is kept constant during heating. As soon as the material has softened, the microstructured tool is pressed into the material. Following cooling and separation of the material from the tool, the inverse tool microsize structure is obtained in the material [60]. The advantages and disadvantages of hot embossing are summarized in Table 2.7.

Table 2.7 Advantages and disadvantages of hot embossing [15, 74, 77]

Advantages	Disadvantages
a) Small flow path and small velocity of the tool contribute to a small flow rate of the material and thus the internal stress induced is rather small and filled structures are homogeneous.	a) High requirements on feedstock rheological behavior.
b) No pressure difference occurs within the mold insert allowing the molding of filigree details.	b) Limited aspect ratio for producing metallic microsize structures.
c) Simple tools particularly suitable for manufacturing large-area microstructured parts.	c) Longer cycle time in comparison with injection molding, 5 to 10 minutes, which is more suitable for prototyping as well as small series production.

As summarized, existing structuring and shaping techniques have their own limitations in fabricating metal microsize structures. For instance, the cost of micro precision casting for large volume production is high and the viscosity requirement on feedstock of hot embossing is strict. Compared to micromachining, micro precision casting and hot embossing, μ PIM has three advantages in general. Firstly, μ PIM can process many types of metals, alloys and even unstable, brittle materials [8]. Secondly, μ PIM inherits the shaping advantages of injection molding; potentially enabling the fabrication of complex shaped microcomponents [78-79]. Thirdly, μ PIM is potentially economically suitable for the mass production of microcomponents [5]. As such, μ PIM is a potential economical method of producing medium and high volume microparts and microstructured parts of metals and ceramics [2].

2.4 Sintering theory

2.4.1 Solid stage sintering

Sintering is a term generally used to represent the interface elimination process during the heat treatment, i.e. the particles bond together by atomic motions that act to eliminate the high surface energy associated with unsintered powder [80]. Solid state sintering occurs at temperature below the melting point of the powder. During sintering, microstructural changes such as pore shape change, pore shrinkage and grain growth take place, which consequently influence the material properties obtained.

It is generally accepted that sintering occurs in three stages, the microstructure changes during which are shown in Figure 2.12 as the bond between the particles grows. The initial sintering stage can be characterized by neck formation between the particles, the intermediate sintering stage, by the shrinkage of open porosity with near-equilibrium surfaces with principal curvatures of opposite sign, and the final sintering stage by the shrinkage of closed rounded pores [81]. Among them, densification at the intermediate sintering stage is fast as retarded grain growth and enhanced diffusion aid densification [82]. Comparatively, final sintering stage is slow where simultaneous coarsening impedes densification. Even though grain growth occurs at all three stages, it is most pronounced in the final sintering stage when the closed pores become smaller and then the grain boundaries are pinned less effectively [83]. Pore migration, coalescence and breakaway (from grain boundaries) all become important at the final sintering stage [84].

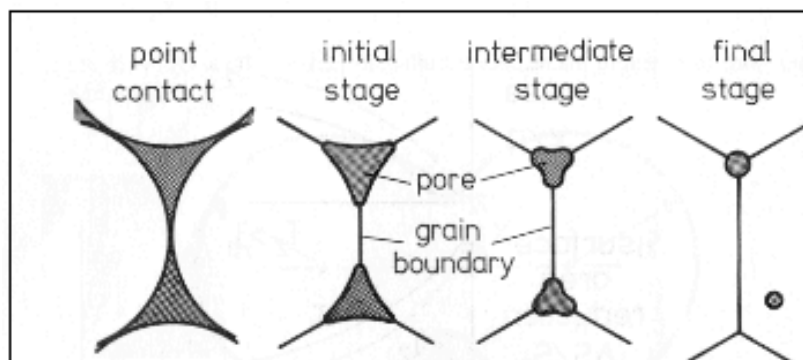


Figure 2.12 Interaction between pores and grain boundary at different sintering stages [85]

2.4.2 Sintering theory overview

Since 1940s, sintering theory has been developed for length scales ranging from atomic through particle to component level [86-90]. Among them, simulation at the atomic level, a representative of which being molecular dynamics (MD), provides successful calculation of the diffusion coefficient for metals. However, the difficulty to migrate the length and time scales beyond atomic level due to the huge calculation involved renders MD just a useful tool when the typical size of a MD model is a few hundred nanometers and the typical physical time is a few nanoseconds [88].

Sintering models at the particle level are the most mature among the three levels. Some of the models are reviewed in Table 2.8. A common weakness of these early models is that they were all based on some strong assumptions about the geometry of the particles and pores. During sintering, the particles and pores experience complex evolution which is difficult to describe quantitatively.

Table 2.8 Reviews of various sintering models [86]

Basic concept	Authors	Critical remarks
Extrapolation of idealized models: two-particle model	Kingery and Berg Coble Rockland	Nonrealistic assumptions on neck shape. Effects of asymmetry and rearrangement not considered. Explicit equations valid only for single mechanism. Not applicable to later sintering stages.
Simple-pore model	Coble	Geometry greatly oversimplified. Empirical grain-growth relationship.
Statistical approach	Kuczynski	Simplifying geometric assumption on pore shape (no convex interface).
Rheological approach	Skorokhod	Defect geometry and interaction porosity-defects not clearly defined. Phenomenological viscosity definition.
Sterological approaches	Johnson Aigeltinger and Drolet	Integration of rate equation not possible. Phenomenological introduction of geometric parameters.

In the last decade, sintering theory at component level has been developed to consider the response of a complex-shaped component with spatial variation in properties. This model is capable of predicting macroscopic characteristics due to shrinkage during sintering of complex porous powder compacts [89]. The different mechanisms of densification are shown schematically in Figure 2.13.

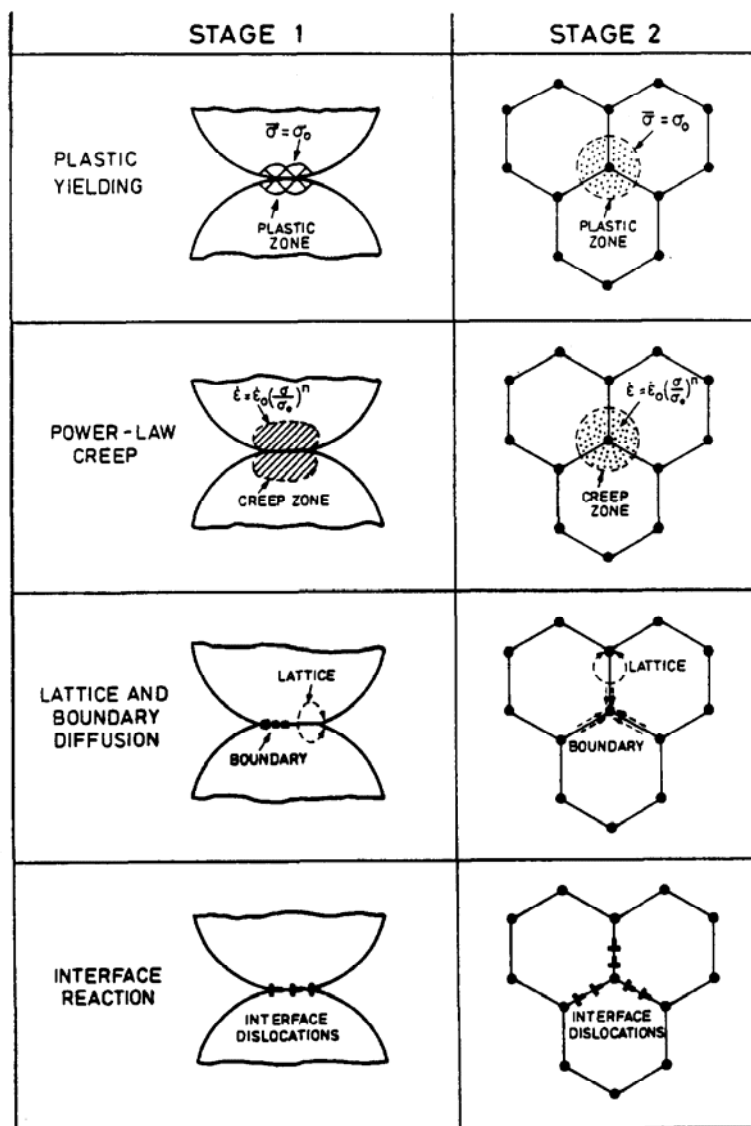


Figure 2.13 Different mechanisms of densification [91]

2.4.3 Sintering stress

The primary driving force for sintering is reduction in the free surface energy of the system [92]. It can be considered as a force acting at the atomic level by means of the curvature differences which create vacancy differences and thus control the direction of transport. An alternative representation is the driving force for atom movement, namely that a flow of atoms stems from the normal pressure differences which occur in regions

of the solid close to surfaces of different curvatures. This concept avoids reliance on atom movement by vacancy and therefore applicable to systems in which atoms move by other defect mechanisms. As atom movement is linked to pressure differences, the diffusional deformation of dense polycrystalline materials caused by an applied stress (creep) can be described directly [93-95]. Physically, the force and the pressure due to curvature differences are equivalent and it is thus a matter of preference.

The sintering stress, a hydrostatic pressure related to pore geometry and to surface and grain boundary energies, is considered to be a true mechanical pressure in the constitutive model of sintering as the driving force [24, 96]. The effective sintering stress corresponds to the result of the collective action of local capillary stresses in a porous material [97]. So far, the sintering stress discussed by several researchers in micromechanical models have been determined as follows: (i) derived from the change in surface energy [98-100] and (ii) derived from the chemical potential at the neck [101-104]. Among them, route (ii) has been used only in model involving diffusion on interparticle boundaries. Sintering stress derived from route (i), however, can be used in model involving diffusion on interparticle boundaries and viscoplastic flow (including lattice or grain boundary diffusion inside the particles) without distinction.

Table 2.9 lists a few sintering stress expressions. The differences between the various sintering stress equations lie with the different geometrical assumptions used by different researchers. Among them, the contribution of grain boundary energy on

sintering stress is only considered in Raj's work [106] where the total free energy associated with all interfaces in polycrystal is attributed to the sum of the net contribution of grain boundaries and the contribution from the surface of the pores. Most early researchers did not take into account the dihedral angle and grain boundary energy in the material system. By excluding grain boundary energy, simplified expressions can be derived while some problems ensue in regard to microstructure representation. For example, the pores located on grain boundary junctions or interfaces tend to be nonspherical owing to grain boundary energy, which is distinct from the spherical pores generally assumed. According to Raj, the sintering stress was defined as the derivative of the total free energy with respect to the volume of the polycrystal [106]. It also can be written as reported by Svoboda *et al* [104]:

$$\sigma_s dV = \gamma_b dA_b + \gamma_s dA_s \quad [104] \quad \text{Eq. 2-1}$$

where dV is a change of the volume of the pores and dA_b and dA_s are the associated changes of the grain boundary area and surface area, respectively. σ_s is sintering stress, γ_b is grain boundary energy and γ_s is surface energy.

The influence of variation in grain number on sintering stress is not considered in either of the work of Arzt, Ashby and Easterling [98, 105], Jagota and Dawson [99], and Raj [106]. For final sintering stage, however, grain growth cannot be neglected and consequently, the grain number varies simultaneously. When the contribution of grain boundary energy on sintering stress is included, the variation in grain number is to be taken into account due to their influence on the grain boundary area.

Table 2.9 Sintering expressions

Geometry assumption	Sintering stress
An aggregate of sphere particles [98, 105]	For open porosity $\sigma_s = \frac{6\gamma_s}{D} \rho^2 \left(\frac{2\rho - \rho_o}{1 - \rho_o} \right)$
A tetrakaidecahedral particle [98, 105]	For closed porosity $\sigma_s = \frac{8\gamma_s}{D} \left(\frac{6}{1 - \rho} \right)^{1/3}$
Nearly spherical grains [106]	$\sigma_s = \frac{2\gamma_b}{G} + \frac{2\gamma_s}{r}$
Cubic unit cell [99]	$\sigma_s = \frac{4\gamma_s}{D} \left(\frac{1}{\rho} - 1 \right)^{-1/3}$

Note: ρ is relative density, ρ_o is initial relative density, G is grain size, D is the particle size and r is the radius of curvature of the pore.

2.4.4 Mass transport mechanisms

In response to the sintering stress, diffusion can proceed by different mechanisms and with different sinks and sources for the vacancies (or atoms) [107]. The commonly documented mass transport mechanisms are shown in Figure 2.14.

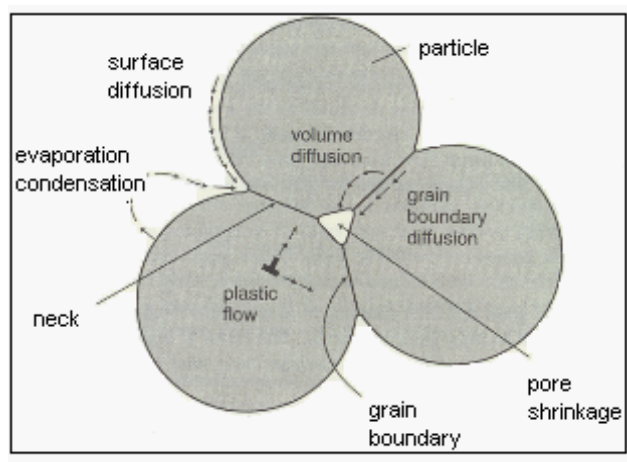


Figure 2.14 Schematic diagram of various transport paths involved in sintering [42]

Surface diffusion

Surface diffusion is a thermally activated process which leads to neck formation without shrinkage [107]. It involves the motion of atoms between the defective sites on the surface, such as vacancies, kinks, ledges and adatoms. Typically, surface diffusion is initiated at a lower temperature during heating, and is slower as particle surface becomes smoother.

Evaporation-condensation

Driving force for evaporation-condensation is the vapor pressure difference between the convex sphere surface and the concave neck region. Material evaporates preferentially from convex particle surfaces and deposits at concave necks between particles. It leads to neck growth but no densification [108]. The contribution to sintering from this mechanism is limited for most metals due to the low vapor pressure of metals.

Volume diffusion (lattice diffusion)

Mass transport driven by volume diffusion involves the motion of vacancies through a sintering body. There are two paths during sintering: one is from the particle surface through the particle interior to the neck surface which shows no densification, and the other involves atom flow to the neck surface from the interparticle grain boundary. The driving force for volume diffusion is the vacancy differences in the sintering microstructure.

Grain boundary diffusion

Grain boundary diffusion is relatively important to the sintering densification for most metals and many compounds [82]. Similar to volume diffusion, the vacancy concentration gradient drives sintering by grain boundary diffusion. It is a densification mechanism involving mass flow along the grain boundary to deposit atoms at the bond that is formed between particles. The activation energy for grain boundary diffusion is usually intermediate between that for surface diffusion and volume diffusion due to the defective character in grain boundaries.

2.4.5 Grain growth

Grain growth is a process by which the average grain size or area increases with time in a material, usually at high temperature. One of the most important driving forces results from the decrease in the total free energy of grain boundaries, which accompanies the reduction in the total boundary area [109]. This force drives the boundary to migrate

towards its curvature center. Consequently, larger grains grow at the expense of smaller grains that diminish in size and even disappear. Other driving forces may originate from the difference in the volume free energy between the grains on either side of a grain boundary, due to difference in chemical composition, defect density or grain orientation. Appropriate evolution equations for grain growth are necessary to formulate constitutive equations of powder components undergoing sintering since porosity and grain size are two variables. The grain growth law has always been developed separately from the constitutive laws [88].

Numerous grain growth equations have been developed by researchers. Some researchers obtained the grain growth equations empirically. Gupta [110-111] reported a linear relationship between the grain size and density during the intermediate stage of sintering based on experimental results. Some other researchers, Nichols [112-113], Brook [25, 114] and Carpay [115], established the grain growth equations through an analysis of the interaction between the migrating grain boundaries and pores, pore drag and pore-boundary separation respectively. A phenomenological model using expressions for pore and boundary mobilities and expressions for the forces on and between pores and boundaries was employed.

With the aid of computer simulation, Hsueh et al. [116], Spears and Evans [117] and Svoboda and Riedel [83, 118] examined the interaction between the grain boundary and pores thoroughly. Hsueh et al. investigated the phenomenon of surface diffusion

controlled pore drag. However, an artificial constraint for the pore shape is imposed on their model by solving the diffusion equation numerically for steady-state motion of a pore attached to a boundary. Svoboda and Riedel's model is not confined to steady-state motions. Classical theories of grain coarsening are modified by using effective mobilities of grain boundaries bearing pores in different configurations: from pore channels along triple grain junctions in the intermediate sintering stage to isolated pores on quadruple-, triple- and two-grain junctions in the final stages are considered. The calculated pore mobilities of Svoboda and Riedel differ substantially from those reported by Hsueh et al. and are closer to the simple estimate used by Brook. It appears that despite the geometry simplification of the dragged pores and migrating boundary, the predictions of Brook's model can still be qualitatively correct [83]. As only surface diffusion controlled pore drag is considered by Svoboda and Riedel, grain growth equations developed by Brook is to be discussed in detail since various diffusion paths are considered.

The effect of mobile second-phase inclusion on grain growth is considered here since it includes the case of porosity and its effect on grain growth, which is technologically important and appropriate for this research. The various grain growth processes are distinguished by the mechanisms of grain boundary motion. The basic assumption in Brook's model is that the instantaneous average rate of grain growth is directly proportional to the instantaneous average rate of grain boundary migration in the structure. When the pore parameters control grain boundary movement, the

instantaneous rate of grain growth is related to the mobilities of the pores [119]. When the boundary movement is controlled by boundary parameters, the instantaneous rate of grain growth is related to the mobility of the boundary itself. Brook's rate equations for grain growth of various mechanisms can be written in a general form [25]:

$$\frac{dG}{dt} = \frac{K'}{G^n} \quad \text{Eq. 2-2}$$

where t is time and K' is a constant related to the temperature and grain growth mechanism. For surface diffusion controlled pore drag, $n = 3$; for lattice diffusion controlled pore drag, $n = 2$ and for boundary diffusion controlled grain growth, $n = 1$.

2.4.6 Densification

Densification indicates the change in density due to sintering. It is widely accepted that the source and sink of matter, as well as the mass transport mechanisms are the determinant parameters in predicting densification [92, 120]. Depending on the porosity of the part and on the sintering conditions, the material densifies more or less rapidly [121]. Initial sintering stage is active for the early portion of neck growth, but there is only a minor level of densification. The intermediate sintering stage extends over a wider range of porosity than the initial or the final sintering stage and results in the largest increase in density [103]. Compared with the initial and intermediate stages, final stage sintering is a slow process. Faster grain growth at the final stage is always attributed to the impeded densification. The densification during the final sintering stage is normally characterized by the shrinkage of isolated pores located at grain corners, junctions and entrapped within the grains [82, 122].

The densification kinetics is very sensitive to grain size since the diffusional distance scales with the grain size [106]. Generally, grain growth and densification are considered as antagonistic phenomena because the grain size increase would lead to a decrease in the grain curvature and, hence, a reduction in driving force for densification [82]. To achieve high density, the aim should be to increase the rate of densification relative to that of grain growth [123]. However, it is important to note that the extent of interference of each of the phenomena on the other can vary from system to system [123-127]. In some cases, abnormal grain growth promoting densification is experimentally observed for some material system [124-125]. Gouvêa and Ricardo [120] proposed an equation relating the relative density and grain size as follows:

$$\frac{d\rho}{dG} = \frac{k' \rho^2}{G^2} \quad \text{Eq. 2-3}$$

where k' is a proportionality factor. When deriving the equation based on geometric evolution during sintering, the contribution of grain boundary energy to sintering was considered in their work. For some material systems, their assumption that the mass transport mechanism for grain growth is the same as that for pore elimination is not realistic.

Assuming that densification results from material transport from grain boundaries to pores by lattice or boundary diffusion and that grain growth is controlled by the pore mobility which is limited by surface, vapor or lattice diffusion, Cannon [123] proposed the following equation to bridge densification and grain growth:

$$\frac{dG}{dr} = \frac{\frac{dG}{dt}}{\left(\frac{\partial r}{\partial t}\right)_d + \frac{r}{G} \frac{dG}{dt}} \quad \text{Eq. 2-4}$$

Here, subscript d refers to the rate of pore size change during densification and relative density can be related to grain growth by virtue of pore size. In application, however, it is hard to distinguish the rate of pore size change during densification and that during grain growth and thus Eq. 2-4 was not used in this research. In comparison, a number of materials systems, SnO_2 , alumina, MgO-doped alumina, alumina- ZrO_2 and Fe, can be applied to Gouvêa and Ricardo's equation (Eq. 2-3) with reasonably accurate fits [120]. Hence, Gouvêa and Ricardo's equation was used in this research.

There have been numerous treatments of the microstructural evolution of a few particles as summarized in Table 2.8, and Coble and Herring's models are reviewed here. This is because diffusional creep that is useful for component level modeling of sintering was discussed in their work. Coble developed phenomenological models for densification during intermediate sintering stage for lattice diffusion and grain boundary diffusion, respectively [21-22]. In the models, cylindrical pores situated along the edges of tetrakaidecahedron grains were assumed. Figure 2.15 shows the sketch of a tetrakaidecahedron grain. It is to be noted that the geometry of the pore phase during the intermediate sintering stage, however, is not as simple as Coble defined in practice [22, 128-129]. The pores form connected channels, but the channels vary in section and surface curvature [130]. According to Coble's models, the densification rate for the lattice diffusion controlled densification is:

$$\frac{d\rho}{dt} = \frac{AD_L\gamma_s\Omega}{G^3kT} \quad [21, 93] \quad \text{Eq. 2-5}$$

The densification rate for grain boundary diffusion controlled densification [22, 93, 131] is:

$$\frac{d\rho}{dt} = \frac{B\delta D_B\gamma_s\Omega}{G^4kT} \quad \text{Eq. 2-6}$$

where T , D_L , D_B , δ , Ω and k are absolute temperature, lattice diffusion coefficient, boundary diffusion coefficient, diffusion thickness of grain-boundary diffusion, the volume occupied by a vacancy and Boltzmann's constant. A and B are constants.

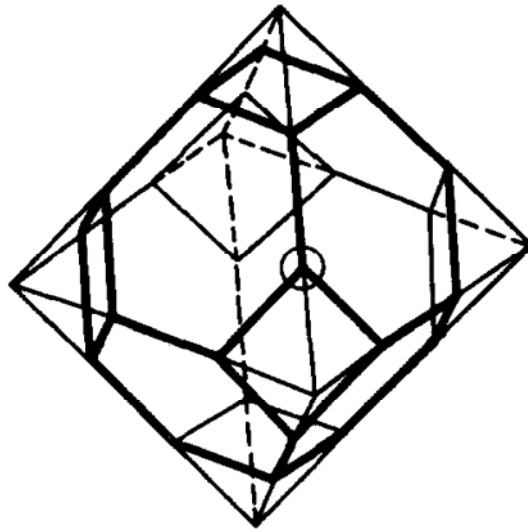


Figure 2.15 A tetrakaidecahedron (dark lines formed from truncated octahedron)

For the final sintering stage, Coble developed a model for lattice diffusion controlled densification based on tetrakaidecahedral grains with spherical pores at 24 corners of a grain [22]. Coble's model has been a standard for interpreting and predicting the densification at final sintering stage governed by lattice diffusion [23, 122]. The densification rate proposed by Coble is:

$$\frac{d\rho}{dt} = \frac{96\pi D_L \gamma_s \Omega}{G^3 kT} \quad \text{Eq. 2-7}$$

For grain boundary diffusion, kinetic equations derived from Herring's flux equations are generally used [23, 122, 132-133]. The densification rate is related to grain size as follows:

$$\frac{d\rho}{dt} \propto \frac{D_B \gamma_s \Omega}{G^4 kT} \quad \text{Eq. 2-8}$$

2.4.7 Constitutive equation for sintering

In constitutive model, the simple geometry assumptions about the microstructure as in particle level of model can be avoided since a powder component is treated as a continuum solid that undergoes time dependent deformation [88]. During sintering, the powder components shrink due to the cohesive force arising from surface tension within the bodies which is represented by an apparent hydrostatic stress, 'sintering stress' [96, 104, 134 - 135]. Continuum mechanics, based upon the theories of plastic deformation of porous bodies and nonlinear-viscous deformation of porous bodies, is applied to the constitutive model. The model is useful for predicting the final shape of complex parts and the optimum sintering condition [97]. Reliable constitutive equation, expressions of

the relation between strain rate and stress, governing the sintering process is required for modeling [136].

The sintering pressure is defined as an effective stress implying that the basic mechanisms responsible for sintering and creep are the same. This hypothesis is in agreement with sintering models proposed in literature [24, 137-138]. The micromechanisms involved in the densification of powder components are generally considered as one or a combination of processes such as plastic yielding [137, 139], power-law creep [138, 140-144] and diffusional densification [101, 137, 145-149] with the exact mechanism depending on the sintering conditions (temperature and external pressure for example) and the stage of sintering [149]. Among them, diffusion includes [150] a) lattice diffusion (Nabarro-Herring creep), b) grain boundary diffusion (Coble creep) and c) interface-reaction controlled diffusional flow. As interface-reaction controlled diffusion typically occurs in situations where the material contains more than one phase [145], it is not discussed here because 316L stainless steel was used in this research.

Ashby and co-workers [105, 137] identified different densification mechanisms for the full range of HIP processing routes. For a powder component under external pressure, deformation is considered as plastic yielding initially. With the increase of average contact area, the effective pressure falls until the yield stress of the material is no longer exceeded and this can change the dominant mechanism. Normally the part enters the

final sintering stage with time dependent deformation processes determining the rate of further densification: power-law creep in the contact zones and diffusion from a grain-boundary source to the void surface [137, 151]. It is rare that the part enters the final stage during plastic flow except when the external pressure is very high [105]. For low external pressure (free sintering as an extreme case) and small-grained materials, diffusional mechanisms tend to be favored [91, 105]. Compared to ceramics where diffusional creep may be the dominant mechanism under most processing conditions [152], diffusional creep controls deformation in metals at high temperatures [93].

Figure 2.16 shows that for hot-isostatic pressing, diffusion is dominant at lower pressure and higher relative density at 1200°C for tool steel. During free sintering, no external pressure is applied to the parts. For alumina throughout free sintering, Hsueh et al. [96] used a constant magnitude of 1MPa for the sintering potential. Kim [153] also obtained a similar sintering potential magnitude of 1MPa for tool steel. Hence, it is acceptable to deduce that during free sintering, the sintering potential of 316L stainless steel is small enough to promote diffusion over power-law creep. High relative density will be obtained for 316L stainless steel sintered from 1200 °C to 1300 °C that is used in this research. Therefore, it is reasonable to presume that diffusion is the dominant mechanism for determining the constitutive equations in this research.

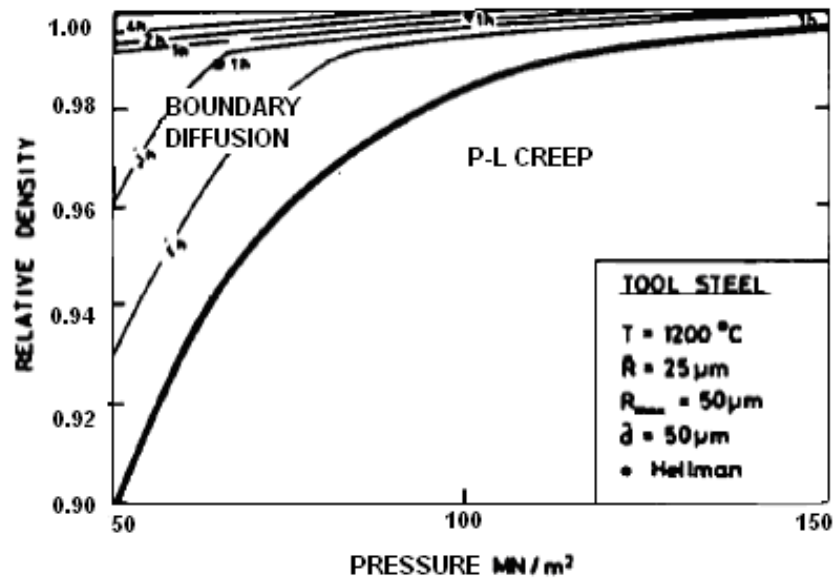


Figure 2.16 Density-pressure diagram for hot-isostatic pressing (HIP) of tool steel [150]

The constitutive equations describing sintering of real crystalline materials systems are unknown for most materials [90]. Due to the large particle size used for metals, application of continuum mechanics to sintering has been mainly concentrated on ceramic rather than metal powder so far [154]. For porous materials during sintering, new constitutive equation is necessary as conventional plasticity theory that applies for pore-free metals is no longer applicable since volume is not constant during the deformation.

Hsueh *et al.* [96] first assumed the system had a viscoelastic behavior and derived a relationship between stress and strain rate by applying creep deformation with a Maxwell model. Using Hsueh's model, Du and Cocks [155] has obtained a reasonable fit of the data. It is pointed out, however, the viscoelastic analysis in their work is

invalidated since the elastic modulus is a function of time or strain for the material [156]. Neglecting the elastic response and allowing for purely viscous deformation, Bordia and Scherer [156-157] have obtained constitutive equations for a porous sintering material using the elastic-viscous analogy. The constitutive equation similar to Bordia and Scherer's work is widely used in a number of researcher's work, e.g. McMeeking and Kuhn [101], Jagota et al. [158] and Svoboda, Riedel, Kraft et al. [104, 147-148], and is expressed as:

$$\dot{\epsilon}_{ij} = \frac{\sigma'_{ij}}{2W} + \delta_{ij} \frac{\sigma_m - \sigma_s}{3Y} \quad \text{Eq. 2-9}$$

In the equation, $\dot{\epsilon}_{ij}$, σ'_{ij} , σ_m , δ_{ij} , W and Y are the strain rate, deviatoric stress, hydrostatic stress, Kronecker symbol, effective shear viscosity and bulk viscosity of porous powder component. Models of this type generally assume a linear-viscous response with the shear and bulk viscosities being functions of the relative density. Different models differ primarily in the predicted ratio of W/Y , which are either derived from experimental fitting or theoretical models [96, 101, 159-160]. McMeeking and Kuhn [101] have used the principle of virtual power and a variational principle from Needleman and Rice [161] to take into account deformation due to diffusion on the particle boundaries and sintering.

Besson and Abouaf et al. [24, 136] have developed another equation to study the deformation behavior of porous materials at elevated temperatures:

$$\dot{\epsilon}_{ij} = \rho \frac{\dot{\epsilon}_{eff}}{\tau_{eff}} \left(\frac{3}{2} c \sigma'_{ij} + f(\sigma_m - 3\sigma_s) \delta_{ij} \right) \quad \text{Eq. 2-10}$$

where $\dot{\epsilon}_{eff}$ is the effective strain rate for a porous powder component, τ_{eff} is the effective pseudo-stress for a porous powder component and c and f are decreasing functions of ρ and they represent the stress localization generated by the porosity.

Shima and Oyane [162] have developed basic equations for porous materials based on plasticity theory in which sintering stress is not incorporated and the effect of temperature is not taken into account. Based on Shima and Oyane's yield function for porous materials, the effects of temperature, power-law creep or diffusional creep are considered by a few researchers [24, 136, 163, 164]. Among them, Besson and Abouaf et al. [24, 136] have taken into account the effect of temperature and used a viscoplastic potential at high temperatures. Both power-law and diffusional creep have been studied. Their model has been applied to both metal and ceramic powder with reasonable fit. c and f in the equation are experimentally determined from tests for powder to provide good agreement between the model and the experiments. However, their work is mainly concerned with HIP and free sintering is not covered.

It is not until recently that researchers [153-154] reported densification modeled by using constitutive equations for free sintering of steel. The limited efforts in developing constitutive equations for metal powders for conventional metal powder processing is attributed to the notion that the large particle sizes used do not have significant densification by free sintering [154]. Kim [165] failed to model the densification of free

sintering for 316L stainless steel compact as little densification, relative density from 0.8 to 0.825 or so, was observed experimentally despite a long sintering time of 100 min and a high sintering temperature from 1250°C to 1300°C. This is due to the large particle size, 110 μm , used in the experiments. However, as the particle size of metal powder for μPIM is small, a few microns or even smaller, constitutive equations for small powder material can be applied to analyze the sintering behavior.

In Kwon *et al.*'s work [154], a constitutive equation from McMeeking *et al.* [101] (Eq. 2-9) has been used for free sintering of injection molded 17-4PH stainless steel. In Kim and Jeon's work [153], Abouaf *et al.*'s model [24, 136] (Eq. 2-10) has been used to predict densification behavior of D7 tool steel powder compact for free sintering under high temperature. Compared to Abouaf *et al.*'s phenomenological approach involving functions determined by experiment, the constitutive model of McMeeking *et al.* is based on the analysis of the deformation of powders considering hollow sphere model. Good agreement between the constitutive models and the experimental data are achieved in the work of both Kwon *et al.* and Kim and Jeon. In sintering forging, however, the model of Abouaf *et al.* agrees reasonable well with experimental data while that of McMeeking *et al.* underestimates the experimental data [165]. In Song *et al.*'s work [166] for copper densification, the model of McMeeking and co-workers also do not have very good agreement in sintering forging. Compared to microstructural approach, the phenomenological modeling which consists of fitting analytical expressions directly from the results of experiments can provide a constitutive equation

describing as precisely as possible the real behavior of the material [121, 132]. Hence, Abouaf *et al.*'s constitutive equation is used in this research with adaptation since lattice diffusion is not included in their model.

In both Kwon *et al.* and Kim and Jeon's work, similar sintering stress expression for the final stage sintering from Ashby [98] has been used. The contribution of grain boundary energy is not included in the sintering stress. In this research, a new sintering stress expression incorporating the variation in grain number is proposed as prominent grain growth takes place at the final stage sintering. In addition, the contribution of grain boundary energy on the sintering stress is taken into account.

2.4.8 Grain size-density plot

Cannon and Yan [167] have proposed a model of simultaneous densification and normal grain growth to construct a trajectory representing microstructure development on a grain size-density plot. Normal sintering is seen to fall on a trajectory between the two extremes of pure grain growth and pure densification. It can be used to predict the coarsening/densification ratio during sintering and recently the trajectories was used for nanocrystalline materials to discover grain size effects [168]. Data from different experiments can be plotted together to show the direction of change in the coarsening / densification ratio caused by changes in processing conditions. It is strictly applicable to final sintering stage, but is considered to be semiquantitative during intermediate sintering stage [123].

2.4.9 Effects of gas atmosphere on sintering

The gas used in sintering may change the densification rate, the limiting density or the grain size [169, 170]. The sign and magnitude of changes in densification rate vary with gaseous species, or with different pressure of a given gas, its defect structure and purity, and on the controlling mechanism. Among them, the density limit due to the gas used is more of interest in this research. During sintering, the gases may get trapped within the sealed pores and form higher internal pressures to prevent complete densification, even under external pressure, and may eventually lead to swelling as pores coarsen at high temperatures [171]. The reduction in density may be attributed to nucleation and growth of grain-boundary pores [172].

Chapter 3 Experimental Work

This chapter describes the experimental work conducted in this research. First, raw materials including powder and binder system were characterized as discussed in sections 3.1 and 3.2. Section 3.3 describes the fabrication of the microstructured parts through the four processing steps of μ PIM, namely mixing, injection molding, debinding and sintering. Finally, the sintered microstructured parts were characterized with respect to density and grain size measurements, and by X-ray photoelectron spectroscopy (XPS) test. The characterization is documented in sections 3.4 to 3.6.

3.1 Powder

Water atomized 316L stainless steel powder (grade PF2, ATMIX Co., Japan) was used in this research. The powder morphology was examined by JEOL JSM-5600LV SEM and is shown in Figure 3.1. As shown in the figure, the particles are generally rounded with some irregular in shape. Table 3.1 summarizes the physical characteristics of the powder. The characteristics such as particle shape and particle size will influence the packing behavior of the molded part and thus affect subsequent debinding and sintering.

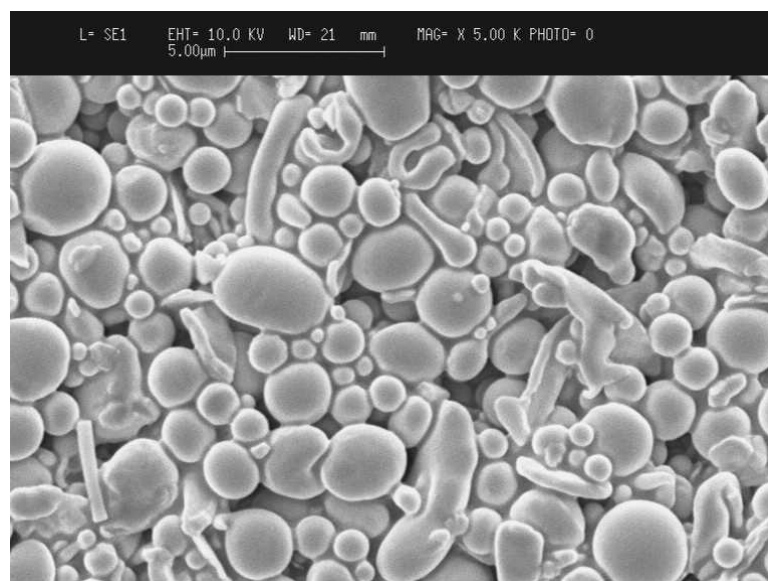


Figure 3.1 Scanning electron micrograph of 316L stainless steel powder

Table 3.1 Physical characteristics of 316L stainless steel powder

Characteristics	Description	Equipment
Particle shape	Generally rounded with some are irregular in shape	JEOL JSM-5600LV SEM
Particle size (μm)	$D_{10}=1.21$ $D_{50}=2.37$ $D_{90}=4.03$	Fritsch Analysette 22 Particle Size Analyzer
True (pycnometer) density (g/cm^3)	8.05	Quantachrome ultra-pycnometer

3.2 Binder system

A multi-component binder system comprising of PAN-250S (ADEKA Fine Chemical Co, Tokyo, Japan) and low density polyethylene (LDPE) was used in this research. Some components of PAN-250S were natural wax, fatty acid wax, stearic acid, poly-oxi-alkylen-ether and olefin-hydrocarbons, etc. The drawback of using PAN-250S alone for μ PIM was its relatively low strength that could not provide successful demolding. To compensate for this, LDPE was added. Being non-polar, high molecular weight crystalline polymer with carbon-carbon bonds in the backbone, it possessed a unique balance of toughness, chemical and solvent resistance [173]. In the present work, the binder system comprised of 50 wt.% LDPE and 50 wt.% PAN-250S.

Table 3.2 lists the characteristics of the binder components that are relevant to mixing (see Appendix A). The melting and recrystallization temperatures were characterized by a Perkin-Elmer differential scanning calorimeter (DSC) Model 7. Start degradation temperatures of the binder components were tested by a Perkin-Elmer thermogravimetric analyzer (TGA) Model 7. The heating/cooling rate was set at 10°C/min under a flow of nitrogen gas at 20 ml/min for both DSC and TGA.

Table 3.2 Characteristics of binder components

Characteristics	PAN-250S	LDPE
Peak melting temperature (°C)	60	126
Recrystallization temperature (°C)	36	103
Start degradation temperature (°C)	170	290
Pycnometer density (g/cm ³)	0.99	0.92

3.3 μ PIM processing steps

3.3.1 Mixing

92 wt.% (58 vol.%) powder loading was used for the production of the feedstock. The mixing of the powder and binder system was conducted in a Herman Linden z-blade mixer. The 316L stainless steel powder was dried in a vacuum oven (Salvis Vacucenter VC-20) at 80 °C for 12 hours to remove any possible moisture. The mixing temperature was set at 140 °C, higher than the highest peak melting temperature of the binder components in the binder system (that is 126 °C, as shown in Table 3.2). A mixing speed of 25 rpm was used. During mixing, LDPE was first fed into the bowl and kneaded until the polymer had melted. PAN-250S was then added and mixed for another 15 minutes. After all the binder components had melted, the powder was loaded into the mixer in small consecutive batches. After all the powder was added into the bowl, the feedstock was then mixed in vacuum for another 30 minutes to evacuate any air that might be trapped in the feedstock. At the end of the mixing, the feedstock was removed and granulated using a granulator.

The granulated feedstock was fed continuously into a Brabender twin screw compounder DSK 42/7 to improve its homogeneity. The barrel temperature was set at 125 °C /130 °C /125 °C (from feed to exit), around the highest melting temperature of the binder components (that is 126 °C) recorded in Table 3.2. A screw speed of 25 rpm was used. Moderate screw speed and low processing temperature were employed to prevent scission of the binder components from the powder and any localized overheating of the barrel, which could cause powder-binder separation. After extrusion, the powder was dispersed homogeneously into the binder as shown in Figure 3.2. The thermal characteristics of the feedstock are listed in Table 3.3 (see Appendix A). The characterization was conducted using the same DSC and TGA equipment and set-up mentioned in section 3.2.

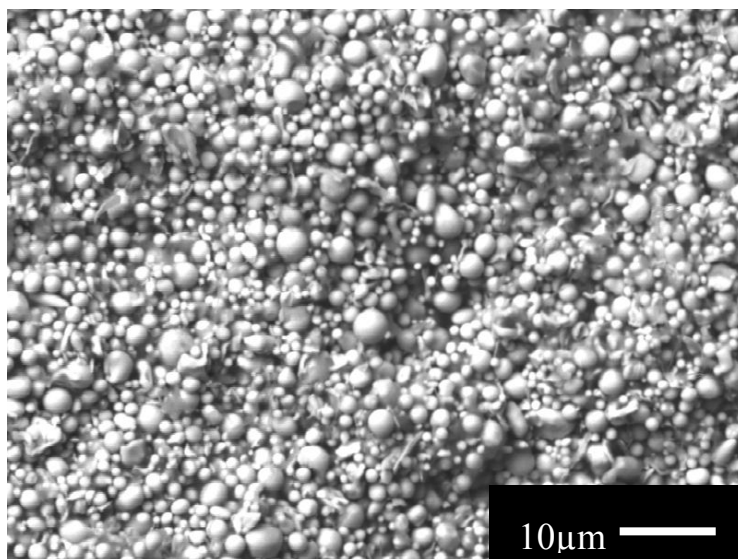


Figure 3.2 Scanning electron micrograph (with back-scattered electron) of feedstock

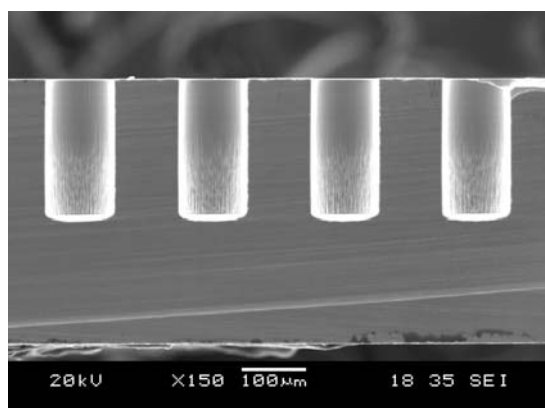
Table 3.3 Thermal characteristics of feedstock

Characteristics	Feedstock
Peak melting temperature (°C)	56, 125
Recrystallization temperature (°C)	30, 110
Start degradation temperature (°C)	160
Onset temperature (°C)	380, 424, 472
End degradation temperature (°C)	501

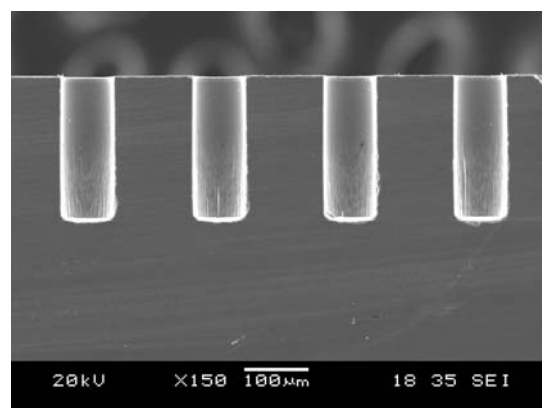
3.3.2 Injection molding

Injection molding was conducted on a Battenfeld BA 250CDC injection molding machine. During molding, the feedstock was melted in the heated barrel and forced into the mold cavity containing a silicon mold insert where it cooled and assumed the topography of the mold cavity. In this research, the mold cavity was a round disc of $\phi 16$ mm and thickness of 1.5 mm. Edge gate and modified trapezoidal cross-sectional runner were used to deliver the melt into the mold cavity. A silicon mold insert of dimensions 5 mm $\times$ 5 mm $\times$ 0.65 mm was employed to replicate the microsize structures. The mold insert had 24 $\times$ 24 (576) microcavities fabricated by inductively coupled plasma (ICP). Three microcavity dimensions were used: $\phi 100$ μ m x height 200 μ m, $\phi 80$ μ m x height 196 μ m and $\phi 60$ μ m x height 191 μ m as shown in Figure 3.3. During molding, the silicon mold insert was mounted on the steel mold cavity. The injection molding parameters summarized in Table 3.4 were used to fabricate the

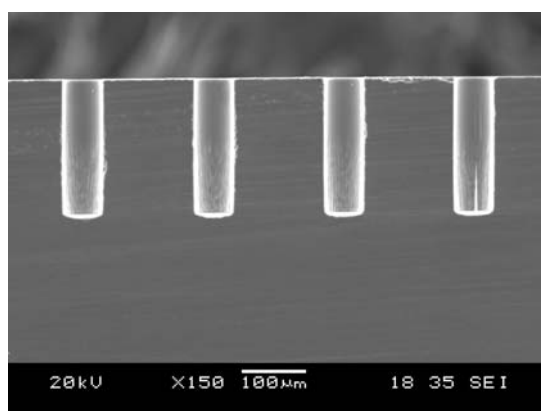
microstructured parts. Figure 3.4 shows the fabricated microsize structures of various sizes on the sub-structure.



(a) Microcavities of $\phi 100\ \mu\text{m}$



(b) Microcavities of $\phi 80\ \mu\text{m}$



(b) Microcavities of $\phi 60\ \mu\text{m}$

Figure 3.3 Cross-sectional view of microcavities on silicon mold insert

Table 3.4 Suitable injection molding parameters

Molding parameters	Value
Injection stroke (mm)	20/17/15.5/13.5
Injection speed profile (stroke 1/2/3/4/5: %)	50/30/20/30/20
Melt temperature profile (nozzle/ zone 1/ zone 2/ zone 3: °C)	157/160/160/157
Follow-up pressure (bar)	80
Follow-up time (s)	2 + 0.5
Mold temperature (°C)	45

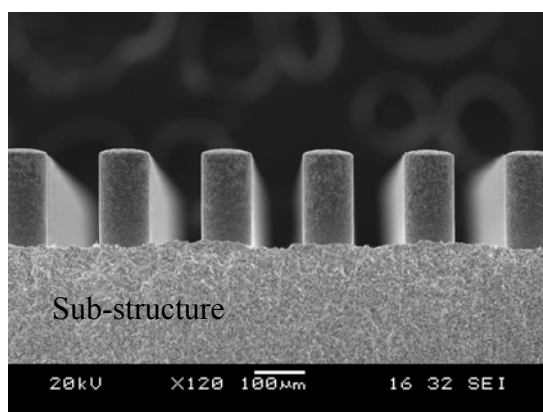
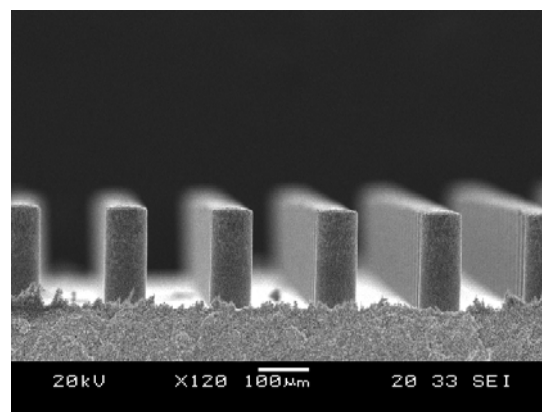
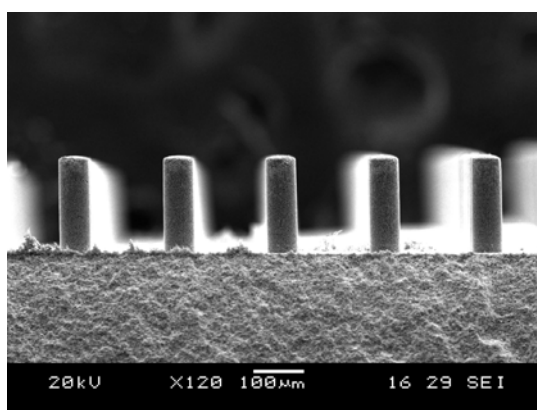
(a) Molded microsize structures of $\phi 100\text{ }\mu\text{m}$ (b) Molded microsize structures of $\phi 80\text{ }\mu\text{m}$ (c) Molded microsize structures of $\phi 60\text{ }\mu\text{m}$

Figure 3.4 Molded microsize structures

The softening temperature of the molded parts was determined on a Perkin-Elmer thermomechanical analyzer (TMA) Model 7. A specimen was pressurized by a penetration probe with a round tip of $\phi 1$ mm at 10 mN pressure. A heating rate of 10 °C/min was used. By measuring the change in the penetration depth, whether or not the molded part can withstand defects at a certain temperature can be determined.

Figure 3.5 shows an increase in the probe position at the beginning of the test, which was due to the expansion of the solid specimen. As the specimen was heated up, the curve started to drop indicating that softening of the specimen occurred. The onset temperature was 95 °C after which the probe penetrated very quickly as the part lost its resistance.

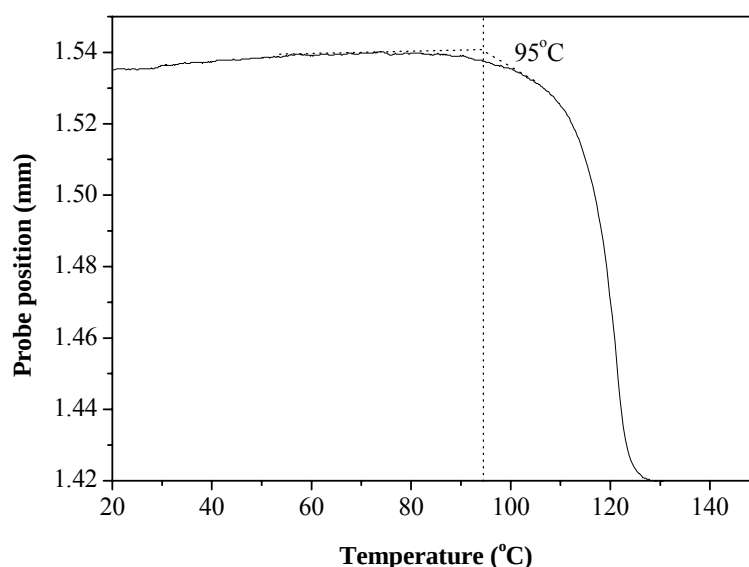


Figure 3.5 TMA curve of molded microstructured part

3.3.3 Debinding

A Lindberg tube furnace was used for the controlled heating in debinding. Porous plates (Coorstek) and a gas mixture of argon and hydrogen (5%) at a continuous flow rate of 279 cc/min were used. Argon will protect the sample from reacting with oxygen and the addition of hydrogen will reduce the oxide. The air in the furnace was purged prior to debinding by flowing the gas mixture for 40 minutes. The thermal characteristics summarized in Table 3.3 and Figure 3.5 was used to establish the debinding schedule. A multi-step debinding schedule as shown in Figure 3.6 and Table 3.5 was used to remove the binder system. The first stage was set at 90 °C, slightly lower than the softening onset temperature of 95 °C (see Figure 3.5), to avoid defects such as slumping. The second stage was set around the higher melting peak temperature of the feedstock, 125 °C (see Table 3.3), for gradual removal of the binder components. The third stage was set at 200 °C to shorten the total debinding time. The fourth and fifth stages were set before the first and the third onset degradation temperatures of 380 °C and 472 °C (see Table 3.3) respectively to avoid deformation caused by abrupt binder removal. The last (sixth) stage was set at 550 °C, above the end degradation temperature of 501 °C (see Table 3.3), to facilitate complete removal of the binder system. The heating rates used in the schedule followed the criteria that a lower heating rate was used at the period with abrupt binder loss to avoid deformation while higher heating rate was used at the period with less binder loss to accelerate the debinding step. The debound microsize structures with good shape retention and without visual defects are shown in Figure 3.7. The density of the debound microstructured parts (with microsize structures of $\phi 100\text{ }\mu\text{m}$) was calculated for three

specimens. The bulk density was obtained by dividing the mass of the specimen to its volume which was established from the dimensions measured using a micrometer with a resolution of 0.01 mm. Using the debinding schedule indicated in Table 3.5, the density of the debound microstructured parts was $4.74 \pm 0.07 \text{ g/cm}^3$.

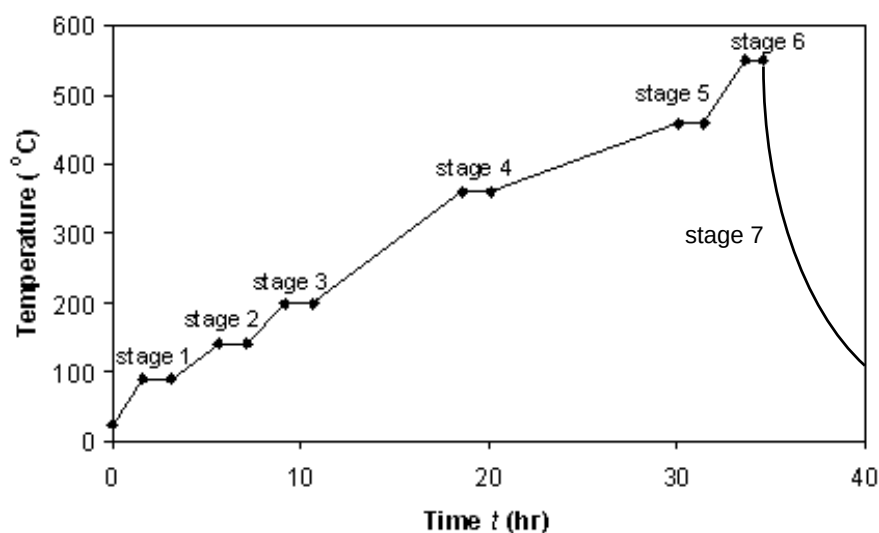


Figure 3.6 Schematic of debinding schedule

Table 3.5 Debinding schedule

	Stage						
	1	2	3	4	5	6	7
Heating rate (°C/hr)	40	20	30	20	10	40	Furnace cooling
Temperature (°C)	90	140	200	360	460	550	
Holding time (min)	90	90	90	90	75	60	

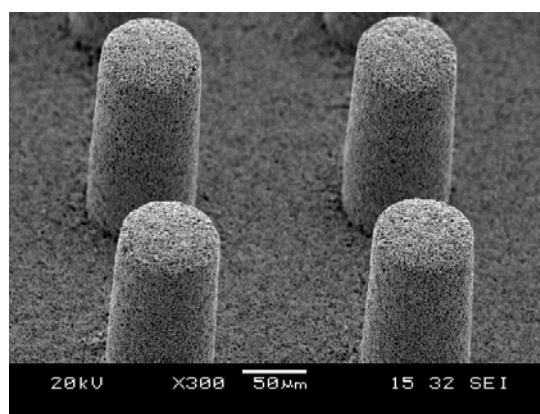
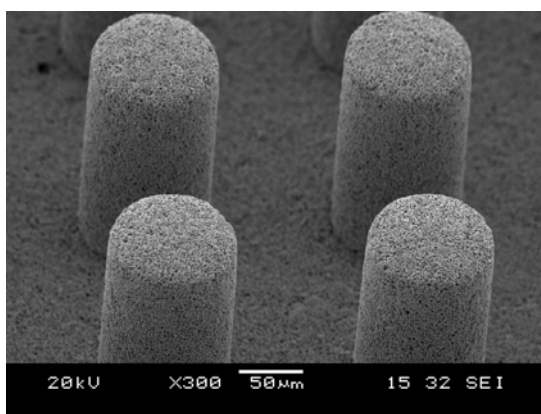
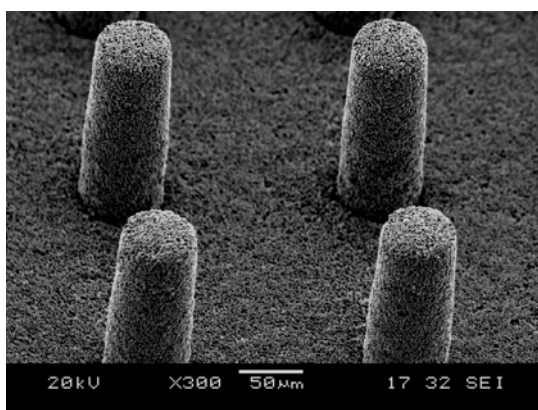
(a) Debound microsize structures of $\phi 100 \mu\text{m}$ (b) Debound microsize structures of $\phi 80 \mu\text{m}$ (c) Debound microsize structures of $\phi 60 \mu\text{m}$

Figure 3.7 Debound microsize structures

3.3.4 Sintering

The debound microstructured parts were sintered in an Oxygon tube furnace under a steady flow of purified H_2 gas at a flow rate of 470 cc/min. Sintering time of 10 min, 30 min, 60 min, 90 min and 120 min were used for temperature of 1200 °C and 1250 °C. Sintering time of 10 min, 30 min, 60 min and 90 min were used at 1300 °C. 120min was not used for 1300 °C during sintering so as to suppress accelerated grain growth beyond high density. Two different heating rates were sequentially used in the sintering schedule as shown in Figure 3.8. Two microstructured parts were tested for each sintering schedule. The microsize structures of various sizes that were sintered at 1300 °C for 60 min are shown in Figure 3.9. The microsize structures showed good shape retention without any visual defects.

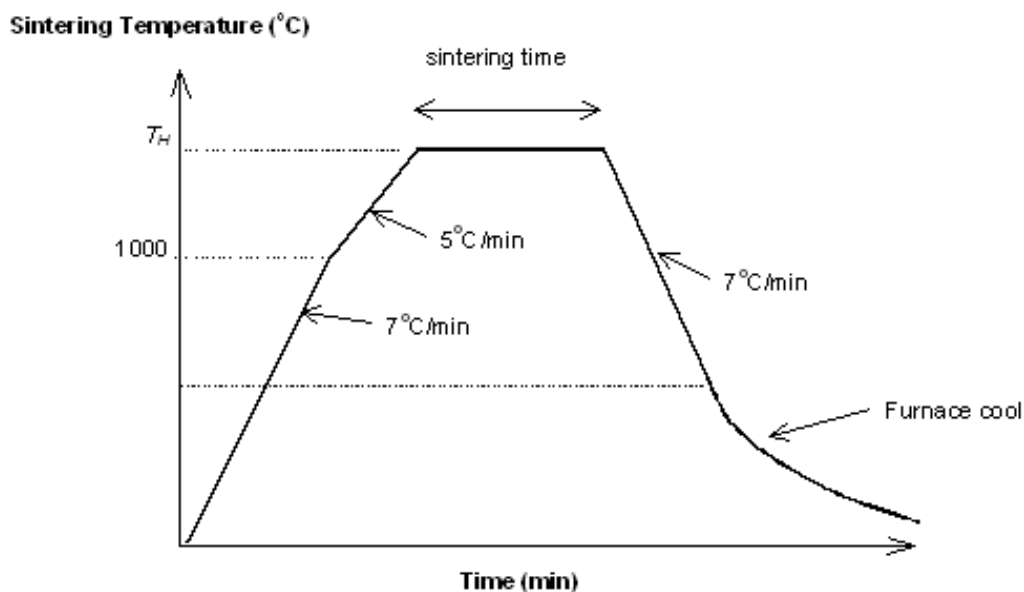
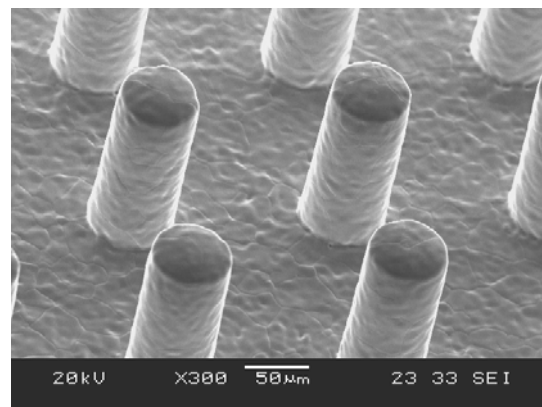
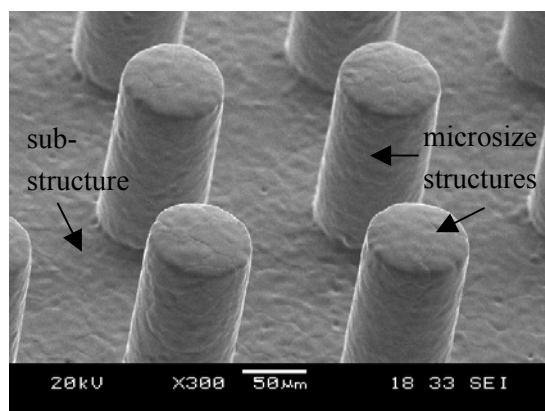
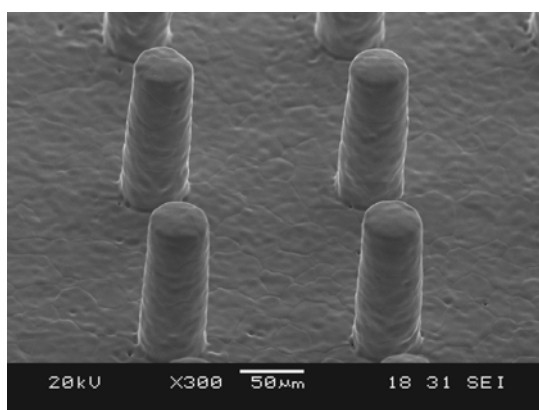


Figure 3.8 Schematic of sintering schedule



(a) Sintered microsize structures of $\phi 100 \mu\text{m}$ (b) Sintered microsize structures of $\phi 80 \mu\text{m}$



(c) Sintered microsize structures of $\phi 60 \mu\text{m}$

Figure 3.9 Sintered microsize structures at 1300 °C for 60 min

3.4 Porosity measurement and density

The porosities of the sub-structure and microsize structures of various sizes were determined on their polished cross sections using image analysis software, Image-Pro Plus, under a lens magnification of $20\times$. The specimens were cut and mounted into thermosetting resin for a series of sanding, 400, 800, 1200, 2400 and 4000 grit in sequence, and final polishing using $1\text{ }\mu\text{m}$ diamond paste. A rotation speed of 60 rpm during polishing was used. For each sintering condition, two specimens were tested and for each specimen, six different microsize structures were measured. Measurement for each reading of the microsize structures covered both the dense layer and core. The relative density (ρ) of the sub-structure and various microsize structures was obtained from the porosity (P_s) measurement due to their relation as follows:

$$\rho + P_s = 1 \quad \text{Eq. 3-1}$$

Appendix B tabulates the experimental data. For each sintering condition, the standard deviation was determined from the mean of each specimen and indicated as an error bar in the graphs in this research.

3.5 Grain size measurement

The grain boundaries on the sub-structure and various microsize structures were revealed using etchant No. 87 as indicated in ASTM E407-99: standard practice for microetching metals and alloys. Grain sizes were obtained by applying the intercept procedure on the micrographs as outlined in ASTM112-96: standard test methods for

determining average grain size. The mean lineal intercept length l' given below was used to determine the ASTM grain size:

$$G = 1.57 l' \quad \text{Eq. 3-2}$$

The readings from a stage micrometer were used for the calibration of the objectives employed. For each sintering condition two specimens were tested and for each specimen, six different microsize structures were measured. Measurement for each reading of the microsize structures covered both the dense layer and core. Over 200 grains were measured for each sintering condition. Appendix C tabulates the experimental data. For each sintering condition, the standard deviation was determined from the mean of each specimen and indicated as an error bar in the graphs in this research.

3.6 X-ray photoelectron spectroscopy (XPS)

The XPS spectra were obtained using a Kratos-Axis Ultra spectrometer. The incident X-ray photons were generated from monochromatic Al K_{α} (1486.7 eV). The etching of various elements was achieved using an ion gun (MiniBeam 1). An argon beam with an accelerating voltage of 4 kV was scanned over 300 μm x 700 μm area of the exposed surface. The pressure in the analysis chamber during Ar etching was around 10^{-8} Torr and the target current was 15 mA. After 20 min of etching, the XPS lines were recorded with step size of 0.1 eV and pass energy at 40 eV. The energy resolution of the electron spectrometer under these conditions was 0.55 eV. The C 1s line of free carbon located

at 284.5 eV binding energy was used as a reference to correct the binding energies for the charge shift on the debound part after ion beam sputtering of surface layer [174]. For the sintered part, O 1s line located at 530.2 eV binding energy was referred to correct the binding energies for the charge shift [175].

Chapter 4 Constitutive Modeling

As shown in Figure 1.1, the microstructured part studied in this research is a circular disc of $\phi 16$ mm and thickness of 1.5 mm with an array of 24×24 microsize structures in the center of the disc. After debinding, the debound microstructured parts are sintered where the dimensions of the microsize structures and the sub-structure (circular disc where the microsize structures are located) shrink. This chapter describes the concepts and development of a constitutive model to predict the densification of the sub-structure and microsize structures based on a continuum-mechanics approach. A new expression for the sintering stress during the final sintering stage has been proposed taking into consideration the variation in grain number. The model is introduced in section 4.1, followed by geometrical assumptions in section 4.2. Section 4.3 details the model development and section 4.4 provides the procedure for modelling. The outline of the model is summarized in section 4.5.

4.1 Introduction of model for densification

A model based on a continuum-mechanics approach is developed to predict the densification during sintering. The constitutive equation is adapted from that developed by Besson and Abouaf et al. [24]. The contribution of lattice diffusion (Nabarro-Herring creep), which was not incorporated in Besson and Abouaf's work, is considered here. Besson and Abouaf's constitutive equation is used here because the effects of temperature and diffusion creep are considered in their equation. The effect of grain

growth on densification is included in the model based on Brook's equations [25]. This is because simultaneous densification and grain growth are typical features during sintering, especially at the final sintering stage. A new sintering stress expression has been developed for the final sintering stage by incorporating the effect of variation in grain number on the change of free energy. Internal gas pressure is also taken into account as the sintering in this research was conducted in a gas atmosphere.

4.2 Geometrical assumptions of the model

The fundamental unit cell in this analysis assumes Kelvin's tetrakaidecahedron grain whose geometry has been used extensively in sintering analysis [22, 119]. The grain structure is assumed to be isotropic and its size G is defined as the distance between two parallel square faces of the polyhedron. The pores are assumed to have a quasi-equilibrium shape; i.e., the surfaces have uniform curvature. According to Coble [22], size G , the volume V_G and surface area S_G of each grain can be expressed in terms of l_p , the edge length of the tetrakaidecahedron as follows:

$$G = 2\sqrt{2} l_p \quad \text{Eq. 4-1}$$

$$V_G = 8\sqrt{2} l_p^3 = \frac{G^3}{2}, \text{ and} \quad \text{Eq. 4-2}$$

$$S_G = (12\sqrt{3} + 6) l_p^2 \approx \left(\frac{3\sqrt{3}}{2} + \frac{3}{4} \right) G^2 \quad \text{Eq. 4-3}$$

Intermediate sintering stage

For the intermediate sintering stage, cylindrical pores, with axis coincident with three-grain edges, are assumed. Within the polyhedron, cylindrical pores of radius r_c distributed along and centered upon the polyhedron edges have volume V_c given by:

$$V_c = 12l_p\pi r_c^2 \quad \text{Eq. 4-4}$$

The porosity P_s is given by:

$$P_s = \frac{V_c}{V_G} = \frac{6\sqrt{2}\pi r_c^2}{G^2} \quad \text{Eq. 4-5}$$

The relative density, ρ , is given by:

$$\rho = 1 - P_s \quad \text{Eq. 4-6}$$

Hence, the radius of the cylindrical pores can be expressed in terms of ρ and G as:

$$r_c = \sqrt{\frac{1-\rho}{6\sqrt{2}\pi}} G \quad \text{Eq. 4-7}$$

Final sintering stage

For the final sintering stage, all the pores are assumed to be closed pores situated on the intersection of four grains in the form of spherical tetrahedrons. All four-grain intersections in the structure are assumed to be occupied by such pores centered on a corner. S_s , the grain boundary area reduction due to the pores at the four-grain junctions per polyhedron, is given by:

$$S_s = 6\alpha r_s^2 \quad \text{Eq. 4-8}$$

where r_s is the radius of curvature of the pore.

A_s , the total pore surface area per polyhedron, is given by:

$$A_s = 6\beta r_s^2 \quad \text{Eq. 4-9}$$

The total pore volume per polyhedron, V_s , is given by:

$$V_s = 6\lambda r_s^3 \quad \text{Eq. 4-10}$$

Here α , β , λ are coefficients depending on the dihedral angle of the pores (see Appendix D).

Thus, the porosity P_s for the final sintering stage is given by:

$$P_s = \frac{V_s}{V_G} = \frac{12\lambda r_s^3}{G^3} \quad \text{Eq. 4-11}$$

Hence, the radius of a spherical pore can be expressed in terms of ρ and G as the following:

$$r_s = \sqrt[3]{\frac{P_s G^3}{12\lambda}} = G \sqrt[3]{\frac{1-\rho}{12\lambda}} \quad \text{Eq. 4-12}$$

4.3 Constitutive model for sintering

4.3.1 Constitutive equation

In the model, the porous part to be sintered is treated as a continuum solid that undergoes time dependent deformation due to the cohesive force arising from surface tension within the part, which is represented by a hydrostatic stress σ_s , also termed the ‘sintering stress’. The porous part is considered as a two-phase material, substance (body skeleton) and voids (pores). The skeleton is assumed be made of individual particles (grains) having nonlinear-viscous incompressible isotropic behavior. The voids (pores) are assumed to be compressible and isotropically distributed. The overall material response is thus assumed as isotropic and unlike conventional plasticity theory, the volume does not remain constant.

Assuming that the basic mechanisms responsible for sintering and creep are the same, Abouaf et al.’s constitutive equation [24, 136] can be used. With regard to the intermediate and final sintering stage, the “snap-through” buckling of the cellular structure formed by large voids (i.e., larger than the individual particles) which exists at low densities can be ignored. Thus, the constitutive equation can be written as:

$$\dot{\epsilon}_{ij} = \rho \frac{\dot{\epsilon}_{eff}}{\tau_{eff}} \left(\frac{3}{2} c \sigma'_{ij} + f(\sigma_m - 3\sigma_s) \delta_{ij} \right) \quad \text{Eq. 4-13}$$

In this research, isotropic shrinkage is assumed for free sintering. Thus, $\sigma_m = 0$ and $\sigma'_{ij} = 0$ and only densification is considered. The effects of external forces such as gravity on densification are not considered [154]. Therefore, Eq. 4-13 can be reduced to:

$$\dot{\epsilon}_{ij} = -3\rho \frac{\dot{\epsilon}_{eff}}{\tau_{eff}} f\sigma_s \delta_{ij} \quad \text{Eq. 4-14}$$

According to Artz et al. [176], the effective strain rate for lattice diffusion controlled creep is given by:

$$\dot{\epsilon}_{eff} = \frac{C_1 \exp\left(\frac{-Q_L}{RT}\right)}{TG^2} \tau_{eff} \quad \text{Eq. 4-15}$$

and the effective strain rate for grain boundary diffusion controlled creep is given by:

$$\dot{\epsilon}_{eff} = \frac{C_2 \exp\left(\frac{-Q_B}{RT}\right)}{TG^3} \tau_{eff} \quad \text{Eq. 4-16}$$

where,

C_1 and C_2 are material constants,

R is gas constant,

Q_L is the activation energy for lattice diffusion and

Q_B is the activation energy for boundary diffusion.

Substituting Eq. 4-15 and 4-16 into Eq. 4-14 respectively, it can be established that for lattice diffusion controlled creep,

$$\dot{\epsilon}_{ij} = -3\rho \frac{C_1 \exp\left(\frac{-Q_L}{RT}\right)}{TG^2} \times f\sigma_s \delta_{ij} \quad \text{Eq. 4-17}$$

and for grain boundary diffusion controlled creep,

$$\dot{\epsilon}_{ij} = -3\rho \frac{C_2 \exp\left(\frac{-Q_B}{RT}\right)}{TG^3} \times f\sigma_s \delta_{ij} \quad \text{Eq. 4-18}$$

The densification rate $\dot{\rho}$ can be expressed in terms of the volumetric strain rate $\dot{\epsilon}_v$ by noting that the mass remains constant during sintering and thus the volume change rate $\dot{V}$ is related to $\dot{\rho}$ by:

$$\frac{\dot{V}}{V} = -\frac{\dot{\rho}}{\rho} \quad \text{Eq. 4-19}$$

The volumetric strain rate $\dot{\epsilon}_v$ and the densification rate are thus related by:

$$\dot{\epsilon}_v = -\dot{\rho} / \rho \quad \text{Eq. 4-20}$$

Substituting Eq. 4-17 and 4-18 into Eq. 4-20, the densification rate for lattice diffusion controlled creep and grain boundary diffusion controlled creep are given by Eq. 4-21 and Eq. 4-22, respectively:

$$\dot{\rho} = 9\rho^2 \frac{C_1 \exp\left(\frac{-Q_L}{RT}\right)}{TG^2} \times f\sigma_s \quad \text{and} \quad \text{Eq. 4-21}$$

$$\dot{\rho} = 9\rho^2 \frac{C_2 \exp\left(\frac{-Q_B}{RT}\right)}{TG^3} \times f\sigma_s \quad \text{Eq. 4-22}$$

4.3.2 Sintering stress

For 1g of porous part, the number of grains, N_g , is given by:

$$N_g = \frac{V}{V_G} = \frac{2}{\rho \rho_T G^3} \quad \text{Eq. 4-23}$$

where V is the volume for 1g of porous part and ρ_T is the theoretical density of the material.

Intermediate sintering stage

For the intermediate sintering stage, the number of grains for 1g of porous part is assumed constant since grain growth is not significant at this stage. Due to limited grain growth, the change in grain boundary energy on the sintering stress is also negligible. Hence, the work done due to the sintering stress is assumed to be equivalent to the decrease in the surface energy alone and is expressed as:

$$\sigma_s dV_c = \gamma_s dA_c \quad \text{Eq. 4-24}$$

where A_c is the surface area of the cylindrical pores of radius r_c within the polyhedron, given by $24l_p \pi r_c$.

Assuming cylindrical pores with the axis coincident with three-grain edges for the open porosity geometry detailed in section 4.2, Eq. 4-24 can be reduced to:

$$\sigma_s = \frac{\gamma_s}{r_c} \quad \text{Eq. 4-25}$$

Substituting Eq. 4-7 into Eq. 4-25 gives the sintering stress as:

$$\sigma_s = \frac{5.15\gamma_s}{(1-\rho)^{1/2}G} \quad \text{Eq. 4-26}$$

Final sintering stage

For the final sintering stage, the work done due to the sintering stress is assumed to be equivalent to the decrease in the surface energy and grain boundary energy as in the sintering stress analysis by Raj [106] since grain growth is evident at this stage. Similar treatment of sintering stress was employed by other researchers [91, 104]. In this research, the effect of variation in grain number on the change of free energy is taken into account. For simplification, the effect of isolated pores on the sintering stress is excluded. The grain boundary area change due to the existence of pores is also included in the model. For grains where all the intersections of four grains in the structure are occupied by pores, the sintering stress is given by:

$$\sigma_s d(V_s N_g) = 0.5\gamma_b d(S_G N_g) - \gamma_b d(S_s N_g) + \gamma_s d(A_s N_g) \quad \text{Eq. 4-27}$$

Where,

$d(V_s N_g)$ is the change of the pore volume for a porous part containing 1g of material,

$0.5d(S_G N_g)$ is the change of the grain boundary area for a porous part containing 1g of material when the pores are excluded, and a weighing factor of 0.5 is prescribed for the surface area as a given grain boundary is shared between two adjacent grains,

$d(S_s N_g)$ is the change of grain boundary area due to the pores for a porous part

containing 1g of material and

$d(A_s N_g)$ is the change of the pores surface area for a porous part containing 1g of material.

Substituting Eqs. 4-3, 4-8, 4-9, 4-10, 4-23 into Eq. 4-27 gives:

$$\sigma_s d\left(\frac{6\lambda r_s^3}{\rho G^3}\right) = \gamma_b d\left[\frac{1}{\rho G}\left(\frac{3\sqrt{3}}{4} + \frac{3}{8}\right)\right] - \gamma_b d\left(\frac{6\alpha r_s^2}{\rho G^3}\right) + \gamma_s d\left(\frac{6\beta r_s^2}{\rho G^3}\right) \quad \text{Eq. 4-28}$$

Substituting Eq. 4-12 into Eq. 4-28 gives:

$$\sigma_s d\left(\frac{1-\rho}{2\rho}\right) = \gamma_b d\left[\frac{1}{\rho G}\left(\frac{3\sqrt{3}}{4} + \frac{3}{8}\right)\right] - \gamma_b d\left[\left(\frac{1-\rho}{12\lambda}\right)^{2/3} \frac{6\alpha}{\rho G}\right] + \gamma_s d\left[\left(\frac{1-\rho}{12\lambda}\right)^{2/3} \frac{6\beta}{\rho G}\right] \quad \text{Eq. 4-29}$$

Differentiating Eq. 4-29 gives:

$$\begin{aligned} \sigma_s d\rho = & \gamma_b \left(\frac{3\sqrt{3}}{2} + \frac{3}{4}\right) \frac{\rho}{G^2} dG + \gamma_b \left(\frac{3\sqrt{3}}{2} + \frac{3}{4}\right) \frac{1}{G} d\rho - \gamma_b \left(\frac{1-\rho}{12\lambda}\right)^{2/3} \frac{12\alpha\rho}{G^2} dG \\ & - \gamma_b \left(\frac{1}{12\lambda}\right)^{2/3} \frac{12\alpha}{G} \left[\frac{2}{3}\rho(1-\rho)^{-1/3} + (1-\rho)^{2/3}\right] d\rho + \gamma_s \left(\frac{1-\rho}{12\lambda}\right)^{2/3} \frac{12\beta\rho}{G^2} dG \\ & + \gamma_s \left(\frac{1}{12\lambda}\right)^{2/3} \frac{12\beta}{G} \left[\frac{2}{3}\rho(1-\rho)^{-1/3} + (1-\rho)^{2/3}\right] d\rho \end{aligned} \quad \text{Eq. 4-30}$$

According to Gouvêa and Ricardo [120], relative density is related to grain size as follows:

$$\frac{d\rho}{dG} = \frac{k' \rho^2}{G^2} \quad \text{Eq. 4-31}$$

where k' can be determined as discussed in Section 4.4. Considering its empirical fitness with experimental results in their research, the equation is used in this model.

Substituting Eq. 4-31 into Eq. 4-30 gives:

$$\sigma_s = \frac{3.35\gamma_b}{k'\rho} + \frac{3.35\gamma_b}{G} + \left(\frac{1}{12\lambda}\right)^{2/3} \frac{12(\beta\gamma_s - \alpha\gamma_b)\left(1 - \frac{1}{3}\rho\right)}{G(1-\rho)^{1/3}} + \left(\frac{1-\rho}{12\lambda}\right)^{2/3} \frac{12(\beta\gamma_s - \alpha\gamma_b)}{k'\rho}$$

Eq. 4-32

4.3.3 Internal gas pressure

During sintering under a gas atmosphere, if the gas diffusivity in the material is not very high, the entrapped gas after pore closure will induce internal gas pressure that affects the densification rate. If the gas cannot diffuse through the part and if ideal gas behavior is assumed, the pressure in the pores is given by:

$$P_i = \frac{P_{cl}V_{cl}T}{T_{cl}V_i}$$

Eq. 4-33

Where,

P_i and P_{cl} are the instantaneous internal gas pressure and the gas pressure at the time of pore closure,

V_i and V_{cl} are the instantaneous pore volume and the pore volume at the time of pore closure for the porous part and

T_{cl} is the temperature at the time of pore closure.

From Kraft and Riedel's equation [148], the pressure in the pores can be expressed by replacing the pore volume with relative density and is expressed as:

$$P_i = \frac{P_{cl}(1-\rho_{cl})\rho T}{T_{cl}(1-\rho)\rho_{cl}} = \frac{H\rho T}{(1-\rho)} \quad \text{Eq. 4-34}$$

Where H represents $\frac{P_{cl}(1-\rho_{cl})}{T_{cl}\rho_{cl}}$ and ρ_{cl} is the relative density at the time of pore closure.

Thus, the effective pressure, P_{eff} , during sintering is given by:

$$P_{eff} = \sigma_s - P_i \quad \text{Eq. 4-35}$$

4.3.4 Grain growth

Densification usually takes place with simultaneous grain growth, particularly during the final sintering stage. Therefore, grain growth based on Brook's equations [25] is included in the model and can be expressed as follows:

(i) For surface diffusion controlled pore drag

$$G^4 - G_0^4 = \frac{K_1}{T} t \exp\left(\frac{-Q_s}{RT}\right) \quad \text{Eq. 4-36}$$

where Q_s is the activation energy for surface diffusion and K_1 is a material constant.

(ii) For lattice diffusion controlled pore drag

$$G^3 - G_0^3 = \frac{K_2}{T} t \exp\left(\frac{-Q_L}{RT}\right) \quad \text{Eq. 4-37}$$

where Q_L is the activation energy for lattice diffusion and K_2 is a material constant.

(iii) For boundary diffusion controlled grain growth

$$G^2 - G_0^2 = \frac{K_3}{T} t \exp\left(\frac{-Q_B}{RT}\right) \quad \text{Eq. 4-38}$$

where Q_B is the activation energy for boundary diffusion and K_3 is a material constant.

4.4 Procedure for the model

(a) Grain growth

To compute grain growth, the dominant mechanism is first determined for the part: grain growth under surface diffusion controlled pore drag or lattice diffusion controlled pore drag or boundary diffusion controlled grain growth. Correspondingly, the respective activation energy for grain growth is determined in order to establish the relationship between the diffusion coefficients and the sintering temperatures. After obtaining the material constants K_1 , K_2 or K_3 , the grain growth can be computed from Eqs. 4-36 to 4-38.

(b) Densification

Two sintering stress expressions are used to describe the densification process: Eq. 4-26 for intermediate sintering stage and Eq. 4-32 for final sintering stage. For the sintering stress at the final sintering stage, Eq. 4-31 is integrated to give the following expression:

$$\frac{1}{\rho} - \frac{1}{\rho_o} = k \left(\frac{1}{G} - \frac{1}{G_o} \right) \quad \text{Eq. 4-39}$$

Where ρ_o is the initial relative density and G_o is the initial grain size. A plot of

$\left(\frac{1}{\rho} - \frac{1}{\rho_o} \right)$ against $\left(\frac{1}{G} - \frac{1}{G_o} \right)$ is made and k' is determined from the slope of the plot.

The dominant mechanism and the respective activation energy for densification of the part as well as material constant are to be determined. For a material system where internal gas pressure exists, H is fitted from the density limit. When Eq. 4-21 or 4-22 is combined with expressions for sintering stress, internal gas pressure and grain growth, the density-time plot at various temperatures can be computed.

4.5 Conclusions

A new sintering stress expression for the final sintering stage is developed and a constitutive model incorporating the expression has been established. The various expressions derived are shown below:

(a) Densification rate

(i) For a material system under lattice diffusion controlled creep, the densification rate is given by:

$$\dot{\rho} = 9\rho^2 \frac{C_1 \exp\left(\frac{-Q_L}{RT}\right)}{TG^2} \times f\sigma_s$$

(ii) For a material system under grain boundary diffusion controlled creep, the densification rate is given by:

$$\dot{\rho} = 9\rho^2 \frac{C_2 \exp\left(\frac{-Q_B}{RT}\right)}{TG^3} \times f\sigma_s$$

The equations given in sections (i) and (ii) above are compared with Johnson's [133] combined-stage sintering model in Appendix E.

(b) Sintering stress

(i) For intermediate sintering stage, the sintering stress is given by:

$$\sigma_s = \frac{5.15\gamma_s}{(1-\rho)^{1/2}G}$$

(ii) For final sintering stage, the sintering stress is given by:

$$\sigma_s = \frac{3.35\gamma_b}{k'\rho} + \frac{3.35\gamma_b}{G} + \left(\frac{1}{12\lambda}\right)^{2/3} \frac{12(\beta\gamma_s - \alpha\gamma_b)\left(1 - \frac{1}{3}\rho\right)}{G(1-\rho)^{1/3}} + \left(\frac{1-\rho}{12\lambda}\right)^{2/3} \frac{12(\beta\gamma_s - \alpha\gamma_b)}{k'\rho}$$

(c) Internal gas pressure and effective pressure

For a material system where internal gas pressure is included, the effective pressure during sintering is given by:

$$P_{eff} = \sigma_s - \frac{H\rho T}{(1-\rho)}$$

where H is an item representing $\frac{P_{cl}(1-\rho_{cl})}{T_{cl}\rho_{cl}}$.

(d) Grain growth based on Brook's equations

Grain growth under surface diffusion controlled pore drag is given by:

$$G^4 - G_0^4 = \frac{K_1}{T} t \exp\left(\frac{-Q_s}{RT}\right)$$

Grain growth under lattice diffusion controlled pore drag is given by:

$$G^3 - G_0^3 = \frac{K_2}{T} t \exp\left(\frac{-Q_L}{RT}\right)$$

Boundary diffusion controlled grain growth is given by:

$$G^2 - G_0^2 = \frac{K_3}{T} t \exp\left(\frac{-Q_B}{RT}\right)$$

Chapter 5 Characterization of Sintered Microstructured Parts

After sintering, sintered microstructured parts with microsize structures of various sizes were characterized with aspect to grain size and porosity. This is to examine the influence of size on the sintering behavior. The grain growth of the sub-structure, in the millimeter regime, and microsize structures of various sizes is covered in section 5.1. Section 5.2 records the densification of the sub-structure and various microsize structures. The effects of internal gas pressure on densification as well as the different sintering behavior between the sub-structure and various microsize structures are discussed in section 5.3 followed by conclusions in section 5.4.

5.1 Grain growth of sub-structure and microsize structures

5.1.1 Microstructure

Figures 5.1 to 5.6 show the etched microstructure of the sub-structure and microsize structures of various sizes sintered at different sintering schedule. It can be seen that grain growth occurred with increasing time and temperature. For different sintering time, from 1200 °C to 1300 °C, the microsize structures all had larger grain size as compared to the sub-structure, which indicates grain growth was promoted when the size of the sintered part reduced into the regime of microns. The difference in grain growth is because the higher porosity at the sub-structure may have hindered grain boundary migration.

The morphology of the pores on the microsize structures is also different from that on the sub-structure. While nearly all the pores on the sub-structure were located at the intersections of the grains, a fraction of the pores on the microsize structures were detached and isolated within the grains. Some pores were located at the two-grain boundary interfaces. During sintering, the detachment of pores from three-grain junctions onto the two-grain interfaces precedes the pore separation and the complete separation of pores from grain boundaries occurs when the pores are located on two-grain boundary interfaces [116]. The observed pores at the two-grain interfaces correspond to the pore separation event.

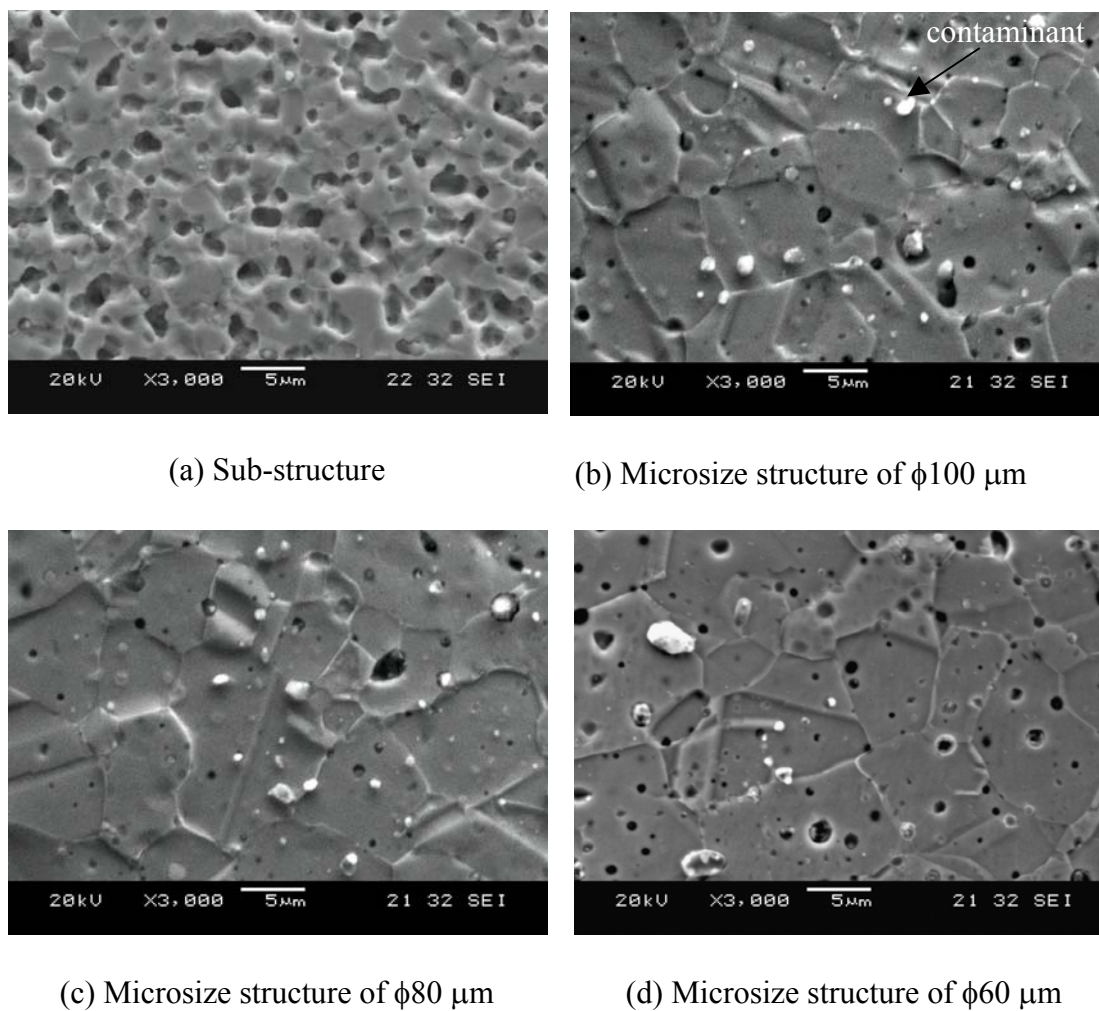
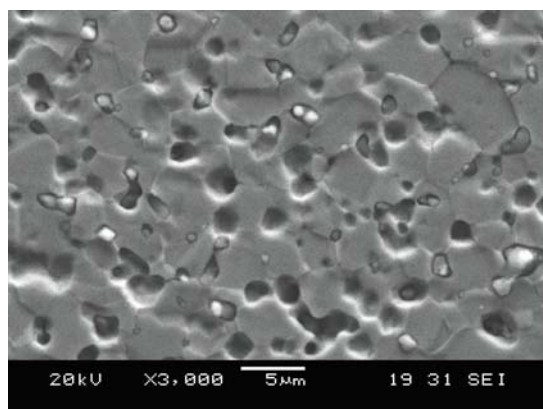
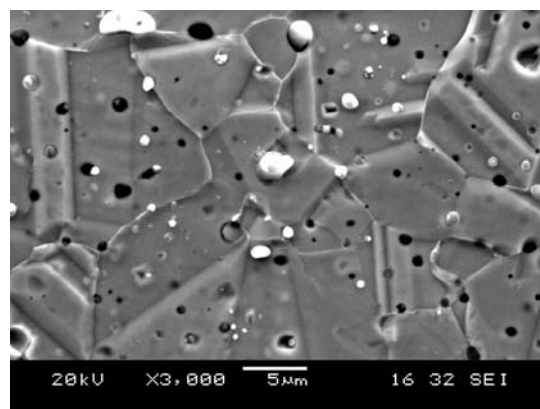


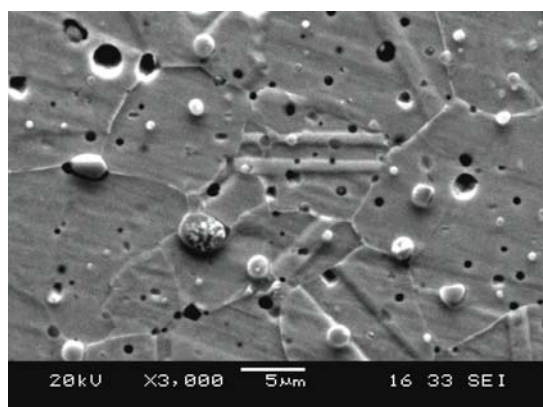
Figure 5.1 Microstructure of microstructured parts sintered at 1200 °C for 10 minutes



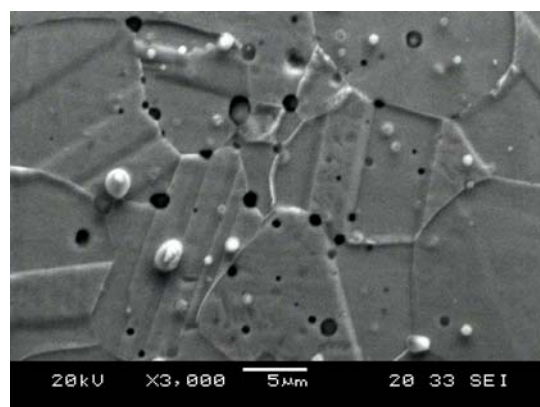
(a) Sub-structure



(b) Microsize structure of $\phi 100 \mu\text{m}$

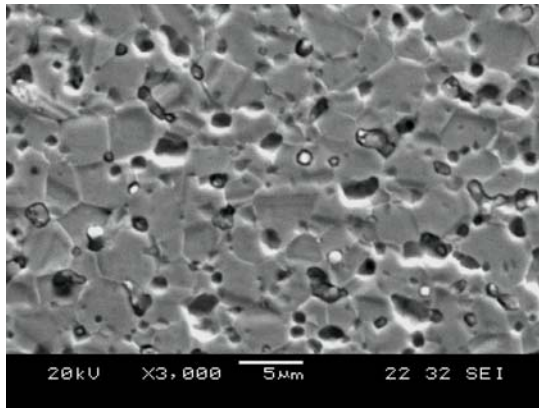


(c) Microsize structure of $\phi 80 \mu\text{m}$

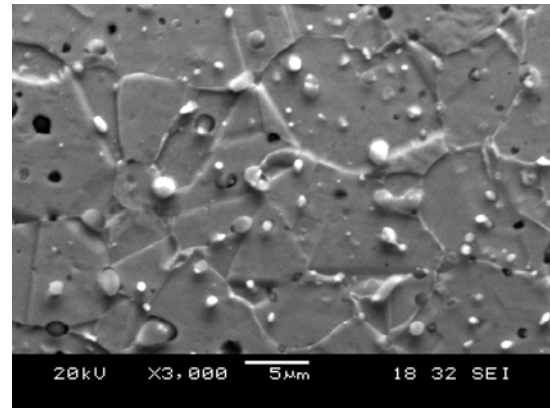


(d) Microsize structure of $\phi 60 \mu\text{m}$

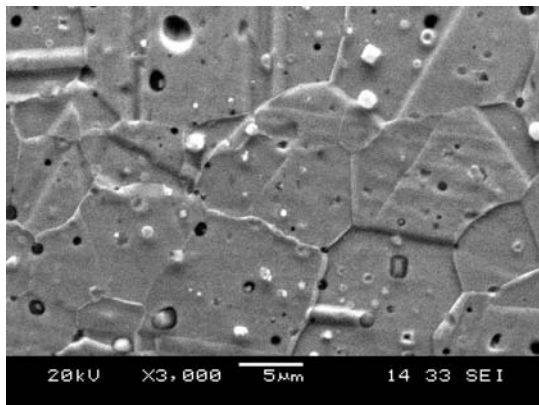
Figure 5. 2 Microstructure of microstructured parts sintered at 1200 °C for 120 minutes



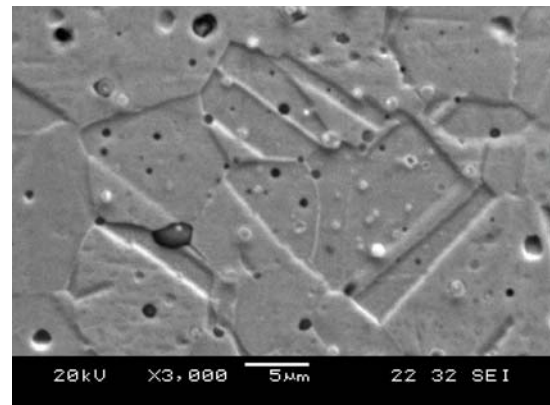
(a) Sub-structure



(b) Microsize structure of $\phi 100 \mu\text{m}$

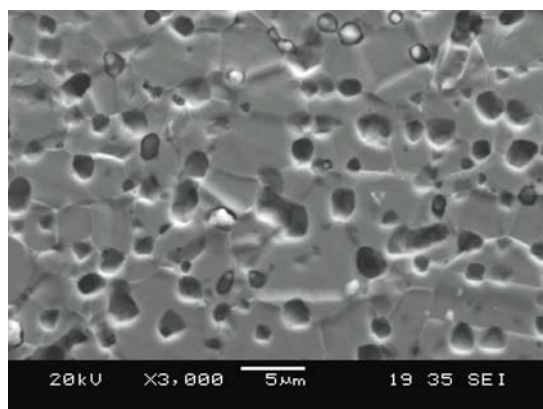


(c) Microsize structure of $\phi 80 \mu\text{m}$

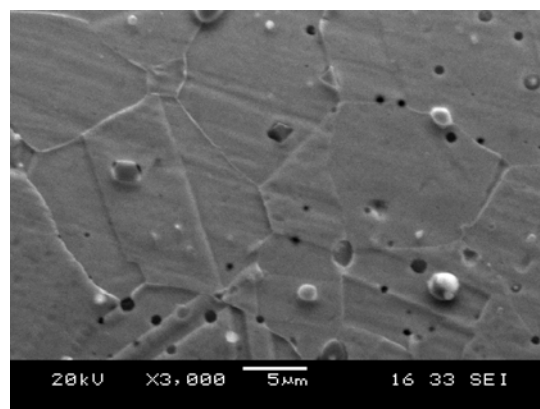


(d) Microsize structure of $\phi 60 \mu\text{m}$

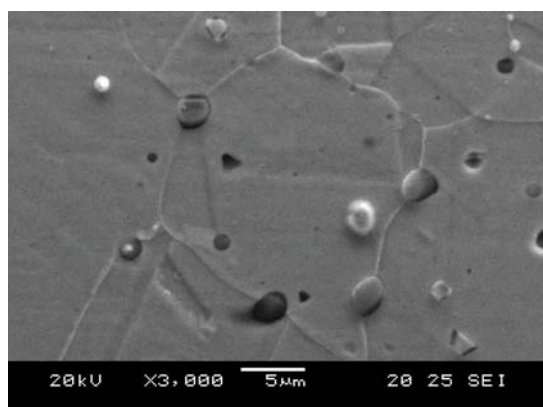
Figure 5.3 Microstructure of microstructured parts sintered at 1250 °C for 10 minutes



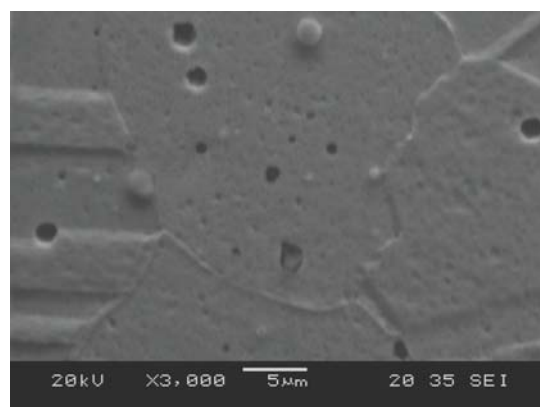
(a) Sub-structure



(b) Microsize structure of $\phi 100 \mu\text{m}$

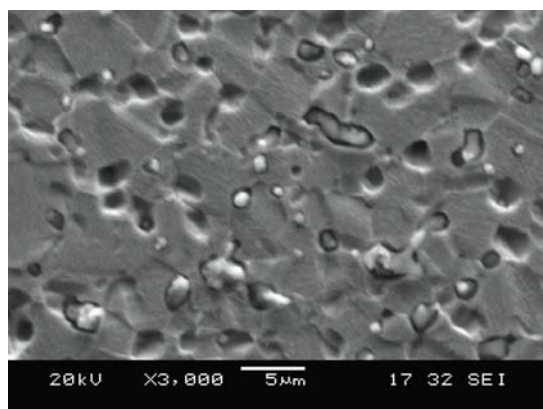


(c) Microsize structure of $\phi 80 \mu\text{m}$

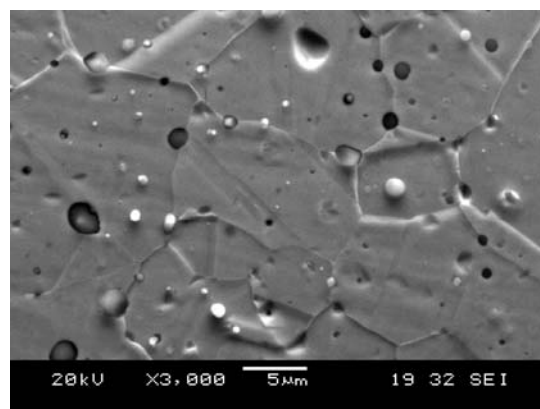


(d) Microsize structure of $\phi 60 \mu\text{m}$

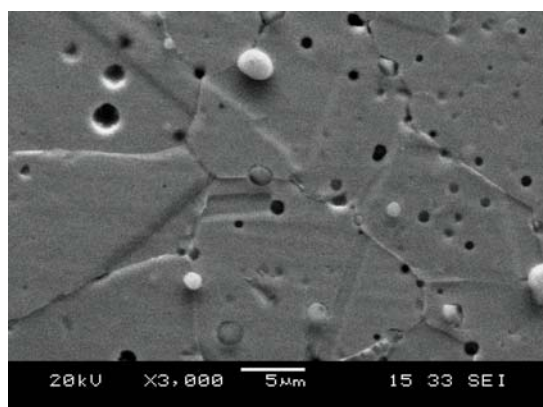
Figure 5. 4 Microstructure of microstructured parts sintered at 1250 °C for 120 minutes



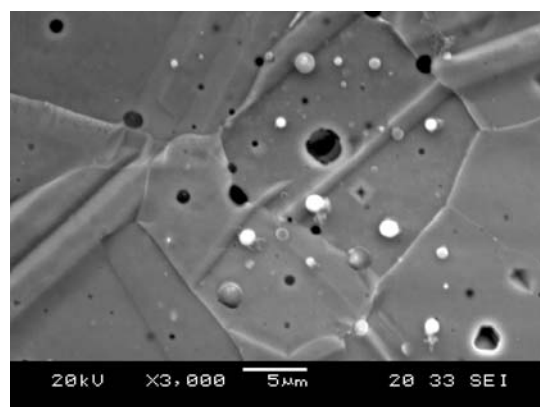
(a) Sub-structure



(b) Microsize structure of $\phi 100 \mu\text{m}$

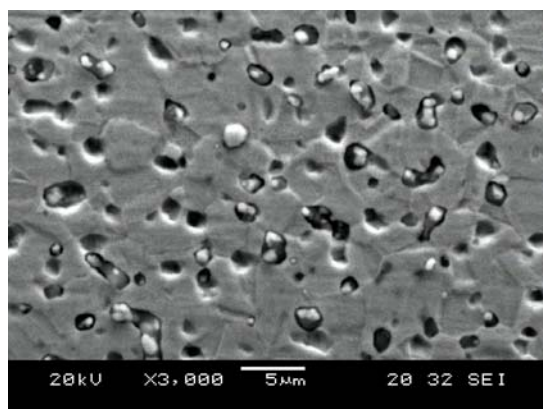


(c) Microsize structure of $\phi 80 \mu\text{m}$

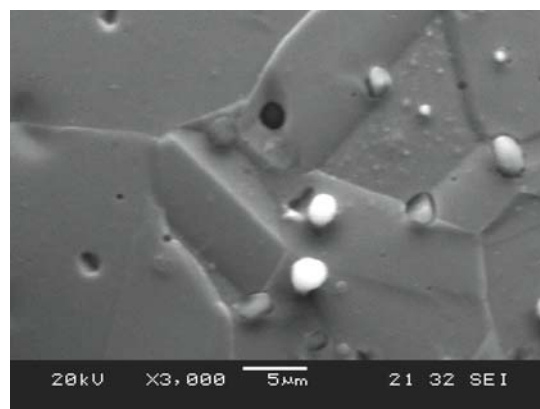


(d) Microsize structure of $\phi 60 \mu\text{m}$

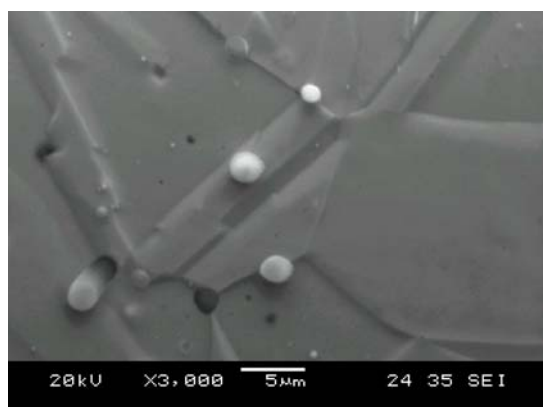
Figure 5. 5 Microstructure of microstructured parts sintered at 1300 °C for 10 minutes



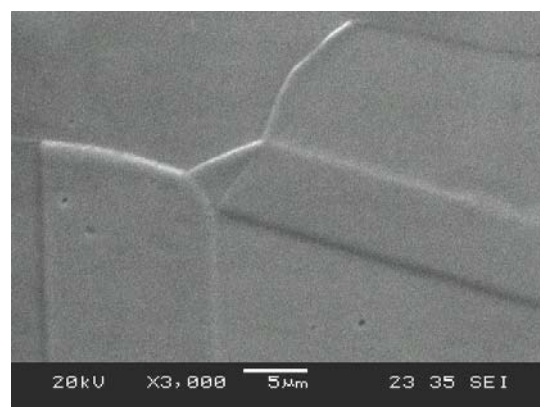
(a) Sub-structure



(b) Microsize structure of $\phi 100 \mu\text{m}$



(c) Microsize structure of $\phi 80 \mu\text{m}$

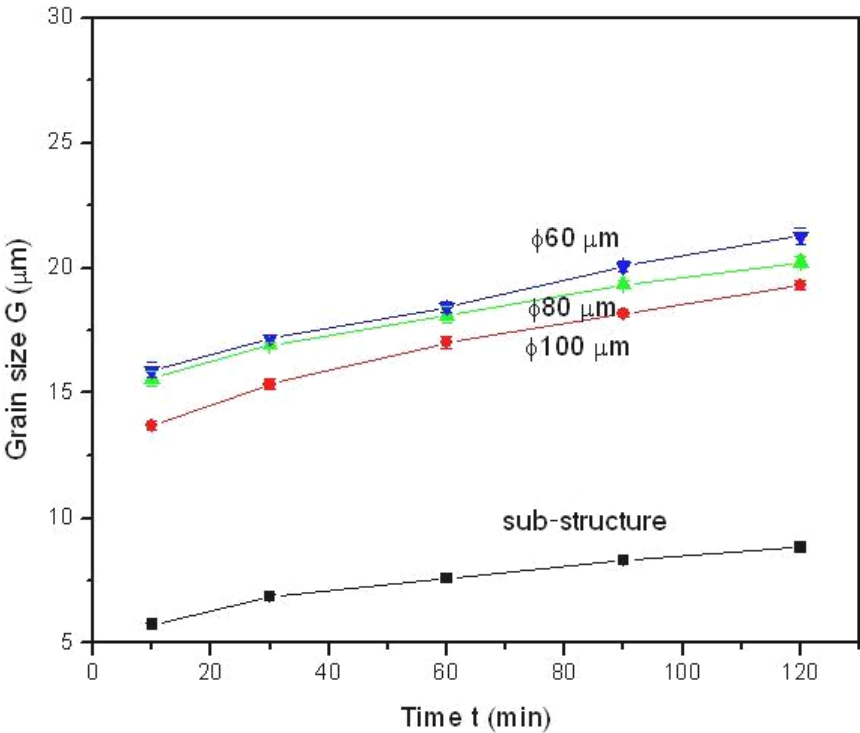


(d) Microsize structure of $\phi 60 \mu\text{m}$

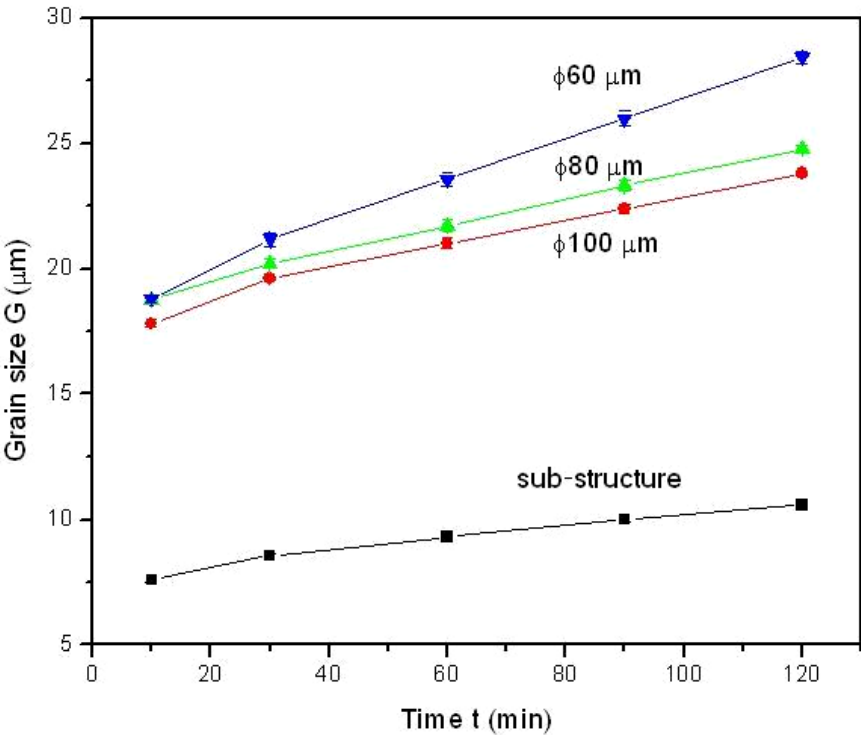
Figure 5.6 Microstructure of microstructured parts sintered at 1300 °C for 90 minutes

5.1.2 Grain size-time plot

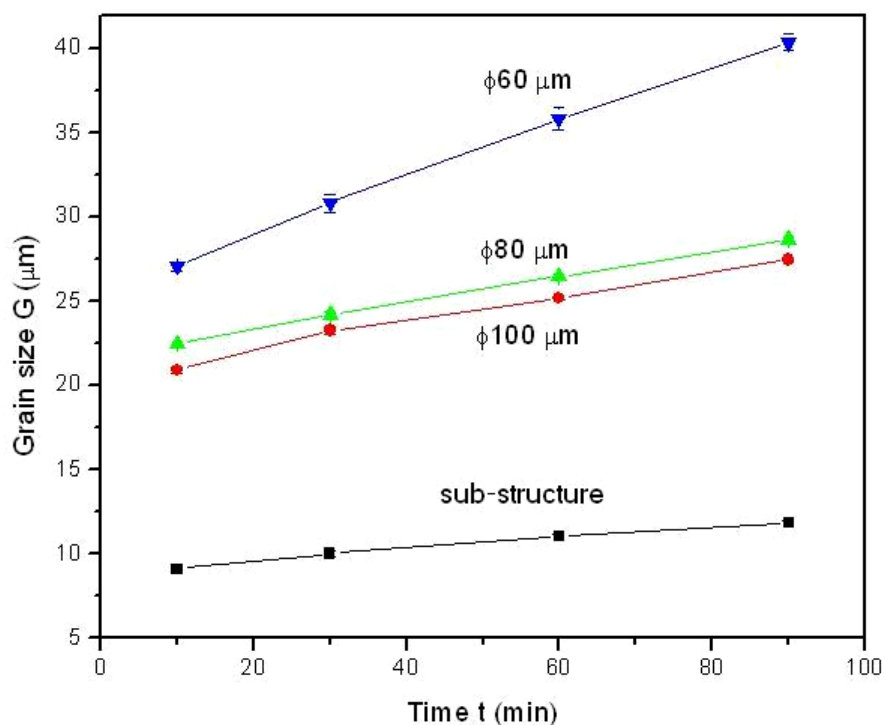
Figure 5.7 compares the grain size between the sub-structure and various microsize structures. Generally, microsize structures of $\phi 60\text{ }\mu\text{m}$ yielded the largest grain size for the same sintering condition. It indicates that size reduction, even within the regime of microns, facilitates grain growth. The slopes of grain size versus time plots show that the rate of grain growth of microsize structures is also higher than that of the sub-structure. The grain size differences between various microsize structures increase with time and temperature. Using a shorter sintering time at a lower temperature, for example 10 min at $1200\text{ }^{\circ}\text{C}$, the average grain size difference between microsize structures of $\phi 100\text{ }\mu\text{m}$ and $\phi 60\text{ }\mu\text{m}$ is just $2.22\text{ }\mu\text{m}$. When time and temperature are increased, such as 90 min at $1300\text{ }^{\circ}\text{C}$, the average grain size difference between microsize structures of $\phi 100\text{ }\mu\text{m}$ and $\phi 60\text{ }\mu\text{m}$ rises to $12.90\text{ }\mu\text{m}$.



(a) $1200\text{ }^{\circ}\text{C}$



(b) $1250\text{ }^{\circ}\text{C}$



(c) 1300 °C

Figure 5.7 Grain size of microstructured parts sintered at different temperatures

5.2 Densification of sub-structure and microsize structures

5.2.1 Microstructure

Figures 5.8 to 5.13 show the porosity of the polished sub-structure and various microsize structures sintered at different time and temperatures. It can be seen that generally the porosity decreases with increasing time and temperature. From 1200 °C to 1300 °C, the microsize structures all had lower porosity as compared to the sub-structure, which indicates densification is promoted when the size of the sintered body

reduces into the regime of micrometer. While some interconnected pores could be observed on the sub-structure, the majority of pores on the microsize structures were nearly spherical closed pores.

On the microsize structures, the majority of pores were circumscribed by a “dense” layer nearly devoid of pores. The thickness of the dense layer was found to increase with increasing sintering temperature and time. At a high temperature for a long time, for example 1300 °C for 90 min, nearly all the pores were absent from the microsize structures of $\phi 60\text{ }\mu\text{m}$ while some pores still remained on the sub-structure and microsize structures of $\phi 100\text{ }\mu\text{m}$ and $\phi 80\text{ }\mu\text{m}$.

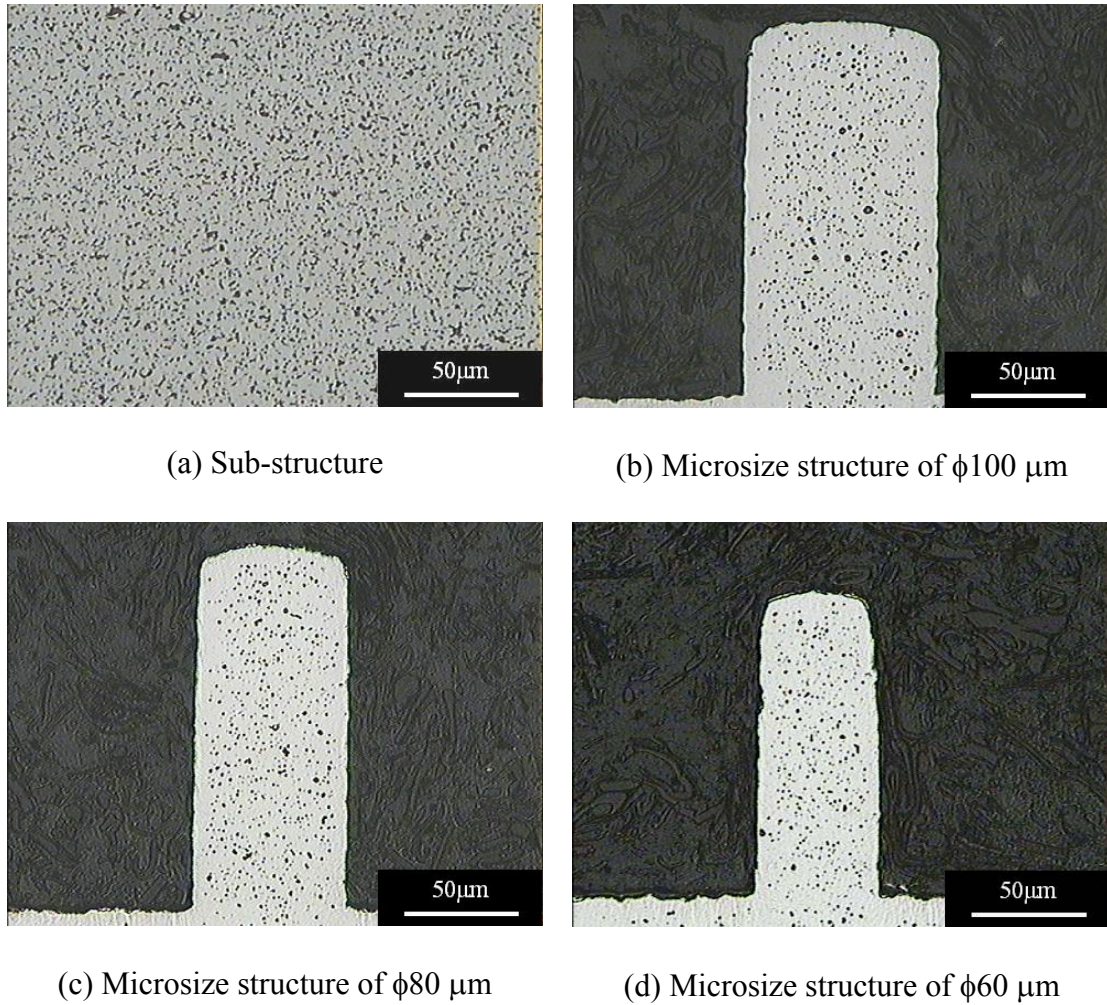


Figure 5.8 Porosity of microstructured parts sintered at 1200 °C for 10 minutes

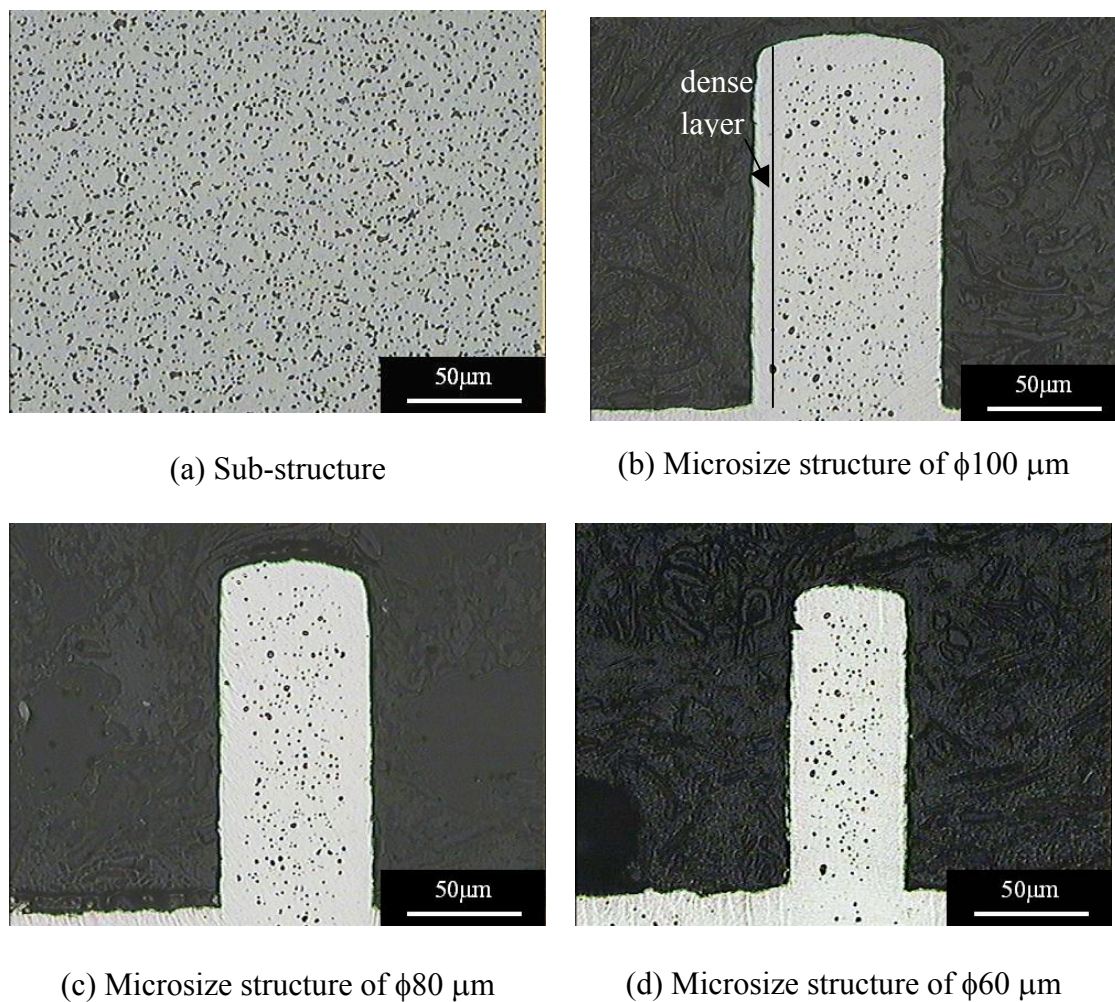


Figure 5.9 Porosity of microstructured parts sintered at 1200 °C for 120 minutes

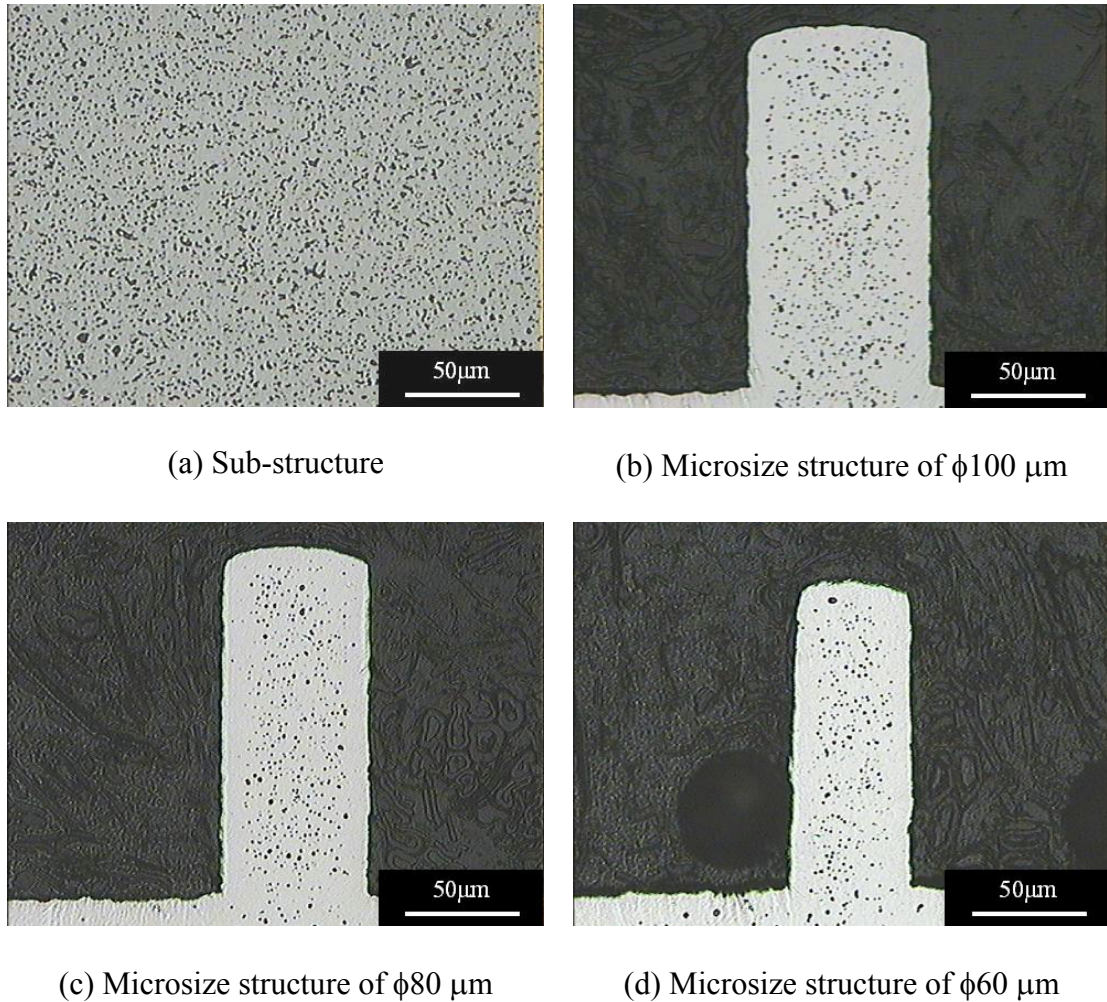


Figure 5.10 Porosity of microstructured parts sintered at 1250 °C for 10 minutes

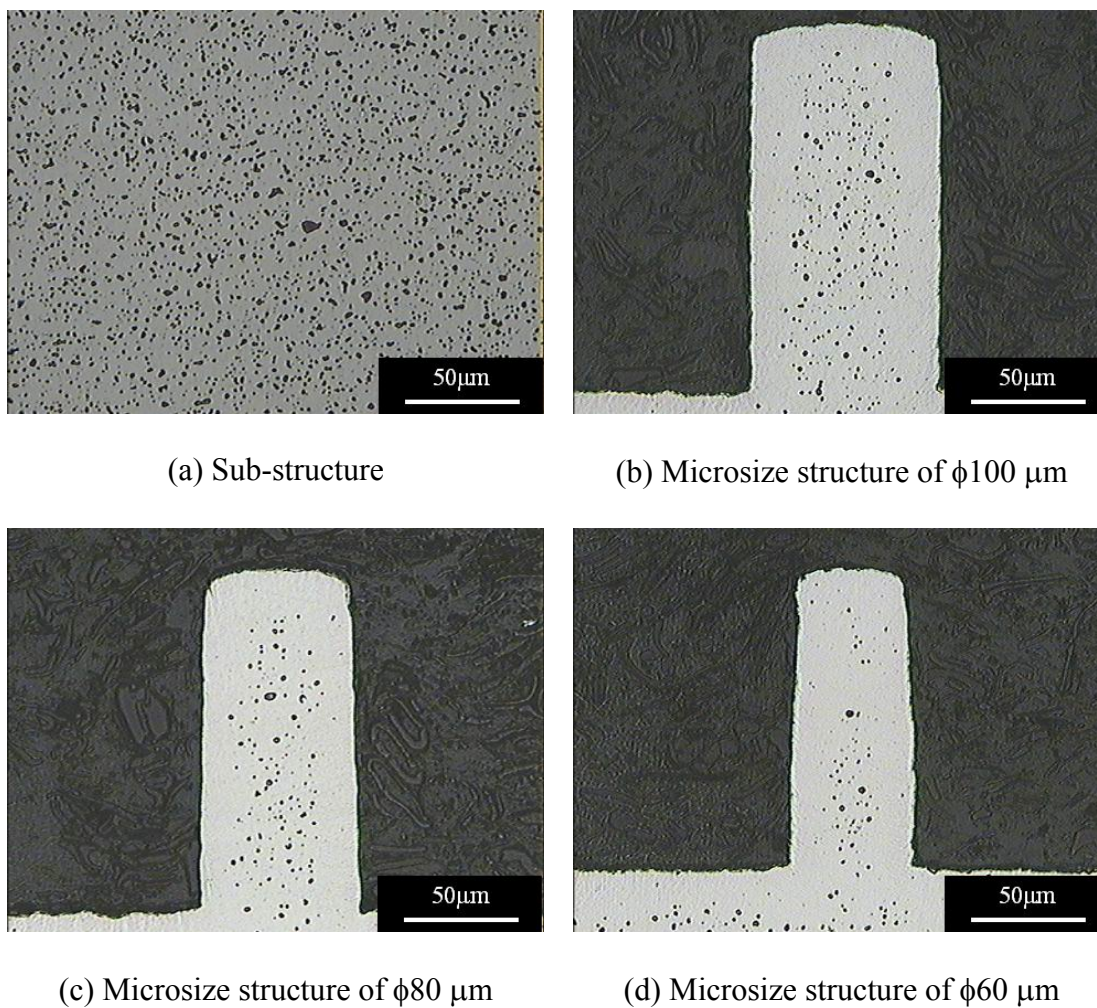


Figure 5.11 Porosity of microstructured parts sintered at 1250 °C for 120 minutes

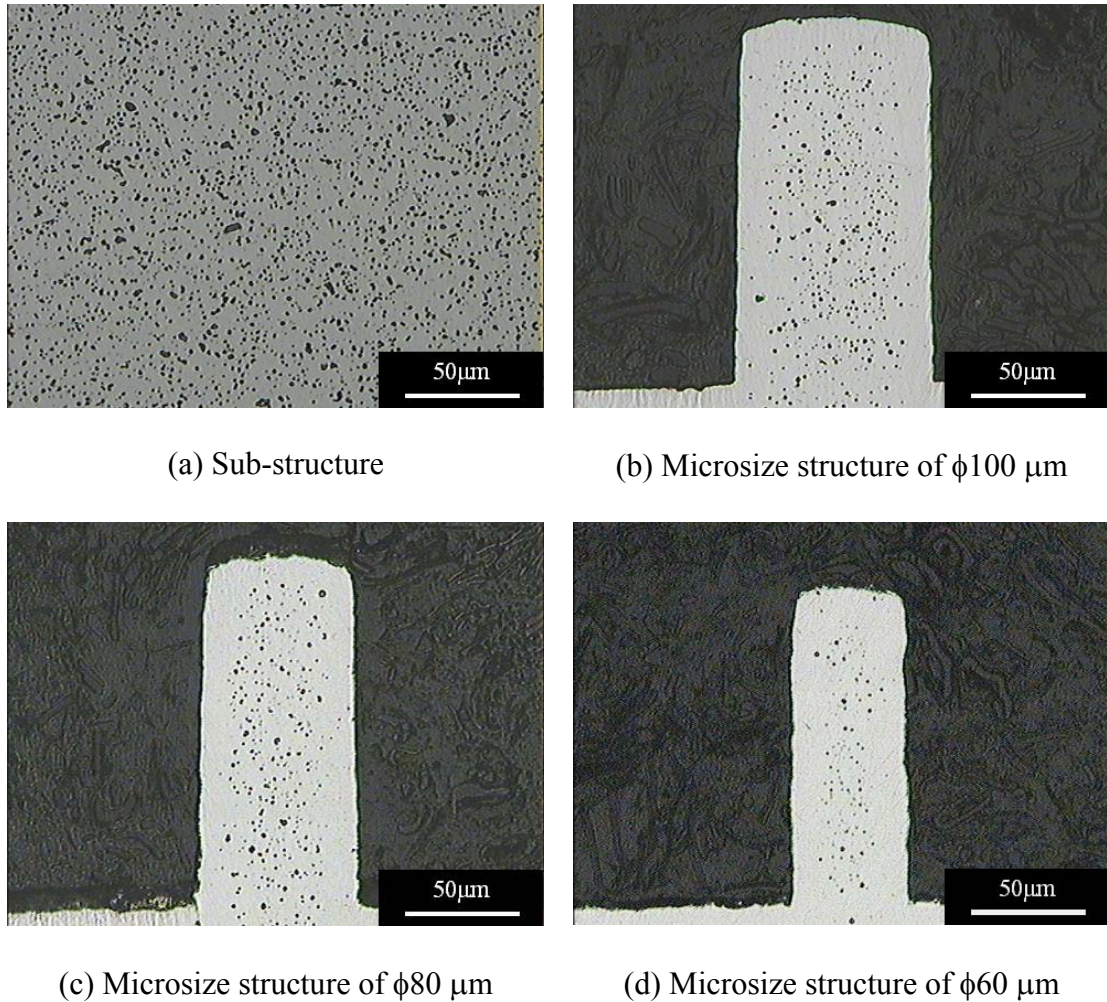


Figure 5.12 Porosity of microstructured parts sintered at 1300 °C for 10 minutes

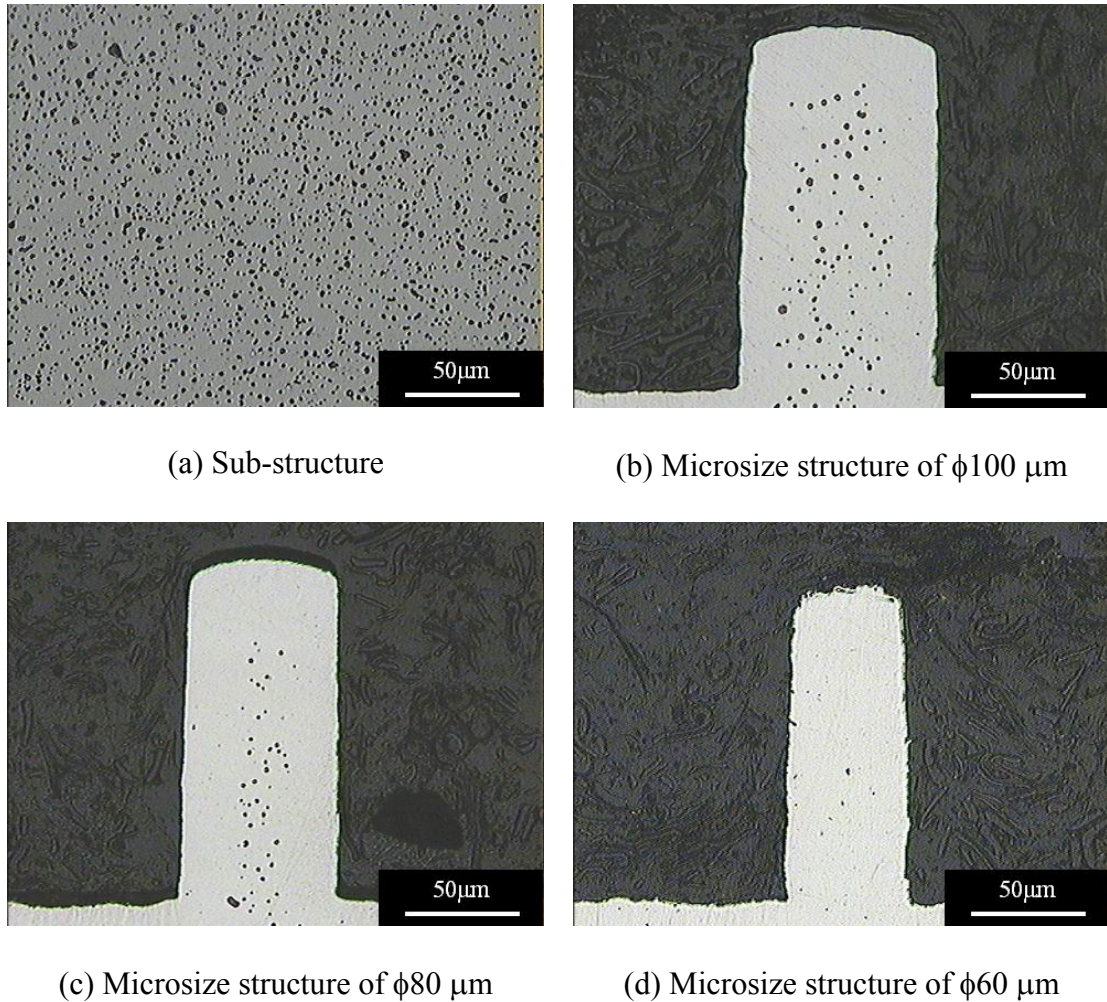
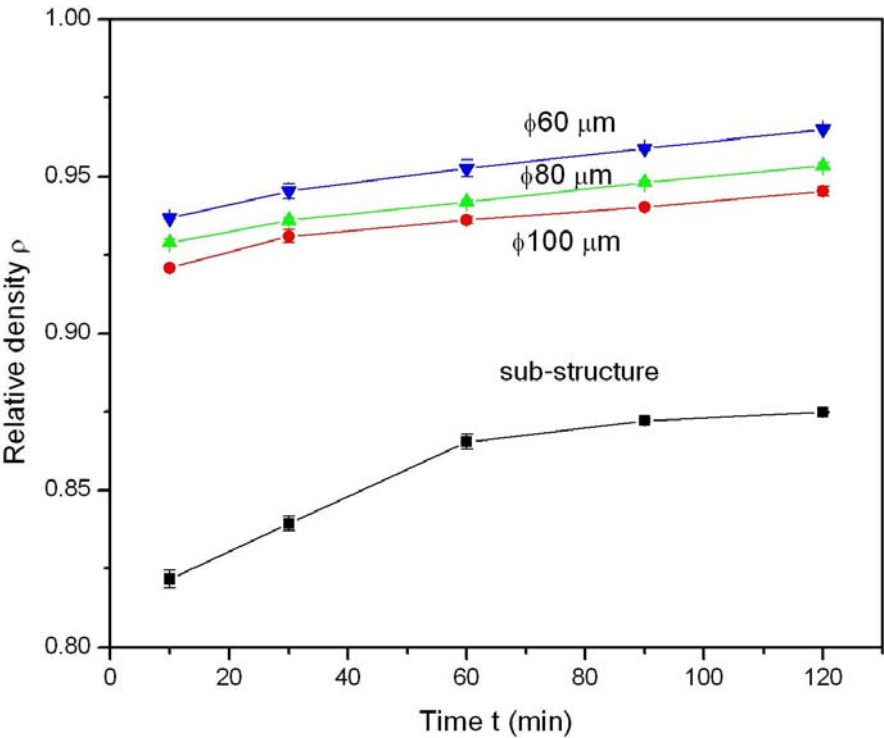


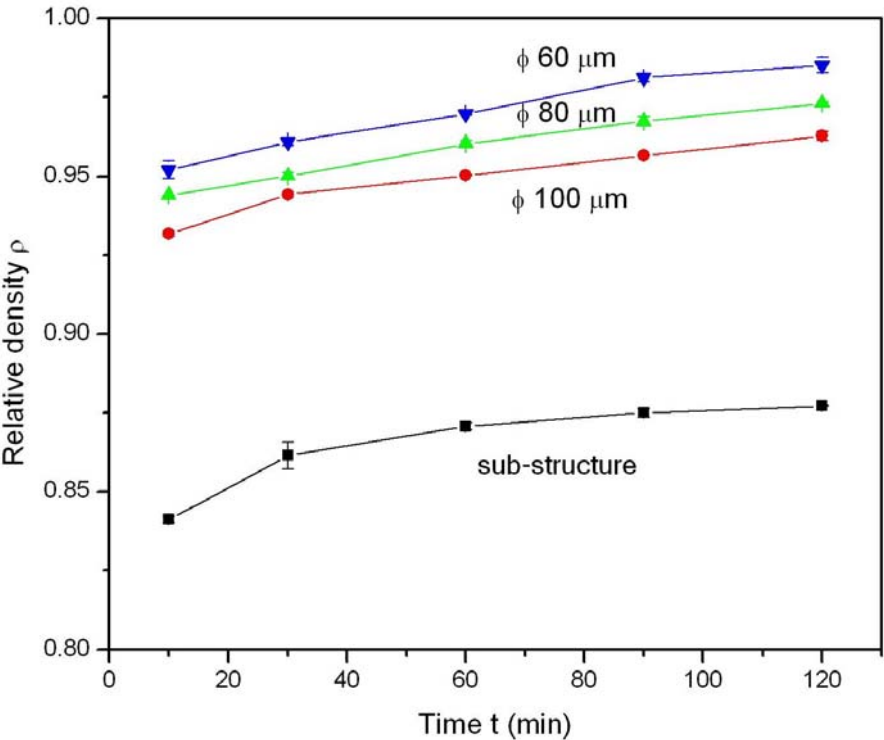
Figure 5.13 Porosity of microstructured parts sintered at 1300 °C for 90 minutes

5.2.2 Density-time plot

Figure 5.14 shows the densities of the sub-structure and the various microsize structures. Generally, smaller dimensions yielded higher density under the same sintering condition. This indicates that size reduction, even within the regime of micrometer, facilitates densification. The densification rate (the slope of ρ versus t) of the sub-structure is faster than that of the microsize structures from 10 min to 60 min at a lower temperature of 1200 °C. This difference in densification rate may be ascribed to the lower density of the sub-structure. As the temperature increases to 1300 °C, however, the densification rate of the sub-structure is no longer higher than that of the microsize structures. It is to be noted that unlike the various microsize structures, a decrease in density is found on the sub-structure with prolong time of 90 min at a high temperature of 1300 °C. The decrease in density is attributed to the internal gas pressure discussed in section 5.3.1.



(a) 1200 °C



(b) 1250 °C

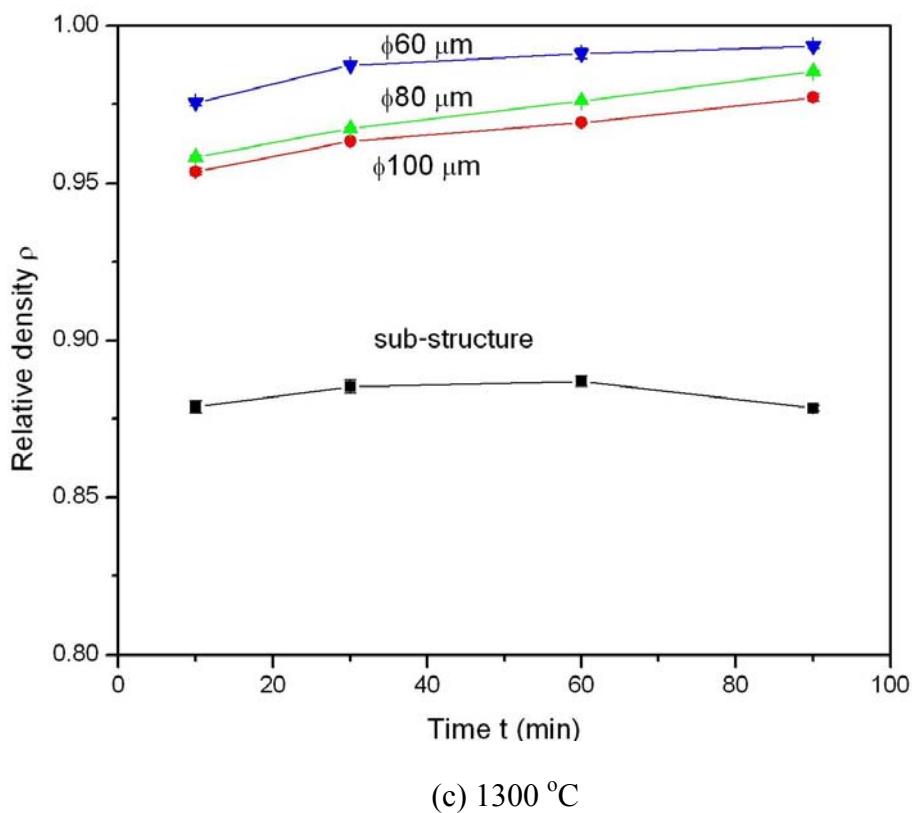


Figure 5.14 Density of microstructured parts sintered at different temperatures

5.3 Discussion

5.3.1 Internal gas pressure

As shown in Figure 5.14, a decrease in the density of the sub-structure was observed when sintered at 1300 °C for 90 min. The effect of internal gas pressure on densification attributes to the decrease in density. For water atomized 316L stainless steel powder, oxides could obstruct the formation of metallic bonds between the powder particles during sintering. Therefore, reducing atmosphere such as hydrogen was used in this

research. During hydrogen sintering, however, internal gas pressure may be generated if a portion of product gas of H_2O gets trapped within the pores after pores closure. The internal gas pressure, assuming ideal gas behavior, increases with time or temperature with pore shrinkage. In the extreme case, the density decreases (as observed in this study) since it counterbalances the sintering stress.

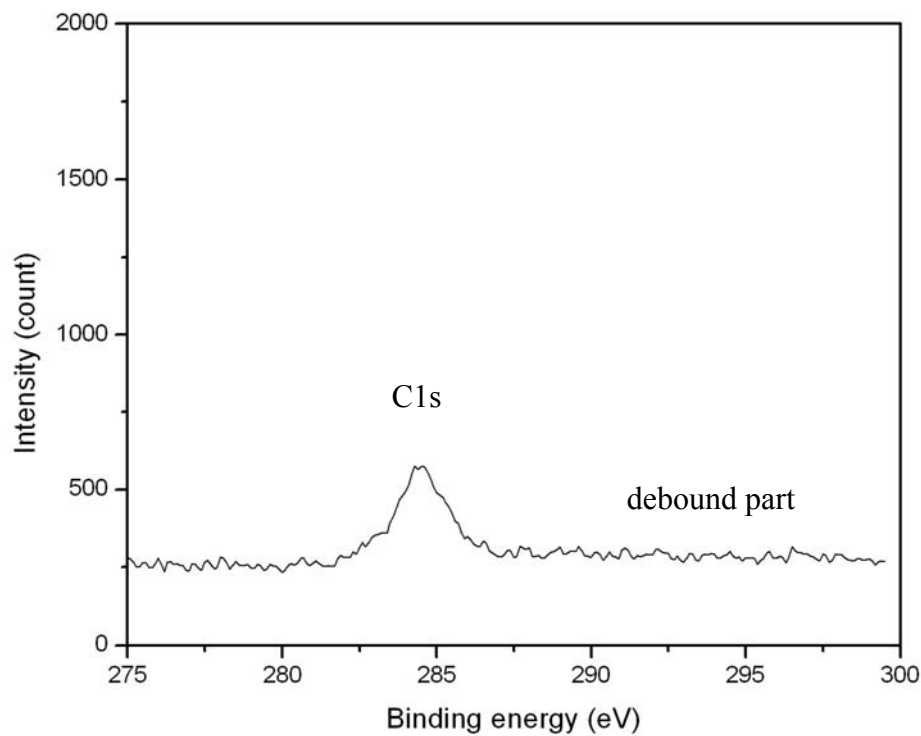
5.3.2 Grain growth and densification of sub-structure and microsize structures

Ashby's method [98] was used to analyze the sintering of microstructured parts: the intermediate stage characterized by $0.8 \leq \rho \leq 0.92$ and final stage, $\rho > 0.92$. According to this, the microsize structures of $\phi 100 \mu m$, $\phi 80 \mu m$ and $\phi 60 \mu m$ are in the final sintering stage while the sub-structure is in the intermediate sintering stage within the temperatures studied. This explains the smaller grain size on the sub-structure where grain growth is retarded with the presence of interconnected pores during the intermediate sintering stage.

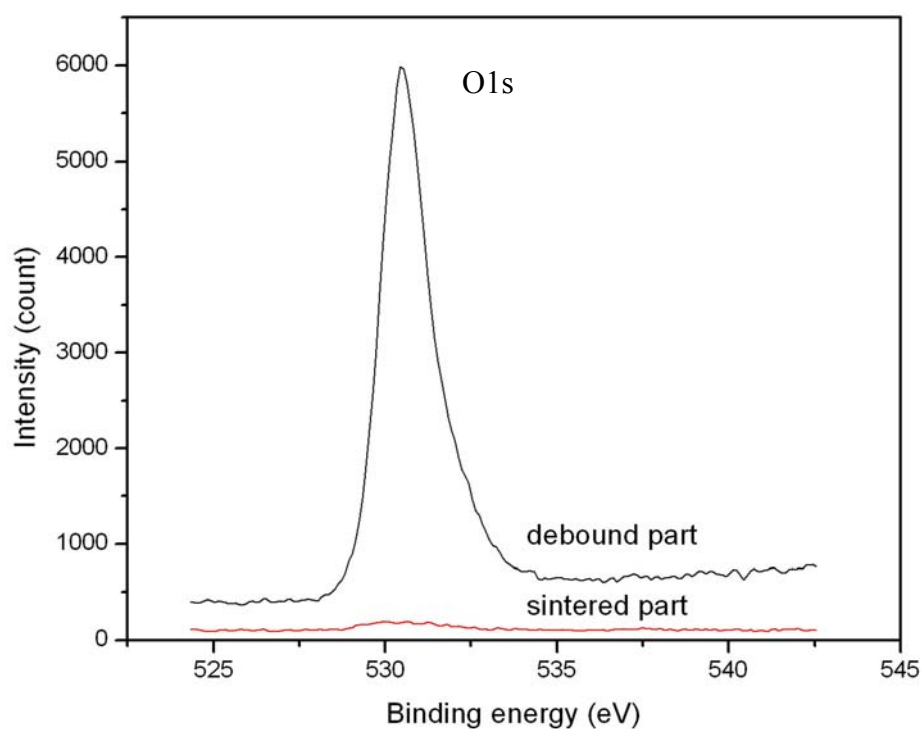
The XPS spectra in Figure 5.15 show that there were carbon and oxygen on the debound part. A $C1s$ peak appearing at 284.5 eV is identified as free carbon according to literature [174]. Oxygen profile was de-convoluted into two binding energies: 530.4 and 531.9 eV, see Figure 5.16, which had been identified as the presence of oxide and hydroxide [175]. Thus, C and O here are ascribed to binder decomposition and oxidation during debinding. After sintering, no carbon was detected by XPS while oxygen, in the form of oxide, still remained even though the amount was reduced

significantly. As C was observed in the form of free carbon on the debound part and no carbide was detected after sintering, its influence on the densification of the microstructured parts is neglected.

The oxides on the microstructured parts and ensuing internal gas pressure during hydrogen sintering are attributed to the difference in sintering behavior between the sub-structure and various microsize structures. During sintering, the soluble hydrogen concentration in the material is not uniform. It decreases inward along the diffusion path, and this induces more effective oxides removal on the smaller microsize structures due to its larger surface-to-volume ratio. With respect to the internal gas pressure, the smaller microsize structure has higher density than the sub-structure because its larger surface-to-volume ratio makes it easier for the gas to egress, which is beneficial to densification.



(a) Carbon



(b) Oxygen

Figure 5.15 XPS spectra of debound and sintered microstructured parts

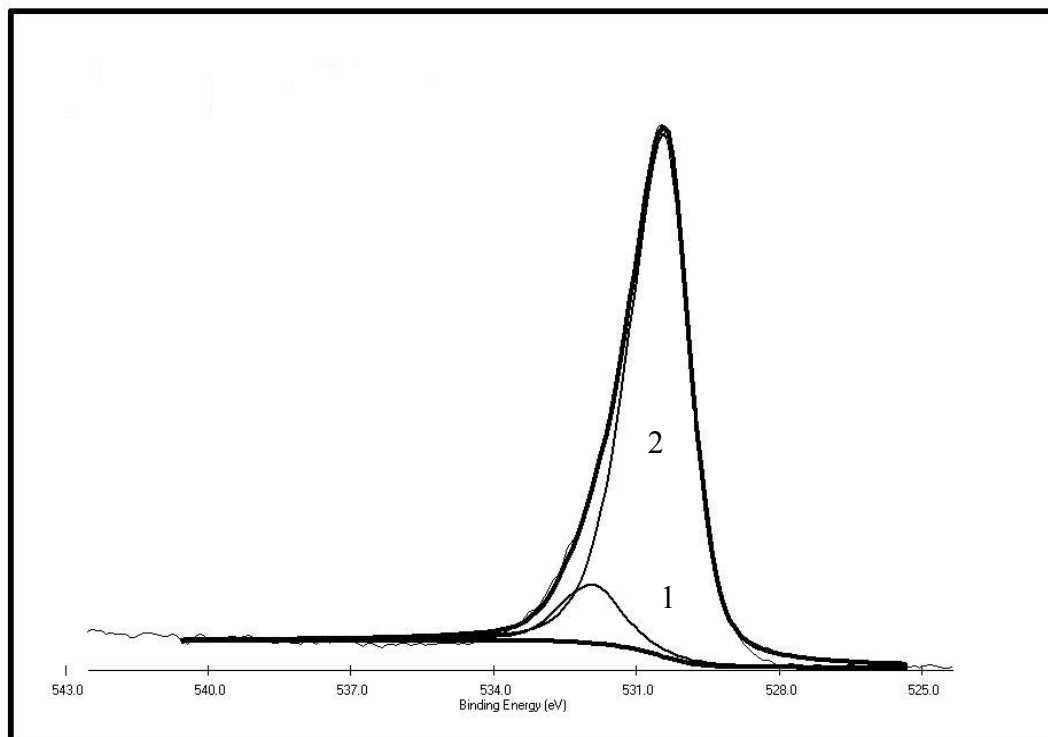


Figure 5.16 Fitting of O1s line of debound part: curves 1 and 2 are fitting peaks

The grain size-density plot is shown in Figure 5.17 to represent the microstructure development of various microsize structures. For relative density < 0.98 , given the same grain size, the trajectory of the microsize structures of $\phi 60 \mu\text{m}$ gives higher density as compared to microsize structures of $\phi 100 \mu\text{m}$. It indicates that for microsize structures of $\phi 60 \mu\text{m}$, densification was promoted over grain growth as compared to microsize structures of $\phi 80 \mu\text{m}$ and $\phi 100 \mu\text{m}$. Above the relative density of 0.98, the increase in density was limited while grain growth was prominent due to less pore drag pinning on the boundary movement.

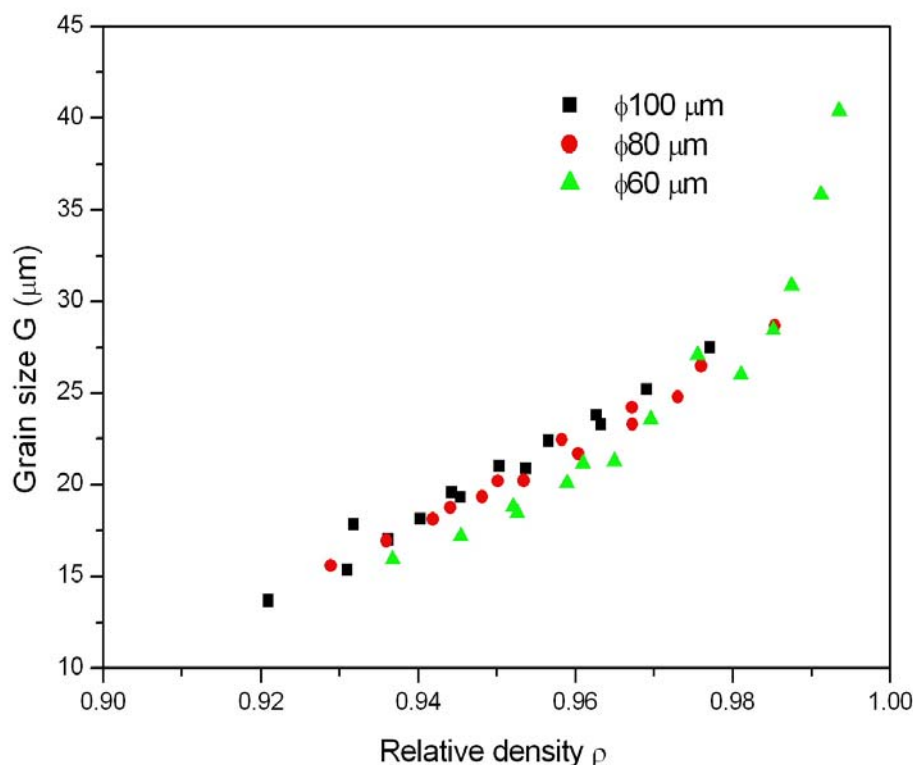


Figure 5.17 Grain size-density trajectories of various microsize structures

5.3.3 Dense layer

The oxides on the debound parts and consequent reduction products during hydrogen sintering such as H_2O attribute to the formation and progression of the dense layers on the sintered microsize structures. During sintering, hydrogen can diffuse into the microsize structures interstitially due to its small molecule and facilitate densification via reaction with the oxides. Nearly no pores existed at areas adjacent to the surface of the microsize structures. This is because it was easier for hydrogen to diffuse into these areas. Meanwhile, the product gas could diffuse out through the open porosity or shorter transport path whereby densification at such areas was enhanced. At the center

of the microsize structures, however, a lower densification level was obtained because it was harder for both hydrogen to enter and product gas to egress, the latter of which might cause internal gas pressure. When hydrogen solubility and permeability increased with rising temperature, densification was promoted simultaneously due to enhanced oxide removal. Hence, the dense layer on microsize structures was augmented with temperature.

5.4 Conclusions

- a) The reduction of the size of the microsize structures into the micrometer regime increases densification. It is found that microsize structures of $\phi 100\ \mu\text{m}$, $\phi 80\ \mu\text{m}$ and $\phi 60\ \mu\text{m}$ are in the final sintering stage while the sub-structure is in the intermediate sintering stage for the various temperatures studied.
- b) Among the various microsize structures, the microsize structures of $\phi 60\ \mu\text{m}$ yielded the highest density within the temperatures studied where densification was promoted over grain growth. The difference in sintering behavior between the sub-structure and various microsize structures was attributed to size effect arising from the presence of oxides on the debound parts and the internal gas pressure.
- c) A reduction in density was observed on the sub-structure with prolonged sintering time of 90 minutes and high temperature of $1300\ ^\circ\text{C}$. The density decrease was attributed to the internal gas pressure generated during hydrogen sintering.

d) Dense layers that increased with time and temperature were observed on various microsize structures. The oxides on the debound parts and consequent reduction products during hydrogen sintering were attributed to the formation and progression of the dense layers.

Chapter 6 Modeling Results and Discussion

This chapter compares the theoretical curves based on the model discussed in chapter 3 with the experimental results of various sintered microstructured parts. Section 6.1 introduces the modeling. The sintering kinetics is investigated in section 6.2 based on particle level sintering theory. The procedure by which how the modeling has been conducted is detailed in section 6.3. In section 6.4, the modeling results, grain growth and densification of various sintered microstructured parts, are examined. The effects of pore location and boundary energy on the densification of the various microsize structures are discussed. The conclusions are summarized in section 6.5.

6.1 Introduction

The controlling mechanism during grain growth and densification, as well as the respective activation energy of the sub-structure and microsize structures of $\phi 100\text{ }\mu\text{m}$, $\phi 80\text{ }\mu\text{m}$ and $\phi 60\text{ }\mu\text{m}$ are investigated based on particle level sintering theory. Material constants required in the model are fitted from experimental results obtained at the sintering temperature of $1250\text{ }^{\circ}\text{C}$. The same material constants are then used for theoretical computations at all the temperatures studied. The theoretical curves of grain growth and densification computed based on the established constitutive model are compared with the experimental results of the sub-structure and microsize structures for validation.

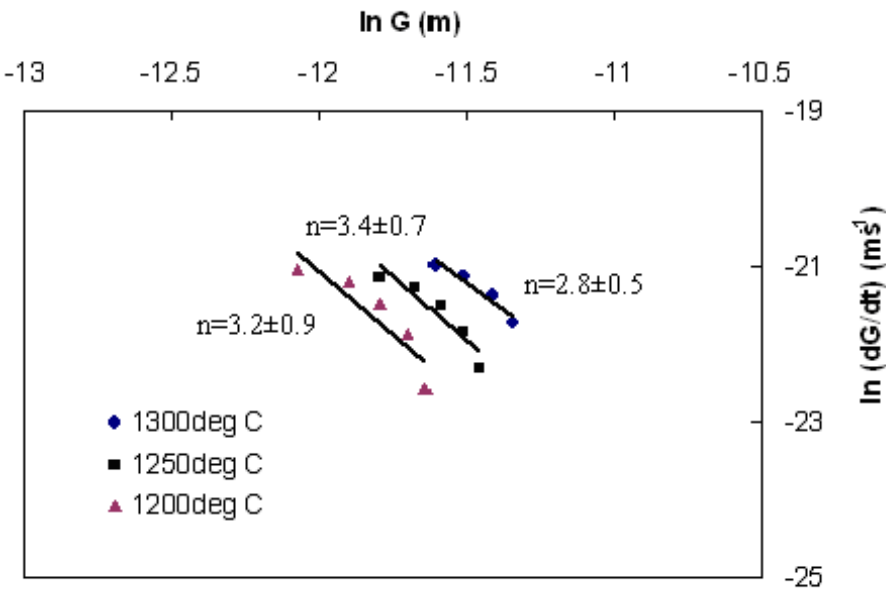
6.2 Sintering kinetics investigation

The controlling mechanism during grain growth and densification for the 316L stainless steel microstructured parts, the corresponding activation energies and parameters required for the modeling discussed in chapter 3 are established here.

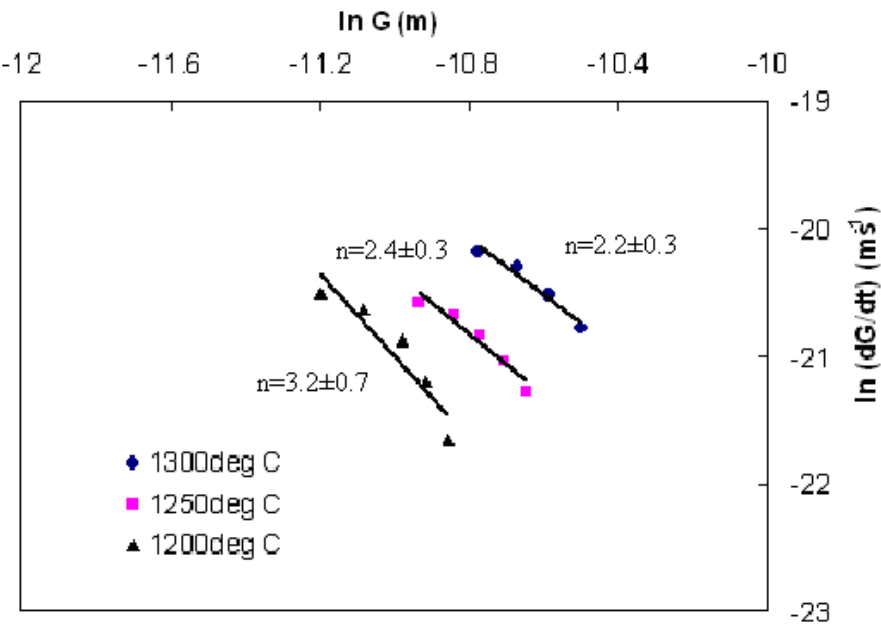
6.2.1 Grain growth kinetics

Grain growth kinetics of the sub-structure and microsize structures were studied based on Brook's model. Assuming monosized pores, the rate equations for various grain growth mechanisms during sintering can be written in a general form as $\frac{dG}{dt} = \frac{K'}{G^n}$ (see section 2.4.5) [25]. $\frac{dG}{dt}$ was derived from the fitted curves of the grain size versus time for the sub-structure and various microsize structures. Based on the results shown in Figure 5.7, the equations of the fitted curves (polynomial fit of grain size versus time, where t is sintering time in seconds, using Excel, Microsoft software) are summarized in Appendix F. $\ln\left(\frac{dG}{dt}\right)$ was plotted against $\ln G$ to determine the grain growth exponent n , which is given by the slope (absolute value) of the plot, for various sintering temperatures using least squares analysis as shown in Figure 6.1. An ideal fit to surface diffusion, lattice diffusion and boundary diffusion will give n of 3, 2 and 1, respectively. The n values obtained from the above curve fitting for the sub-structure and various microsize structures are listed in Table 6.1.

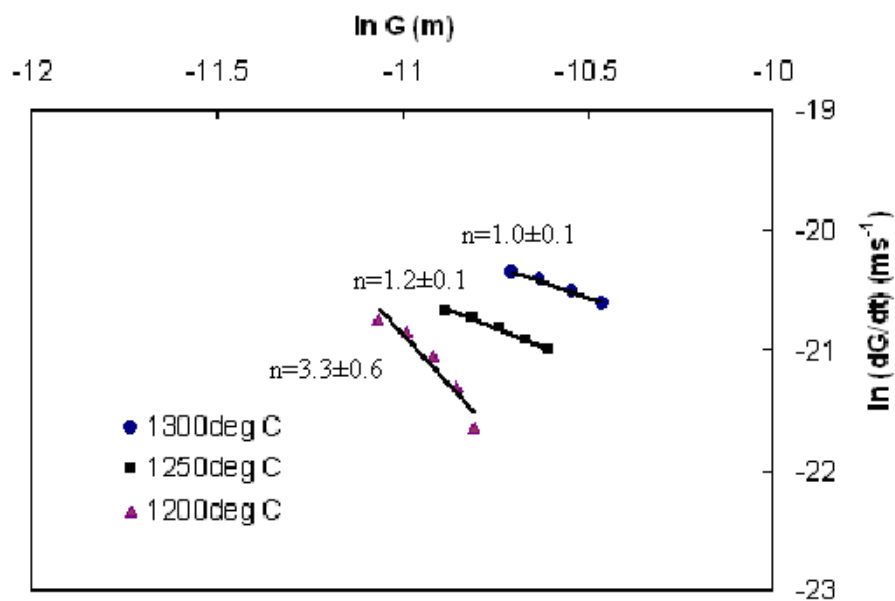
Table 6.1 shows that for the sub-structure, grain growth is governed by surface diffusion controlled pore drag for the three temperatures studied: 1200 °C, 1250 °C and 1300 °C. For the microsize structures of $\phi 100\ \mu\text{m}$, grain growth is governed by surface diffusion controlled pore drag at 1200 °C and lattice diffusion for 1250 °C and 1300 °C. For the microsize structures of $\phi 80\ \mu\text{m}$, grain growth is governed by surface diffusion controlled pore drag at 1200 °C and boundary diffusion for 1250 °C and 1300 °C. For the microsize structures of $\phi 60\ \mu\text{m}$, grain growth is governed by boundary diffusion for all the three temperatures studied: 1200 °C, 1250 °C and 1300 °C. It indicates that for the sub-structure and microsize structures of $\phi 60\ \mu\text{m}$, the grain growth is dominated by a single mechanism. For the microsize structures of $\phi 100\ \mu\text{m}$ and $\phi 80\ \mu\text{m}$, however, a mixture of mechanisms operates for grain growth.



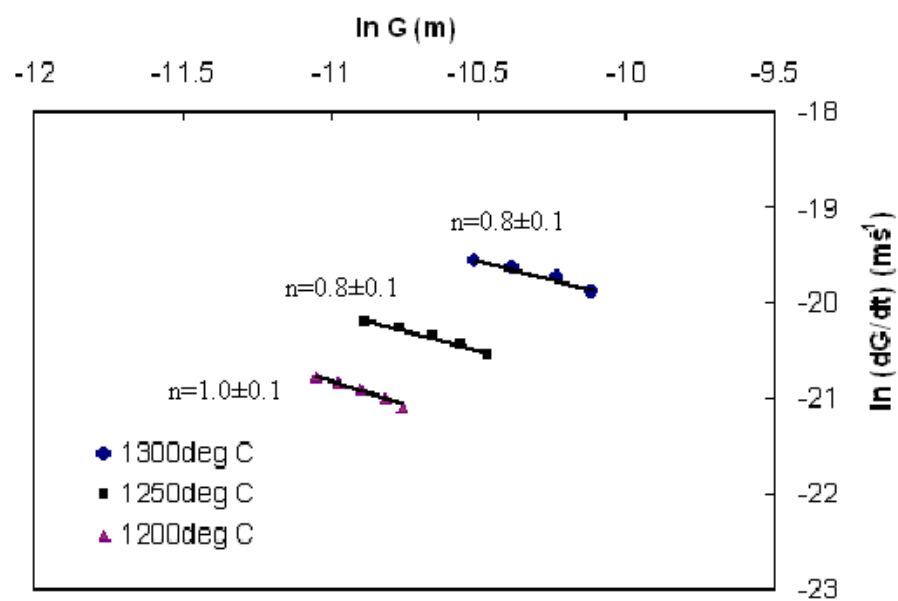
(a) Sub-structure



(b) Microsize structures of $\phi 100 \mu m$



(c) Microsize structures of $\phi 80 \mu\text{m}$



(d) Microsize structures of $\phi 60 \mu\text{m}$

Figure 6.1 $\ln\left(\frac{dG}{dt}\right)$ versus $\ln G$ for sub-structure and microsize structures

Table 6.1 Calculated grain growth exponent n for sub-structure and microsize structures

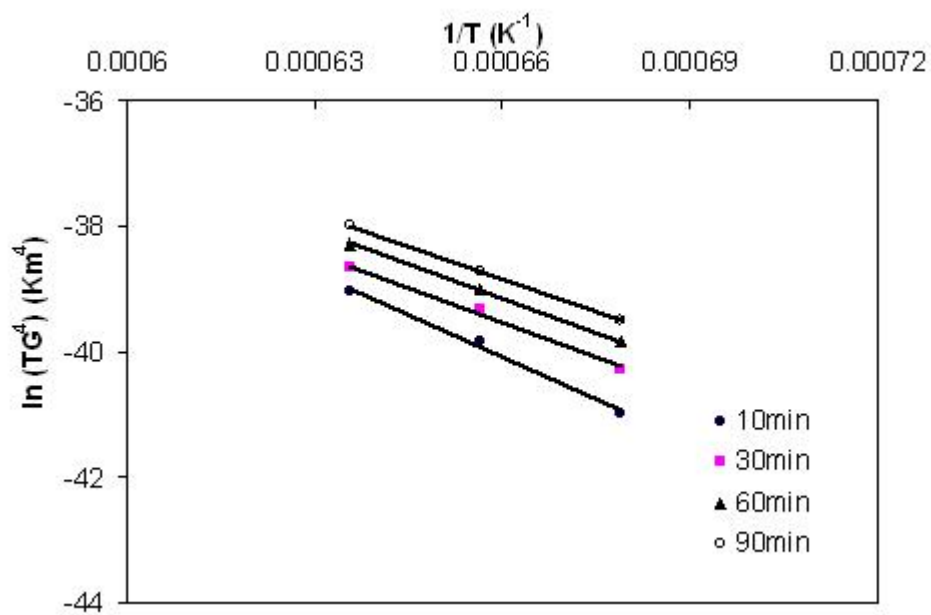
Sintered part	n		
	1200 °C	1250 °C	1300 °C
Sub-structure	3.2 ± 0.9	3.4 ± 0.7	2.8 ± 0.5
Microsize structures of $\phi 100 \mu\text{m}$	3.2 ± 0.7	2.4 ± 0.3	2.2 ± 0.3
Microsize structures of $\phi 80 \mu\text{m}$	3.3 ± 0.6	1.2 ± 0.1	1.0 ± 0.1
Microsize structures of $\phi 60 \mu\text{m}$	1.0 ± 0.1	0.8 ± 0.1	0.8 ± 0.1

6.2.2 Activation energy for grain growth

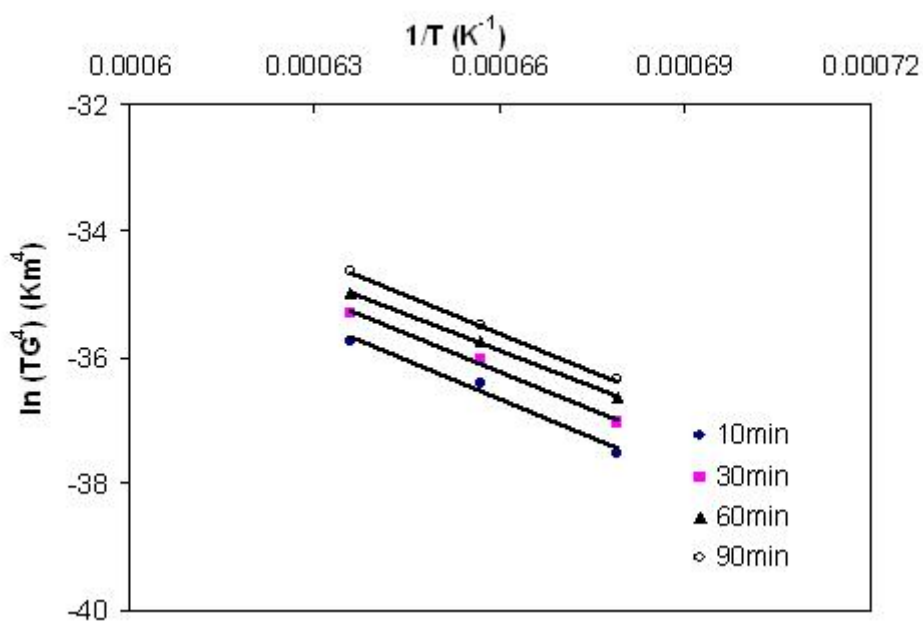
The activation energies for grain growth of the sub-structure and various microsize structures were calculated based on the slopes on the Arrhenius plots of $\ln(TG^{n+1})$ versus $1/T$, applying different n values for different mechanisms, as shown in Figure 6.2. Table 6.2 summarizes the calculated activation energies for various possible mechanisms. It can be seen that the calculated activation energy based on surface diffusion for the sub-structure and boundary diffusion for the microsize structures of $\phi 60 \mu\text{m}$ are higher than the values obtained with radioactive tracer diffusion method [82]. German [82] pointed out that diffusivities could vary widely with impurity content and atmosphere. As discussed in section 5.3.2, the influence of carbon on the diffusivities of 316L stainless steel microstructured parts during sintering is negligible and therefore the higher activation energy is attributed to the presence of oxides on the debound and sintered microstructured parts.

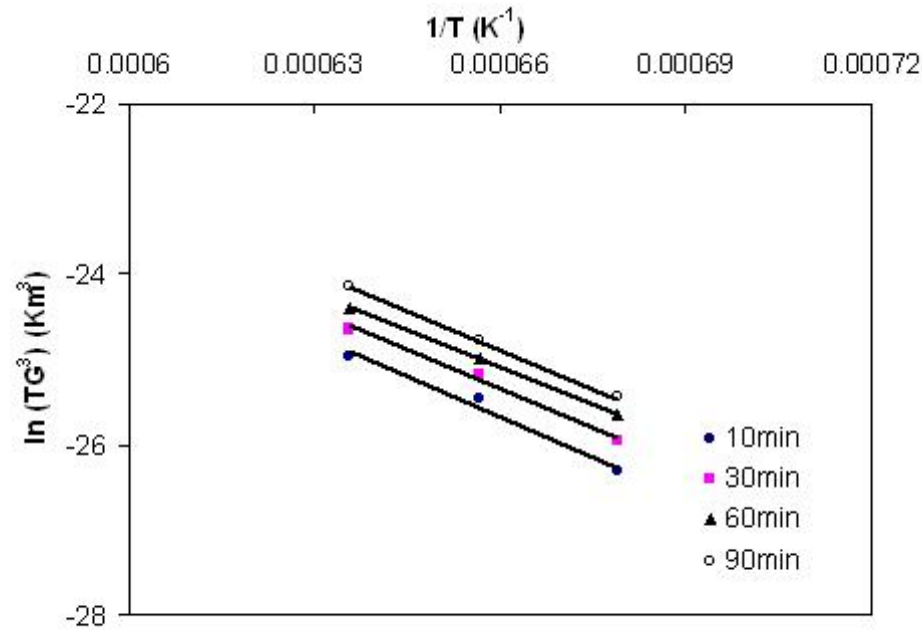
For the microsize structures of $\phi 100\ \mu\text{m}$ and $\phi 80\ \mu\text{m}$, when surface diffusion controlled pore drag is assumed, the calculated activation energies are higher than the values obtained with radioactive tracer diffusion method as shown in Table 6.2. However, when grain growth under lattice diffusion controlled pore drag is assumed for the microsize structures of $\phi 100\ \mu\text{m}$, the calculated activation energy of 251 kJ/mol is smaller than the 280 kJ/mol obtained with radioactive tracer diffusion method. Likewise, when boundary diffusion controlled grain growth is assumed for the microsize structures of $\phi 80\ \mu\text{m}$, the calculated activation energy of 157 kJ/mol is also smaller than the 167 kJ/mol obtained with radioactive tracer diffusion method. On the assumption that the presence of oxides increases the activation energy for different transport paths, surface diffusion controlled pore drag is assumed during grain growth of the microsize structures of $\phi 100\ \mu\text{m}$ and $\phi 80\ \mu\text{m}$ for all the temperatures studied.

For the sub-structure, surface diffusion controlled pore drag is considered. For the microsize structures of $\phi 60\ \mu\text{m}$, boundary diffusion is assumed. Considering the microsize structures as a system containing mobile second-phase inclusions of pores, the results indicate that when the size reduces to $\phi 60\ \mu\text{m}$, boundary parameters, not pore parameters, control the boundary movement for temperatures from 1200 °C to 1300 °C. This might be because that the microsize structures of $\phi 60\ \mu\text{m}$ has higher density and thus less pore drag is superimposed on the grain boundary to restrain its movement. The summarized mechanisms and activation energies for grain growth of the sub-structure and various microsize structures are shown in Table 6.3.

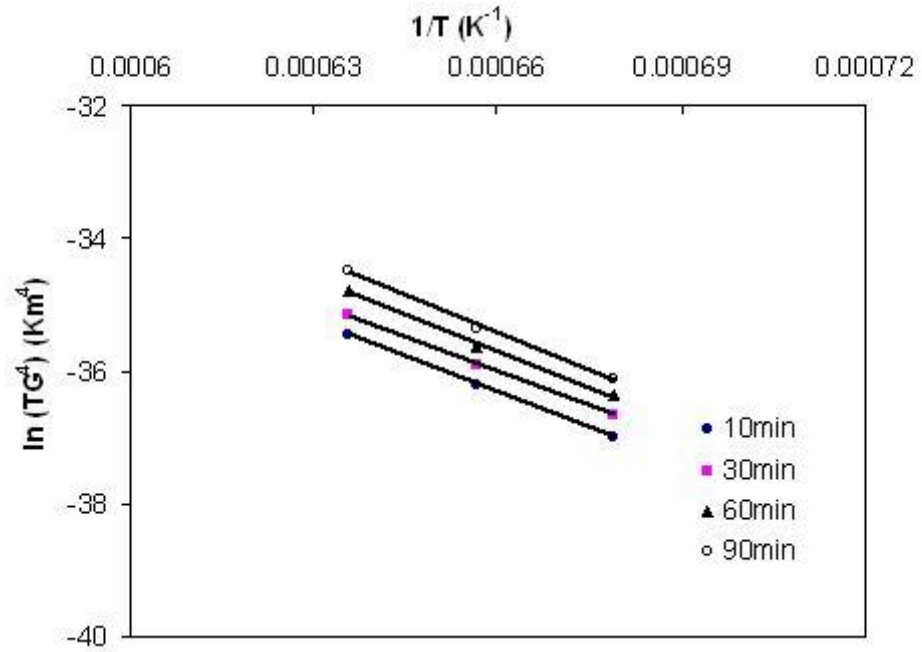


(a) Sub-structure

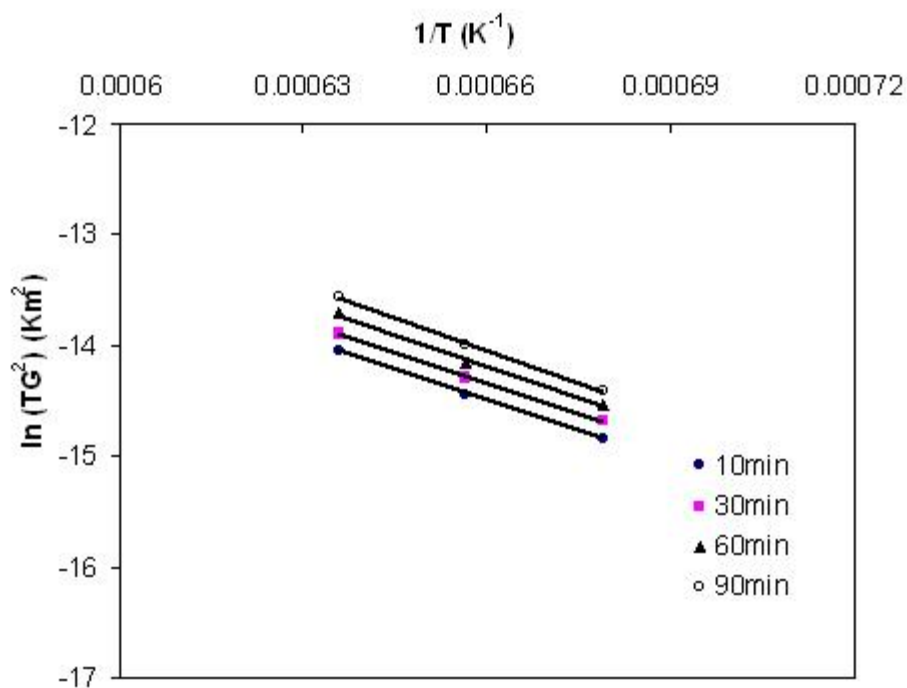
(b) Microsize structures of $\phi 100 \mu\text{m}$ fitted based on surface diffusion



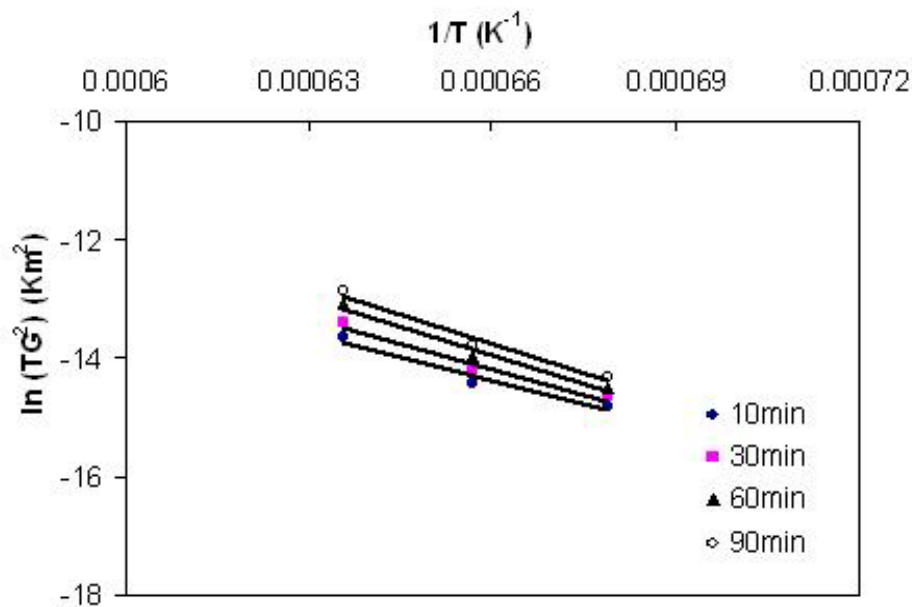
(c) Microsize structure of $\phi 100 \mu\text{m}$ fitted based on lattice diffusion



(d) Microsize structures of $\phi 80 \mu\text{m}$ fitted based on surface diffusion



(e) Microsize structures of $\phi 80 \mu\text{m}$ fitted based on boundary diffusion



(f) Microsize structures of $\phi 60 \mu\text{m}$

Figure 6.2 Plot of $\ln(TG^{n+1})$ against $\frac{1}{T}$ for sub-structure and microsize structures

Table 6.2 Calculated activation energies for grain growth for sub-structure and
microsize structures

Sintered part	Calculated activation energies (kJ/mol)		
	Surface diffusion Q_S	Lattice diffusion Q_L	Boundary diffusion Q_B
Sub-structure	318 ± 36	_____	_____
Microsize structures of $\phi 100 \mu\text{m}$	331 ± 10	251 ± 8	_____
Microsize structures of $\phi 80 \mu\text{m}$	301 ± 12	_____	157 ± 6
Microsize structures of $\phi 60 \mu\text{m}$	_____	_____	251 ± 29
From reference [82]	250	280	167

Table 6.3 Grain growth: diffusion mechanisms and activation energies for sub-structure
and microsize structures

Sintered part	Activation energy
Sub-structure	Surface diffusion: 318 ± 36 kJ/mol
Microsize structures of $\phi 100 \mu\text{m}$	Surface diffusion: 331 ± 10 kJ/mol
Microsize structures of $\phi 80 \mu\text{m}$	Surface diffusion: 301 ± 12 kJ/mol
Microsize structures of $\phi 60 \mu\text{m}$	Boundary diffusion: 251 ± 29 kJ/mol

6.2.3 Densification kinetics

For densification, Coble's models for lattice and grain boundary diffusion at the intermediate sintering stage and lattice diffusion at the final sintering stage as well as kinetic equations derived from Herring's flux equations for boundary diffusion were used in this work [21-23]. The rate equations for densification during the intermediate and final stage sintering can be written in a general form [23]:

$$\frac{d\rho}{dt} = \frac{K''}{TG^m} \quad \text{Eq. 6-1}$$

where,

K'' is a constant related to the temperature and densification mechanism,

$m = 3$ for lattice diffusion controlled densification and

$m = 4$ for boundary diffusion controlled densification.

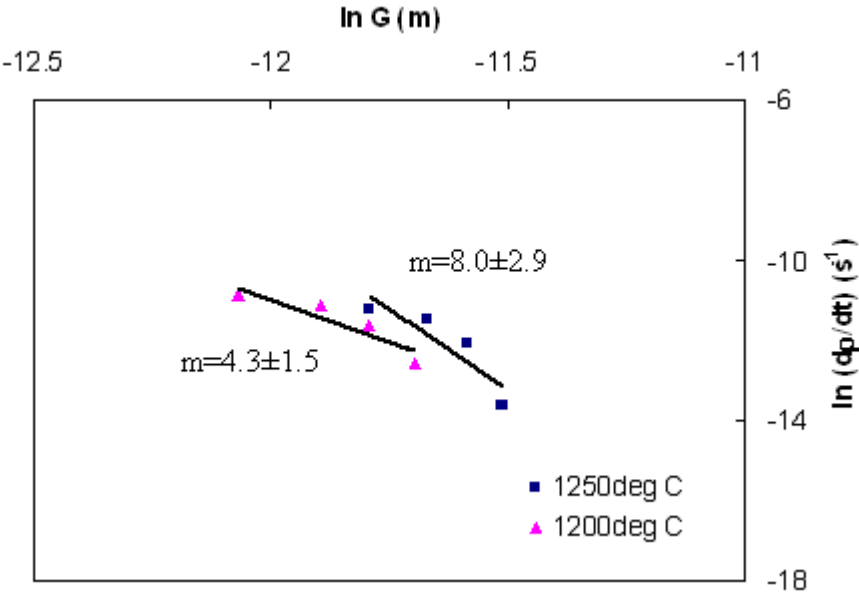
$\frac{d\rho}{dt}$ was derived from the fitted curves of relative density versus time. Based on the results of Figure 5.14, the equations of the fitted curves (polynomial fit of relative density versus time, where t is sintering time in seconds, using Excel, Microsoft software) are summarized in Appendix G. The densification of the sub-structure and microsize structures was studied based on Eq. 6-1 and the results are shown in Figure

6.3. $\ln\left(\frac{d\rho}{dt}\right)$ was plotted against $\ln G$ to determine m , the slope (absolute value) of the plot, for various temperatures using least squares analysis. An ideal fit to the boundary or lattice diffusion will give m of 4 or 3, respectively. The fitting was not performed for the sub-structure at 1300 °C as a reduction in density was observed at 90 min. The

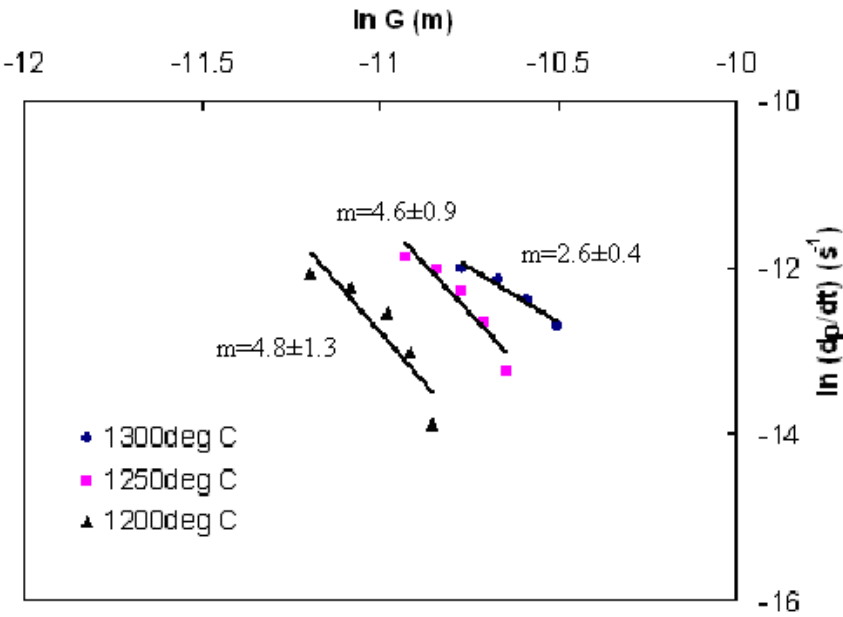
densification rate of the microsize structures of $\phi 60 \mu\text{m}$ at 1300°C for 90 min was not included for analysis as the density increase here is relatively small.

The calculated m values for the sub-structure and microsize structures at various sintering temperatures are listed in Table 6.4. For the sub-structure, m is closer to 4 despite a significant deviation and boundary diffusion controlled densification is herein assumed. The calculated m value of 7.98 deviates from the value of 4 in Coble's model [21-22] because the internal gas pressure was not included in Coble's model. Acting opposite to the sintering stress, the internal gas pressure increases with time and consequently results in an increasing decline in the densification rate, which increases the value of m . Therefore, m is larger than the idealized value where internal gas pressure is excluded. The higher the internal gas pressure, the larger m is. The experimental results show that m of 7.98 at 1250°C is higher than that of 4.31 at 1200°C .

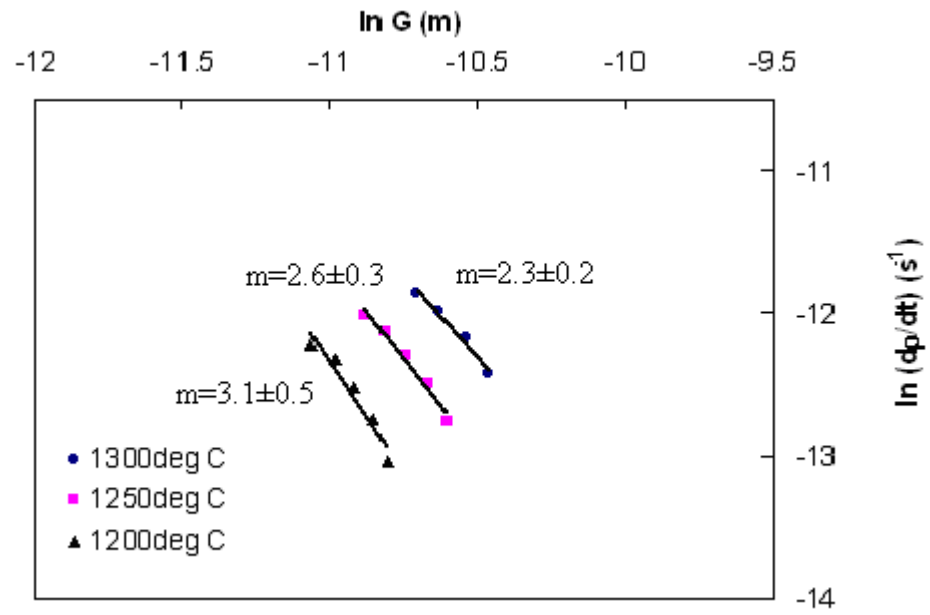
The calculated m values are rounded to the nearest m value of 4 or 3. Thus, for the microsize structures of $\phi 80 \mu\text{m}$, lattice diffusion controlled densification is assumed. For the microsize structures of $\phi 100 \mu\text{m}$, boundary diffusion is assumed for 1200°C and 1250°C and lattice diffusion is assumed for 1300°C . For the microsize structures of $\phi 60 \mu\text{m}$, lattice diffusion is assumed for 1200°C and 1250°C and boundary diffusion is assumed for 1300°C .



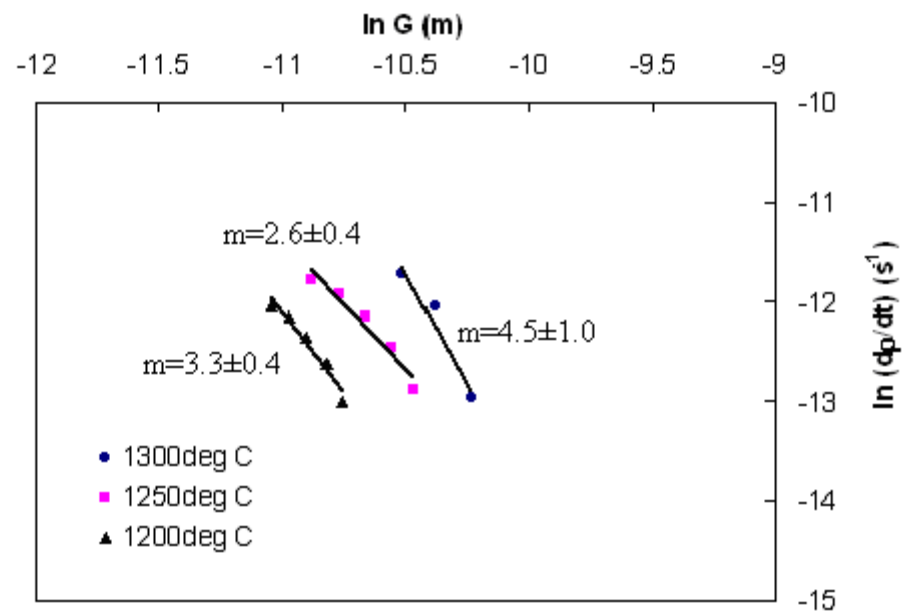
(a) Sub-structure



(b) Microsize structures of $\phi 100 \mu m$



(c) Microsize structures of $\phi 80 \mu\text{m}$



(d) Microsize structures of $\phi 60 \mu\text{m}$

Figure 6.3 Plot of $\ln\left(\frac{d\rho}{dt}\right)$ versus $\ln G$ of sub-structure and microsize structures

Table 6.4 m values for sub-structure and microsize structures from curve fitting

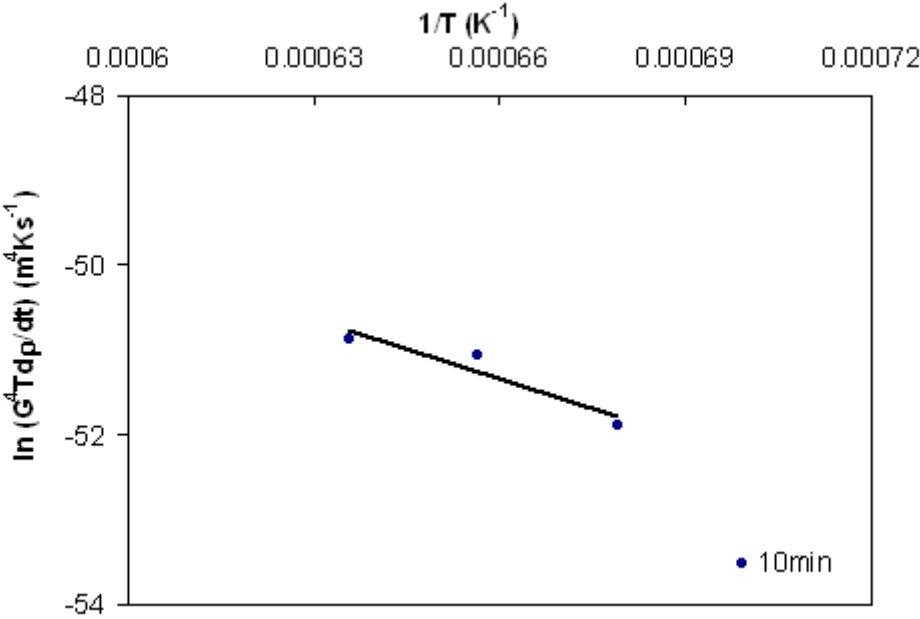
Sintered parts	<i>Calculated m</i>		
	1200 °C	1250 °C	1300 °C
Sub-structure	4.3 ± 1.5	8.0 ± 2.9	NA
Microsize structures of $\phi 100 \mu\text{m}$	4.8 ± 1.3	4.6 ± 0.9	2.6 ± 0.4
Microsize structures of $\phi 80 \mu\text{m}$	3.1 ± 0.5	2.6 ± 0.3	2.3 ± 0.2
Microsize structures of $\phi 60 \mu\text{m}$	3.3 ± 0.4	2.6 ± 0.4	4.5 ± 1.0

6.2.4 Activation energy for densification

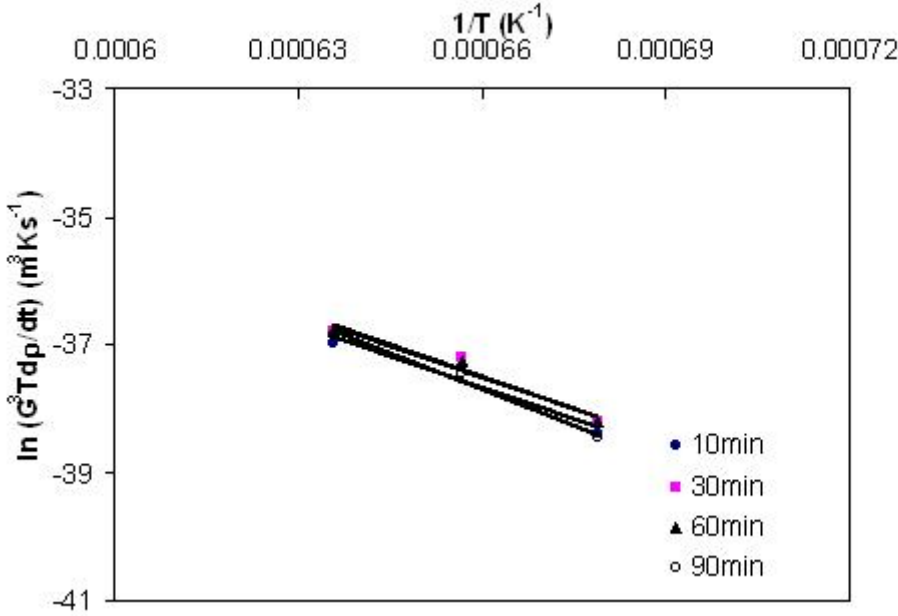
The activation energies for the densification of the sub-structure and various microsize structures were calculated from the slopes of the Arrhenius plots of $\ln\left(TG^m \frac{d\rho}{dt}\right)$ versus $1/T$ as shown in Figure 6.4. For boundary diffusion, $m = 4$ and for lattice diffusion $m = 3$. The calculated activation energies are summarized in Table 6.5. For the sub-structure and microsize structures of $\phi 80 \mu\text{m}$, the calculated activation energies for boundary diffusion and lattice diffusion are higher than the respective value obtained by radioactive tracer diffusion methods. This corresponds to the assumption in Section 6.2.2 that the presence of oxides increases the activation energy for different transport paths.

For the microsize structures of $\phi 100\ \mu\text{m}$ and $\phi 60\ \mu\text{m}$, the respective calculated activation energy for boundary diffusion, 363 and 456 kJ/mol, are much higher than both the value measured via radioactive tracer diffusion methods and the value calculated for the sub-structure. Comparatively, the calculated activation energy for lattice diffusion, 283 and 342 kJ/mol, exhibits a lower increase from 280 kJ/mol reported in [82]. Hence, lattice diffusion was assumed during the densification of the microsize structures of $\phi 100\ \mu\text{m}$ and $\phi 60\ \mu\text{m}$ for all the temperatures studied. The mechanisms assumed and the respective activation energies for densification of the sub-structure and various microsize structures are summarized in Table 6.6 and used for subsequent computations.

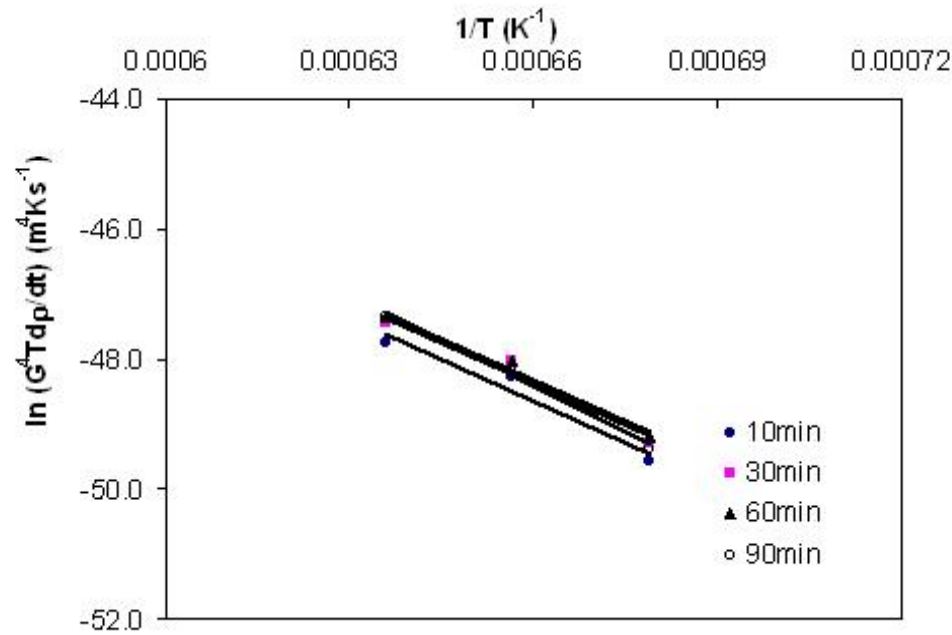
The results indicate that the corresponding densification mechanism changes as the size of the sintered part varies. During densification, boundary diffusion is assumed for the sub-structure whereas lattice diffusion is assumed for the various microsize structures. As the grain size of the sub-structure is smaller than that of the microsize structures, the result corresponds to the scale effect of sintering mechanisms where the relative contribution of grain boundary over lattice diffusion is enhanced with a reduction in scale [122]. The removal of some isolated pores within grains as shown in Figures 5.1 to 5.6 corroborates the assumed lattice diffusion as the entrapped pores can only be removed via lattice diffusion.



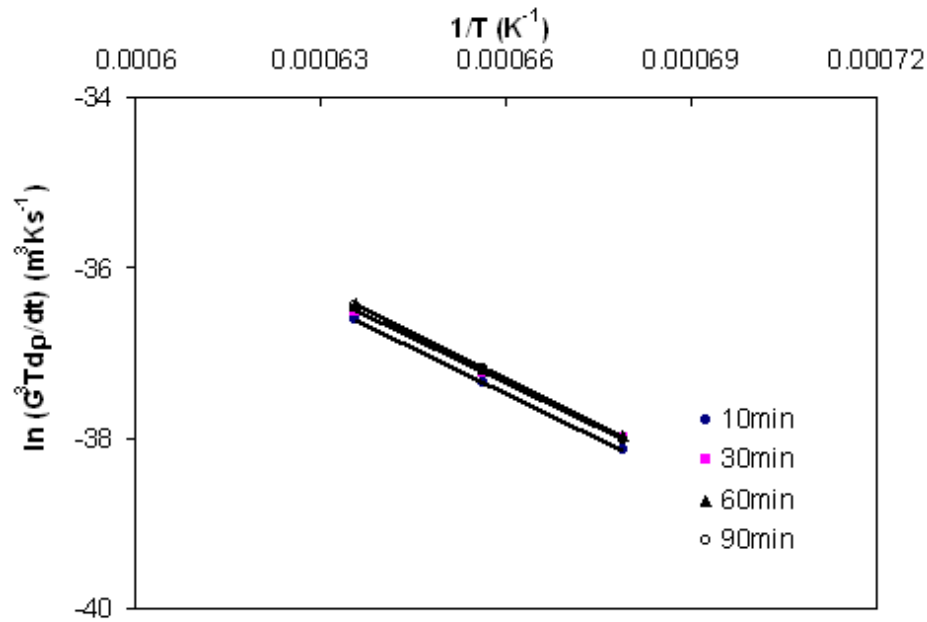
(a) Sub-structure



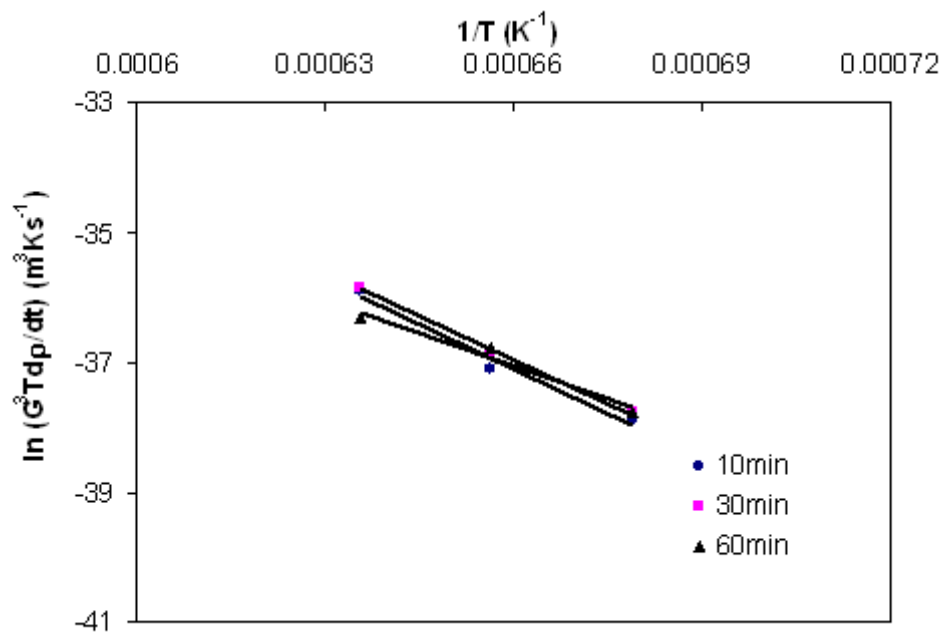
(b) Microsize structures of $\phi 100 \mu\text{m}$ fitted based on lattice diffusion



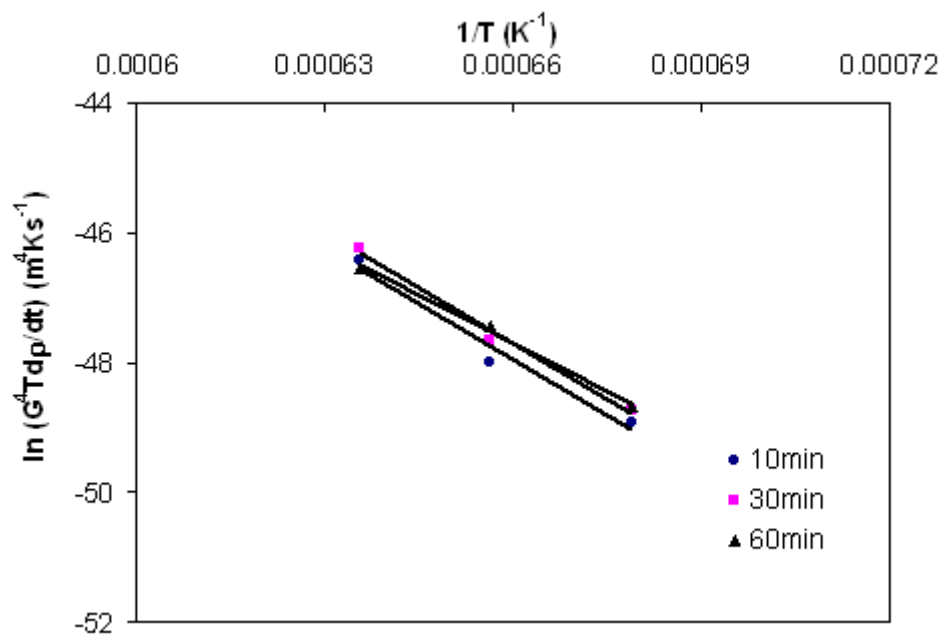
(c) Microsize structures of $\phi 100\ \mu m$ fitted based on boundary diffusion



(d) Microsize structures of $\phi 80\ \mu m$



(e) Microsize structures of $\phi 60 \mu\text{m}$ fitted based on lattice diffusion



(f) Microsize structures of $\phi 60 \mu\text{m}$ fitted based on boundary diffusion

Figure 6.4 Plot of $\ln\left(G^m T \frac{d\rho}{dt}\right)$ against $\frac{1}{T}$ for sub-structure and microsize structures

Table 6.5 Calculated activation energies for densification for sub-structure and
microsize structures

Sintered part	Calculated activation energies (kJmol ⁻¹)	
	Lattice diffusion	Boundary diffusion
Sub-structure	————	194
Microsize structures of $\phi 100\ \mu\text{m}$	283 ± 19	363 ± 19
Microsize structures of $\phi 80\ \mu\text{m}$	295 ± 7	————
Microsize structures of $\phi 60\ \mu\text{m}$	342 ± 54	456 ± 42
From reference [82]	280	167

Table 6.6 Densification: diffusion mechanisms and activation energies for sub-structure
and microsize structures

Sintered part	Activation energy
Sub-structure	Boundary diffusion: 194 kJmol ⁻¹
Microsize structures of $\phi 100\ \mu\text{m}$	Lattice diffusion: 283 ± 19 kJmol ⁻¹
Microsize structures of $\phi 80\ \mu\text{m}$	Lattice diffusion: 295 ± 7 kJmol ⁻¹
Microsize structures of $\phi 60\ \mu\text{m}$	Lattice diffusion: 342 ± 54 kJmol ⁻¹

6.3 Modeling of sintering

6.3.1 Sintering stress

As discussed in section 5.3.2, the microsize structures of $\phi 100 \mu\text{m}$, $\phi 80 \mu\text{m}$ and $\phi 60 \mu\text{m}$ entered the final sintering stage while the sub-structure was at the intermediate sintering stage within the temperatures studied. Hence, sintering stress expressions for two stages are used for the sub-structure (in the millimeter size) and various microsize structures (in the micrometer size) to incorporate the effect of size on densification. For the sub-structure, Eq. 4-26 is used and for the microsize structures, $\phi 100 \mu\text{m}$, $\phi 80 \mu\text{m}$ and $\phi 60 \mu\text{m}$, Eq. 4-32 is used.

From Eq. 4-39, $\left(\frac{1}{G} - \frac{1}{G_o} \right)$ can be plotted against $\left(\frac{1}{\rho} - \frac{1}{\rho_o} \right)$ for the microsize structures of $\phi 100 \mu\text{m}$, $\phi 80 \mu\text{m}$ and $\phi 60 \mu\text{m}$ that were sintered at 1250°C . Grain size obtained at 10 min was used as G_o and relative density obtained at 10 min was used as ρ_o here. k' in Eq. 4-32 was determined by calculating the slope of the plot.

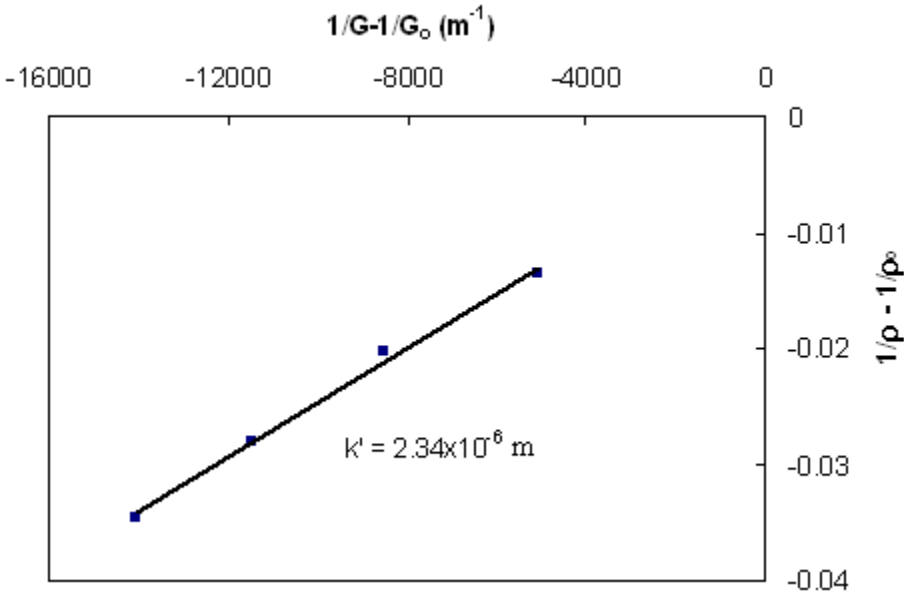
Figure 6.5 shows the determined k' for the various microsize structures:

$$k' = 2.34 \times 10^{-6} \text{ m for microsize structures of } \phi 100 \mu\text{m}$$

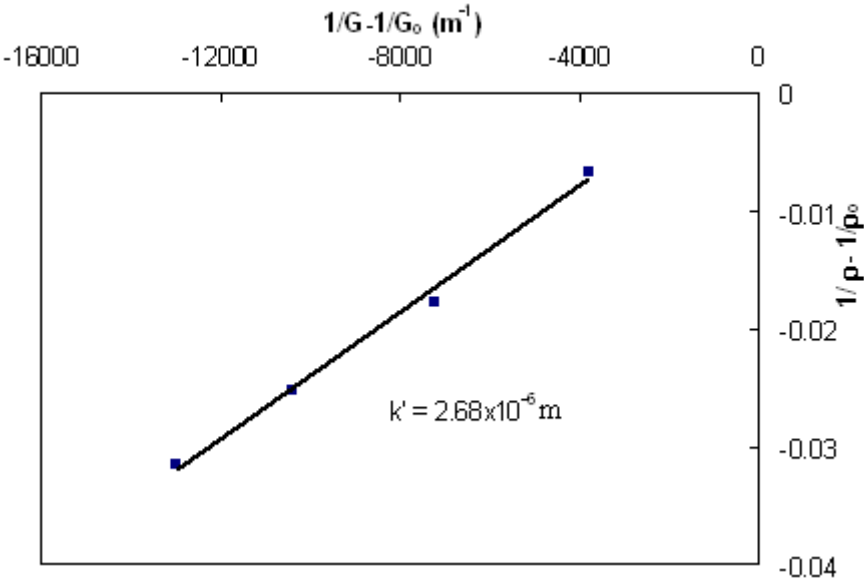
$$k' = 2.68 \times 10^{-6} \text{ m for microsize structures of } \phi 80 \mu\text{m}$$

$$k' = 2.19 \times 10^{-6} \text{ m for microsize structures of } \phi 60 \mu\text{m}.$$

The above k' values are used for subsequent computations.



(a) Microsize structures of $\phi 100 \mu\text{m}$



(b) Microsize structures of $\phi 80 \mu\text{m}$

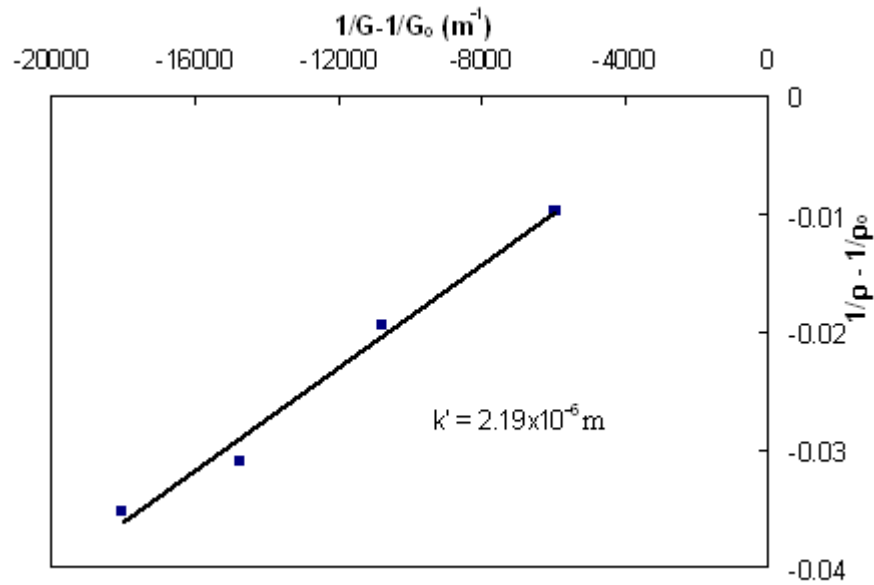
(c) Microsize structures of $\phi 60 \mu\text{m}$

Figure 6.5 Plot of $\left(\frac{1}{\rho} - \frac{1}{\rho_o} \right)$ against $\left(\frac{1}{G} - \frac{1}{G_o} \right)$ for microsize structures sintered at $1250 \text{ }^\circ\text{C}$

Since crystallographic orientation varies from grain to grain, the magnitude of grain boundary energy depends on the true dihedral angle between grain boundary planes meeting at triple edges in polycrystals [177]. In this model, a statistical average of grain boundary energy was employed. The surface energy γ_s of 2 Jm^{-2} [82] and grain boundary energy γ_b of 0.67 Jm^{-2} [178] for 316L stainless steel are used for computation. Hence, for this materials system and pores as spherical tetrahedrons, $\alpha = 5.64$, $\beta = 8.89$ and $\lambda = 2.32$. The k' value of $2.34 \times 10^{-6} \text{ m}$ for microsize

structures of $\phi 100 \mu\text{m}$, $2.68 \times 10^{-6} \text{ m}$ for microsize structures of $\phi 80 \mu\text{m}$ and $2.19 \times 10^{-6} \text{ m}$ for microsize structures of $\phi 60 \mu\text{m}$ is substituted into Eq. 4-32. Hence, the sintering stress for the sub-structure and various microsize structures are expressed as:

For sub-structure:

$$\sigma_s = \frac{10.30}{(1-\rho)^{1/2} G} \quad \text{Eq. 6-2}$$

For microsize structures of $\phi 100 \mu\text{m}$:

$$\sigma_s = \frac{9.59 \times 10^5}{\rho} + \frac{2.24}{G} + \frac{7.82 \times 10^6 (1-\rho)^{2/3}}{\rho} + \frac{18.29 \left(1 - \frac{1}{3}\rho\right)}{G(1-\rho)^{1/3}} \quad \text{Eq. 6-3}$$

For microsize structures of $\phi 80 \mu\text{m}$:

$$\sigma_s = \frac{8.37 \times 10^5}{\rho} + \frac{2.24}{G} + \frac{6.83 \times 10^6 (1-\rho)^{2/3}}{\rho} + \frac{18.29 \left(1 - \frac{1}{3}\rho\right)}{G(1-\rho)^{1/3}} \quad \text{Eq. 6-4}$$

For microsize structures of $\phi 60 \mu\text{m}$:

$$\sigma_s = \frac{1.02 \times 10^6}{\rho} + \frac{2.24}{G} + \frac{8.35 \times 10^6 (1-\rho)^{2/3}}{\rho} + \frac{18.29 \left(1 - \frac{1}{3}\rho\right)}{G(1-\rho)^{1/3}} \quad \text{Eq. 6-5}$$

6.3.2 Grain growth

Different grain growth mechanisms are assumed for the sub-structure and various microsize structures as shown in Table 6.3. Material constants were determined by fitting grain size-time data at 1250 °C for the sub-structure and various microsize structures: $K_I = 1.68 \times 10^{-10} \text{ m}^4\text{Ks}^{-1}$ for the sub-structure, $K_I = 1.11 \times 10^{-8} \text{ m}^4\text{Ks}^{-1}$ for microsize structures of $\phi 100 \text{ }\mu\text{m}$, $K_I = 1.22 \times 10^{-9} \text{ m}^4\text{Ks}^{-1}$ for microsize structures of $\phi 80 \text{ }\mu\text{m}$ and $K_3 = 0.04 \text{ m}^2\text{Ks}^{-1}$ for microsize structures of $\phi 60 \text{ }\mu\text{m}$. G_o was obtained from the polynomial fit of grain size versus time for the sub-structure and microsize structures as shown in Appendix F. The material constants coupled with activation energies determined in Table 6.3 were then used in all subsequent computations. The theoretical curves for grain growth were computed for different sintering temperatures with the aid of Matlab.

The grain growth of the sub-structure is computed according to:

$$G^4 - G_o^4 = \frac{1.68 \times 10^{-10}}{T} t \exp\left(\frac{-38249}{T}\right) \quad \text{Eq. 6-6}$$

The grain growth of the microsize structures of $\phi 100 \text{ }\mu\text{m}$ is computed according to:

$$G^4 - G_o^4 = \frac{1.11 \times 10^{-8}}{T} t \exp\left(\frac{-39812}{T}\right) \quad \text{Eq. 6-7}$$

The grain growth of the microsize structures of $\phi 80 \text{ }\mu\text{m}$ is computed according to:

$$G^4 - G_o^4 = \frac{1.22 \times 10^{-9}}{T} t \exp\left(\frac{-36204}{T}\right) \quad \text{Eq. 6-8}$$

The grain growth of the microsize structures of $\phi 60 \mu\text{m}$ is computed according to:

$$G^2 - G_0^2 = \frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) \quad \text{Eq. 6-9}$$

6.3.3 Gas pressure

During hydrogen sintering, the magnitude of change in sintering stress brought forth by internal gas pressure due to unescaped gas is taken into account for the sub-structure. For microsize structures whose shorter diffusion path makes it easier for the gas to escape, the influence of internal gas pressure on densification is less significant and thus not considered in the model. H in Eq. 4-34 was obtained for the sub-structure by equating sintering stress at 1300 °C for 60 min with the internal gas pressure. This is because a density limit was observed experimentally in Figure 5.14. Thus, the effective pressure, P_{eff} , during sintering for the sub-structure is given by:

$$P_{eff} = \sigma_s - P_i = \frac{10.30}{(1-\rho)^{1/2} G} - \frac{224.37 \rho T}{1-\rho} \quad \text{Eq. 6-10}$$

6.3.4 Constitutive equation for model

For the 316L stainless steel powder used in this research, Eqs 4-21 and 4-22 give the densification rate for lattice diffusion controlled creep and boundary diffusion controlled creep, respectively. Based on the investigation on the densification kinetics discussed in section 6.2, different mechanisms as shown in Table 6.6 are assumed for the sub-structure and various microsize structures. In the model, $f = 0.16 \left(\frac{1-\rho}{\rho-0.69} \right)$

obtained from Kim and Jeon [165] is used.

(a) For the sub-structure, grain size G in Eq. 4-22 was replaced with particle size D of $2.37 \mu\text{m}$ for simplification due to insignificant grain growth in the intermediate sintering stage. Substitute Equations 6-6 and 6-10 into Equation 4-22 gives:

$$\dot{\rho} = \frac{1.44\rho^2 C_2 \exp\left(\frac{-23334}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{TD^3} \times \left[\frac{10.30}{(1-\rho)^{1/2} \left[\frac{1.68 \times 10^{-10}}{T} t \exp\left(\frac{-38249}{T}\right) + G_o^4 \right]^{1/4}} - \frac{224.37\rho T}{1-\rho} \right]$$

Eq. 6-11

(b) For microsize structure of $\phi 100 \mu\text{m}$, substitute Equations 6-3 and 6-7 into Equation 4-21 gives:

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-34039}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{1/2}} \times \left[\frac{0.96 + 7.82(1-\rho)^{2/3}}{\rho} \times 10^6 + \frac{2.24 + \frac{18.29\left(1-\frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{1/4}} \right]$$

Eq. 6-12

(c) For microsize structure of $\phi 80 \mu\text{m}$, substitute Equations 6-4 and 6-8 into Equation 4-21 gives:

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-35482}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{1/2}} \times \left[\frac{0.84 + 6.83(1-\rho)^{2/3}}{\rho} \times 10^6 + \frac{2.24 + \frac{18.29\left(1-\frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{1/4}} \right]$$

Eq. 6-13

(d) For microsize structure of $\phi 60 \mu\text{m}$, substitute Equations 6-5 and 6-9 into Equation 4-21 gives:

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-41135}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]} \times \left[\frac{1.02 + 8.35(1-\rho)^{2/3}}{\rho} \times 10^6 + \frac{2.24 + \frac{18.29\left(1-\frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]^{1/2}} \right]$$

Eq. 6-14

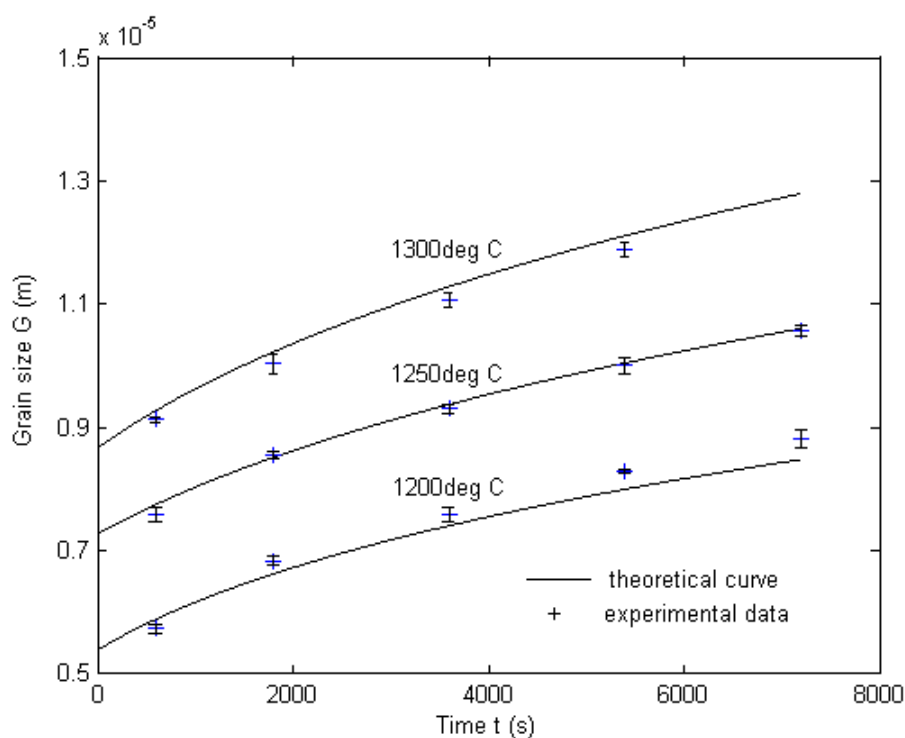
The density-time curves were computed with the aid of a computer, using Matlab, by iteration of the integral forms of the densification rate equations, Eq. 6-11 to Eq. 6-14, for the sub-structure and the microsize structures. The material constant, C_1 or C_2 in Eqs 4-21 or 4-22, was fitted from the density-time data at 1250 °C and used for all the subsequent computations. For the sub-structure, $C_2 = 8.72 \times 10^{-19} \text{ s}^{-1}\text{N}^{-1}\text{m}^5\text{K}$; for the microsize structures of $\phi 100 \mu\text{m}$, $C_1 = 1.61 \times 10^{-8} \text{ s}^{-1}\text{N}^{-1}\text{m}^4\text{K}$; for the microsize structures of $\phi 80 \mu\text{m}$, $C_1 = 5.48 \times 10^{-8} \text{ s}^{-1}\text{N}^{-1}\text{m}^4\text{K}$ and for the microsize structures of $\phi 60 \mu\text{m}$, $C_1 = 3.58 \times 10^{-6} \text{ s}^{-1}\text{N}^{-1}\text{m}^4\text{K}$.

6.4 Modeling results and discussion

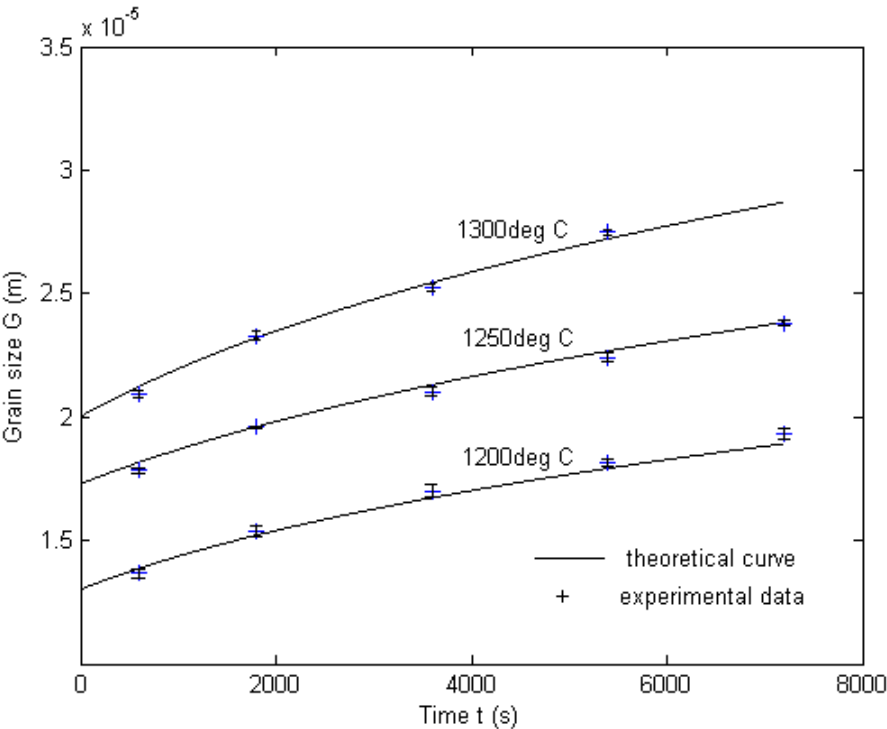
6.4.1 Grain growth

Figure 6.6 compares the theoretical grain size-time curves for 316L stainless steel sub-structure and microsize structures of $\phi 100 \mu\text{m}$, $\phi 80 \mu\text{m}$ and $\phi 60 \mu\text{m}$ from 1200 °C to 1300 °C with the experimental results. In each case, higher temperature and longer sintering time promotes grain growth. It is noted that larger grain size is obtained for

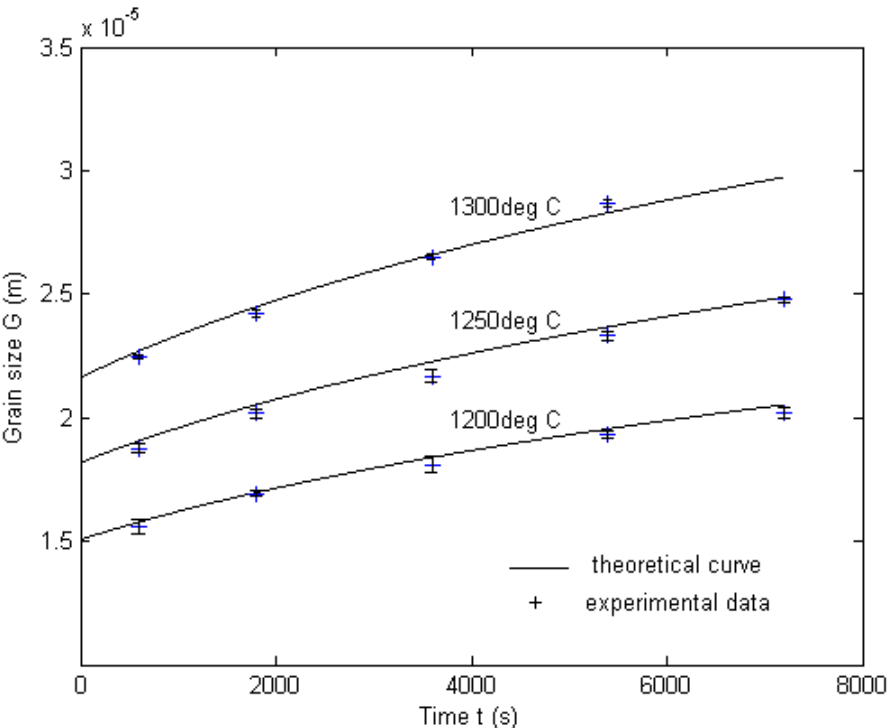
smaller dimensions of the structure given the same sintering condition. Higher grain growth rate is predicted on smaller sintered body at high temperature, i.e. an average of $1.85 \times 10^{-9} \text{ ms}^{-1}$ for the microsize structures of $\phi 60 \text{ }\mu\text{m}$ as compared to an average of $1.21 \times 10^{-9} \text{ ms}^{-1}$ for the microsize structures of $\phi 100 \text{ }\mu\text{m}$ at $1300 \text{ }^{\circ}\text{C}$. For microsize structures of $\phi 60 \text{ }\mu\text{m}$, larger deviation from theoretical curves is observed at $1300 \text{ }^{\circ}\text{C}$. The deviation might be ascribed to the high density obtained at $1300 \text{ }^{\circ}\text{C}$ for microsize structures of $\phi 60 \text{ }\mu\text{m}$, near to the relative density of 1, which promotes coarsening.



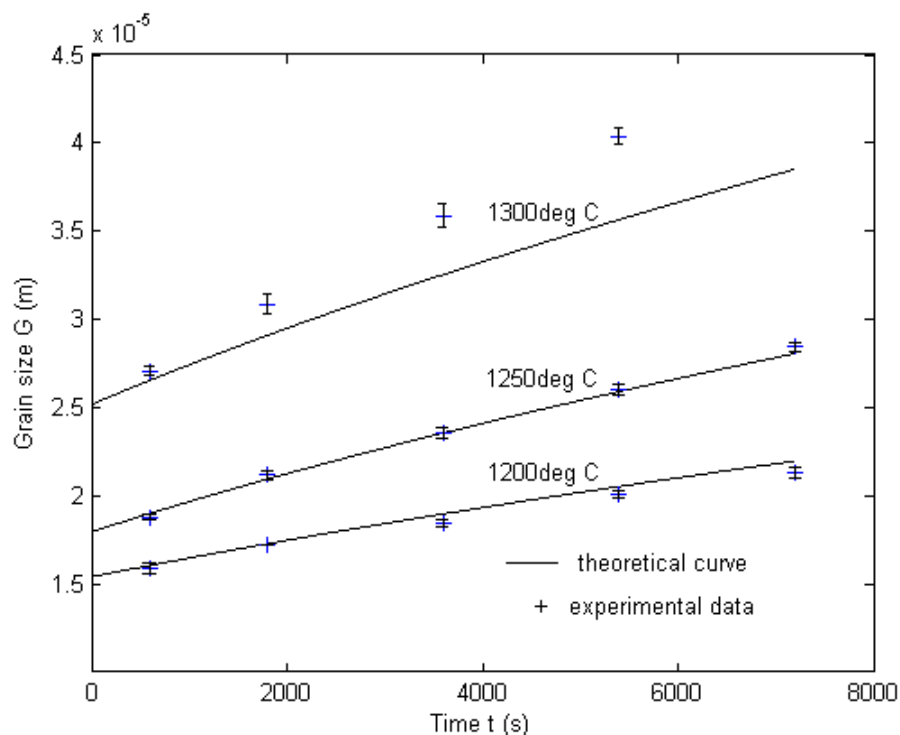
(a) Sub-structure (theoretical curve based on Eq. 6-6)



(b) Microsize structures of $\phi 100 \mu\text{m}$ (theoretical curve based on Eq. 6-7)



(c) Microsize structures of $\phi 80 \mu\text{m}$ (theoretical curve based on Eq. 6-8)



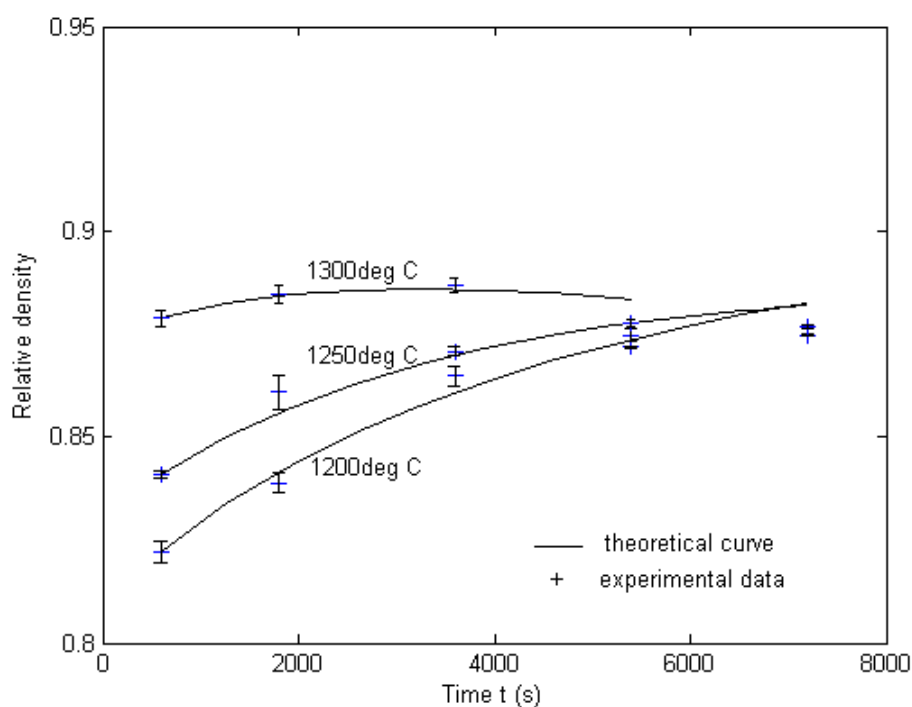
(d) Microsize structures of $\phi 60 \mu\text{m}$ (theoretical curve based on Eq. 6-9)

Figure 6.6 Comparison of theoretical and experimental grain size-time results

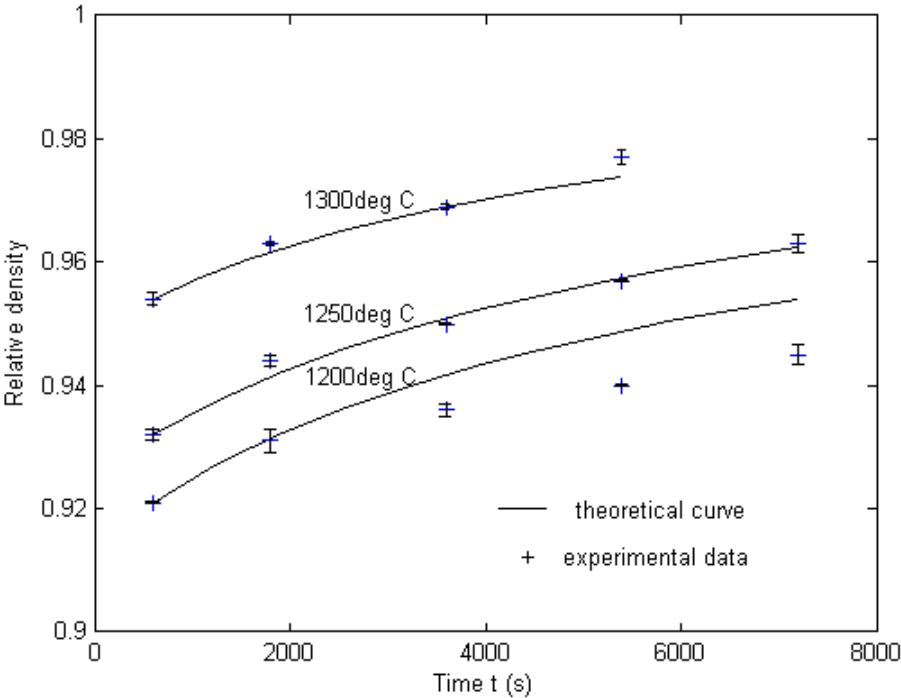
6.4.2 Densification

Figure 6.7 compares the theoretical density-time curves with the experimental data. By including the internal gas pressure in the model for the sub-structure, a reduction in density is predicted at 1300 °C when the sintering time is prolonged. For the microsize structures, however, higher temperature and longer sintering time both give higher density. Another feature to be noted in comparing the theoretical densification of the sub-structure and the microsize structures is that higher density is obtained as the size

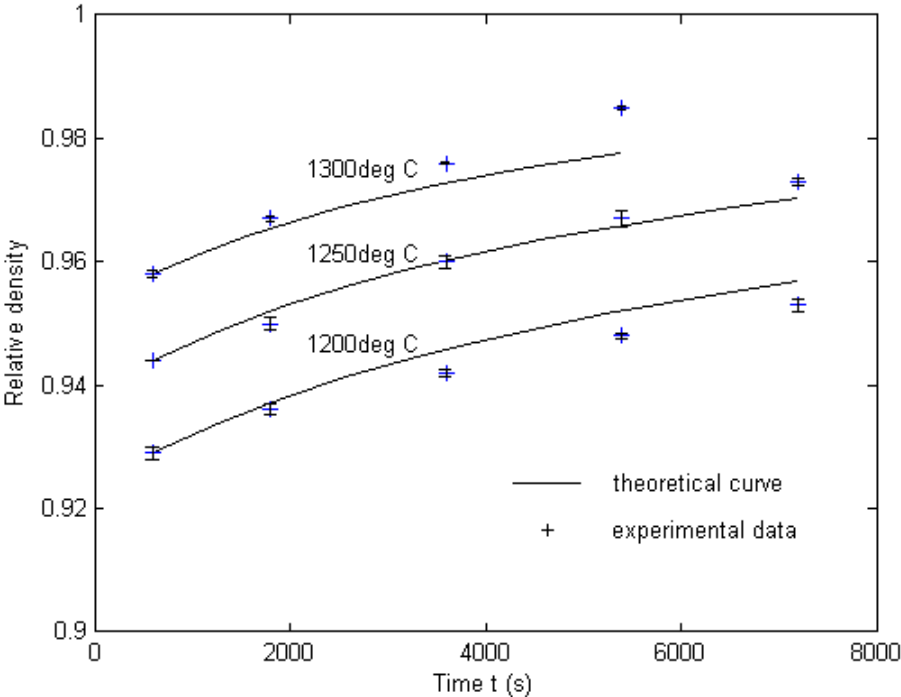
decreases for the same sintering condition. For the microsize structures, the theoretical curves overestimate the densities slightly at the lower temperature of 1200 °C, in particular microsize structures of $\phi 100\text{ }\mu\text{m}$. At higher temperature such as 1300 °C, the model slightly underestimates the densities for microsize structures of $\phi 80\text{ }\mu\text{m}$ and $\phi 60\text{ }\mu\text{m}$. Comparison of experimental results with theoretical curves based on different sintering stress expressions can be found in Appendix H.



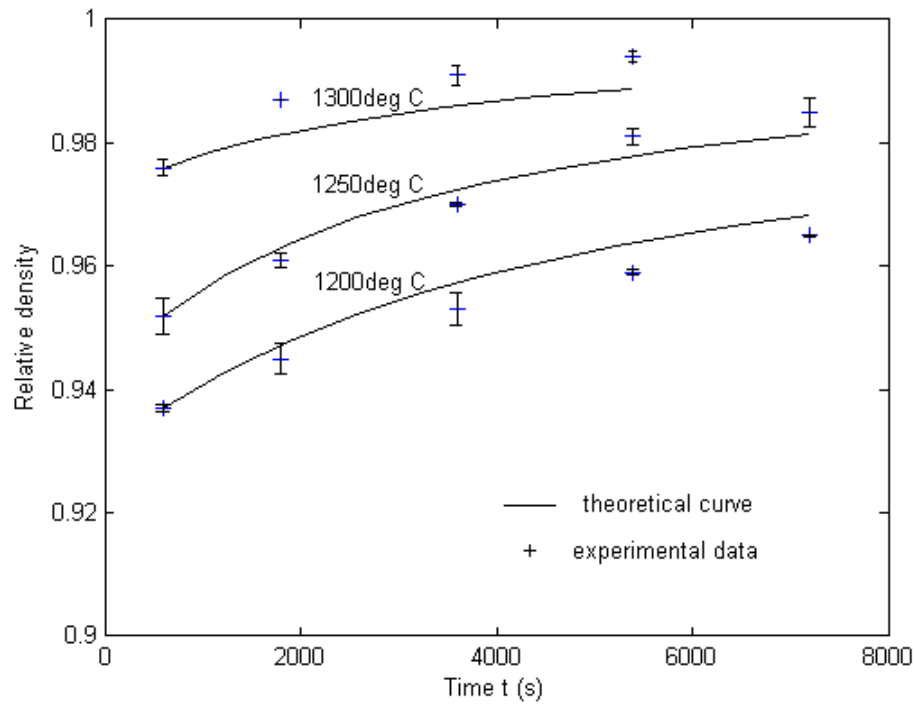
(a) Sub-structure (theoretical curve based on Eq. 6-11)



(b) Microsize structures of $\phi 100 \mu\text{m}$ (theoretical curve based on Eq. 6-12)



(c) Microsize structures of $\phi 80 \mu\text{m}$ (theoretical curve based on Eq. 6-13)



(d) Microsize structures of $\phi 60 \mu\text{m}$ (theoretical curve based on Eq. 6-14)

Figure 6.7 Comparison of theoretical and experimental density-time results

(Theoretical curves assume pores located at four-grain junctions)

6.4.3 Effects of pore location on densification of microsize structures

In the earlier model discussed in chapter 3, all the pores are assumed to be closed pores situated on the intersection of four grains in the form of spherical tetrahedrons for the final stage sintering. In reality, however, it is not necessary for all the pores to be situated at the four-grain junctions. When entering into the final sintering stage, the pore changes from continuous channels along three-grain junctions into closed pores at the three-grain junctions by means of Rayleigh instability and some of them may move

from three-grain junctions onto two-grain interfaces [116, 179]. This corresponds to the observed pores at the two-grain interfaces in section 5.1.1. Besides, a fraction of the pores on the two-grain interfaces broke away from the grain boundaries and formed separated pores as observed in Figures 5.1 to 5.6. Therefore, the effects of pores located at two-grain interfaces and separated pores on the densification of microsize structures are considered here.

(a) Considering pores located at two-grain interfaces

If all the pores are assumed as lenticular pores located at two-grain interface instead of spherical tetrahedrons at four-grain junctions, the grain boundary area reduction due to the pores per polyhedron S_s is given by:

$$S_s = 12\alpha r_s^2 \quad \text{Eq. 6-15}$$

The pore surface area per polyhedron A_s is given by:

$$A_s = 12\beta r_s^2 \quad \text{Eq. 6-16}$$

The pore volume per polyhedron, V_s , is given by:

$$V_s = 12\lambda r_s^3 \quad \text{Eq. 6-17}$$

Here α , β , λ are coefficients that depends on the dihedral angle of the pores (see Appendix D).

Substituting Eqs. 6-15 to 6-17 into sintering stress Eq. 4-27 gives

$$\sigma_s d \left(\frac{12\lambda r_s^3}{\rho G^3} \right) = \gamma_b d \left[\frac{1}{\rho G} \left(\frac{3\sqrt{3}}{4} + \frac{3}{8} \right) \right] - \gamma_b d \left(\frac{12\alpha r_s^2}{\rho G^3} \right) + \gamma_s d \left(\frac{12\beta r_s^2}{\rho G^3} \right) \quad \text{Eq. 6-18}$$

As $1 - \rho = \frac{V_s}{V_G} = \frac{24\lambda r_s^3}{G^3}$, Eq. 6-18 can be rewritten as:

$$\begin{aligned} \sigma_s d\rho = & \gamma_b \left(\frac{3\sqrt{3}}{2} + \frac{3}{4} \right) \frac{\rho}{G^2} dG + \frac{\gamma_b \left(\frac{3\sqrt{3}}{2} + \frac{3}{4} \right)}{G} d\rho - \gamma_b \frac{6\alpha \left(\frac{1-\rho}{3\lambda} \right)^{2/3} \rho}{G^2} dG - \gamma_b \frac{6\alpha \left(\frac{1}{3\lambda} \right)^{2/3} \left(1 - \frac{1}{3}\rho \right)}{G(1-\rho)^{1/3}} d\rho \\ & + \gamma_s \frac{6\beta \left(\frac{1-\rho}{3\lambda} \right)^{2/3} \rho}{G^2} dG + \gamma_s \frac{6\beta \left(\frac{1}{3\lambda} \right)^{2/3} \left(1 - \frac{1}{3}\rho \right)}{G(1-\rho)^{1/3}} d\rho \end{aligned} \quad \text{Eq. 6-19}$$

Substituting Eq. 4-31 into Eq. 6-19 yields:

$$\sigma_s = \gamma_b \frac{\left(\frac{3\sqrt{3}}{2} + \frac{3}{4} \right)}{k' \rho} + \frac{\gamma_b \left(\frac{3\sqrt{3}}{2} + \frac{3}{4} \right)}{G} + \frac{\left(\frac{1-\rho}{3\lambda} \right)^{2/3} (6\beta\gamma_s - 6\alpha\gamma_b)}{k' \rho} + \frac{\left(\frac{1}{3\lambda} \right)^{2/3} \left(1 - \frac{1}{3}\rho \right) (6\beta\gamma_s - 6\alpha\gamma_b)}{G(1-\rho)^{1/3}} \quad \text{Eq. 6-20}$$

For this material system, $\alpha = 3.05$, $\beta = 10.42$ and $\lambda = 3.13$. The densification rate for the various microsize structures is shown below:

(i) Microsize structures of $\phi 100 \mu\text{m}$

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-34039}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{1/2}} \times \left[\frac{0.96 + 10.83(1-\rho)^{2/3}}{\rho} \times 10^6 + \frac{2.24 + \frac{25.34 \left(1 - \frac{1}{3}\rho \right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{1/4}} \right] \quad \text{Eq. 6-21}$$

(ii) Microsize structures of $\phi 80 \mu\text{m}$

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-35482}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{\frac{1}{2}}} \times \left[\frac{0.84 + 9.46(1-\rho)^{\frac{2}{3}}}{\rho} \times 10^6 + \frac{2.24 + \frac{25.34 \left(1 - \frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{\frac{1}{4}}} \right]$$

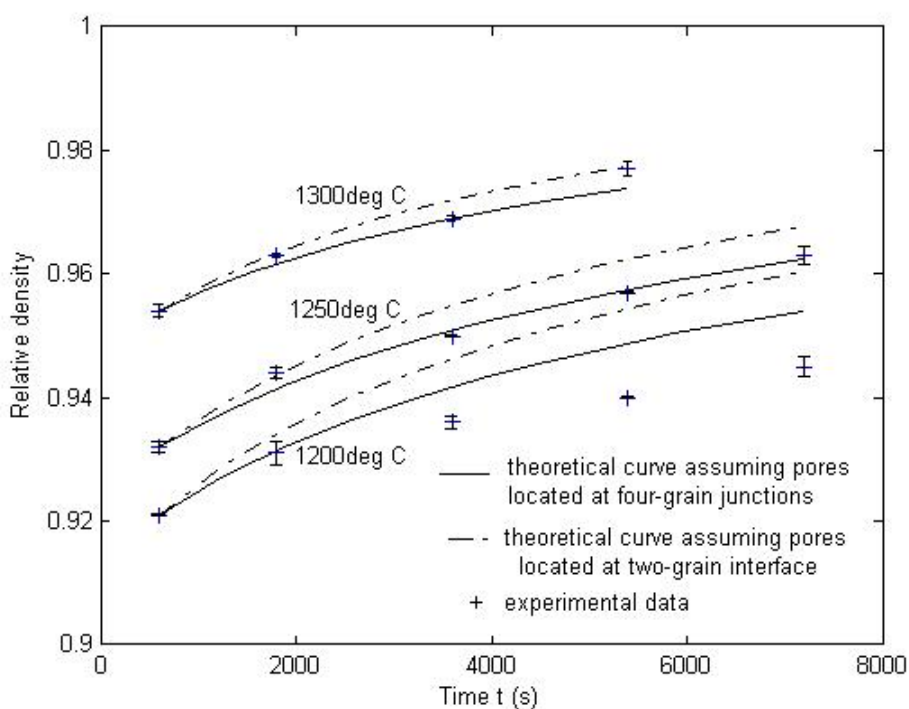
Eq. 6-22

(iii) Microsize structures of $\phi 60 \mu\text{m}$

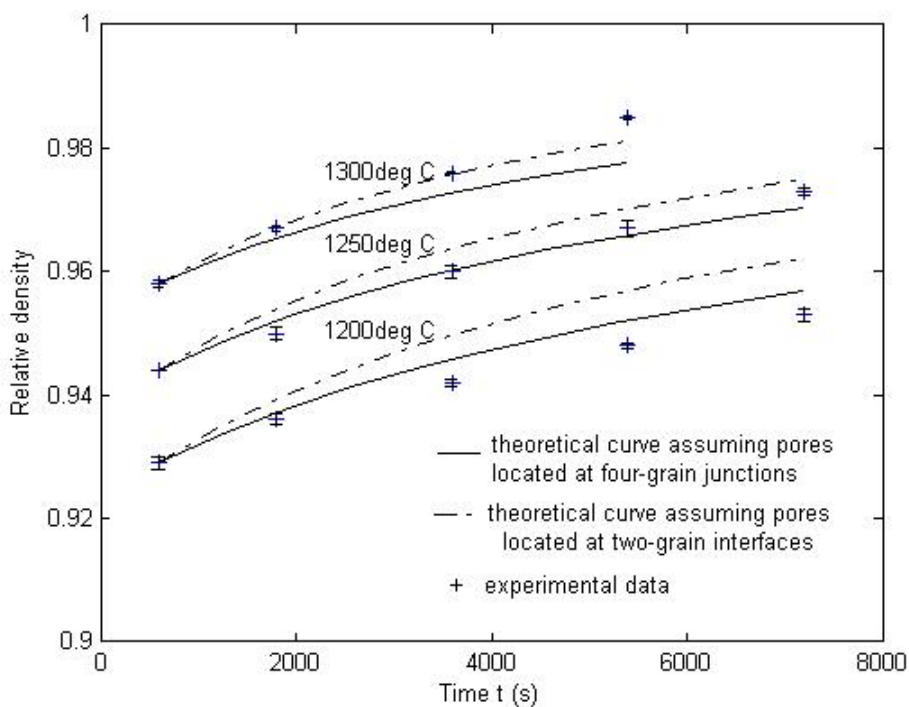
$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-41135}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]} \times \left[\frac{1.02 + 11.57(1-\rho)^{\frac{2}{3}}}{\rho} \times 10^6 + \frac{2.24 + \frac{25.34 \left(1 - \frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]^{\frac{1}{2}}} \right]$$

Eq. 6-23

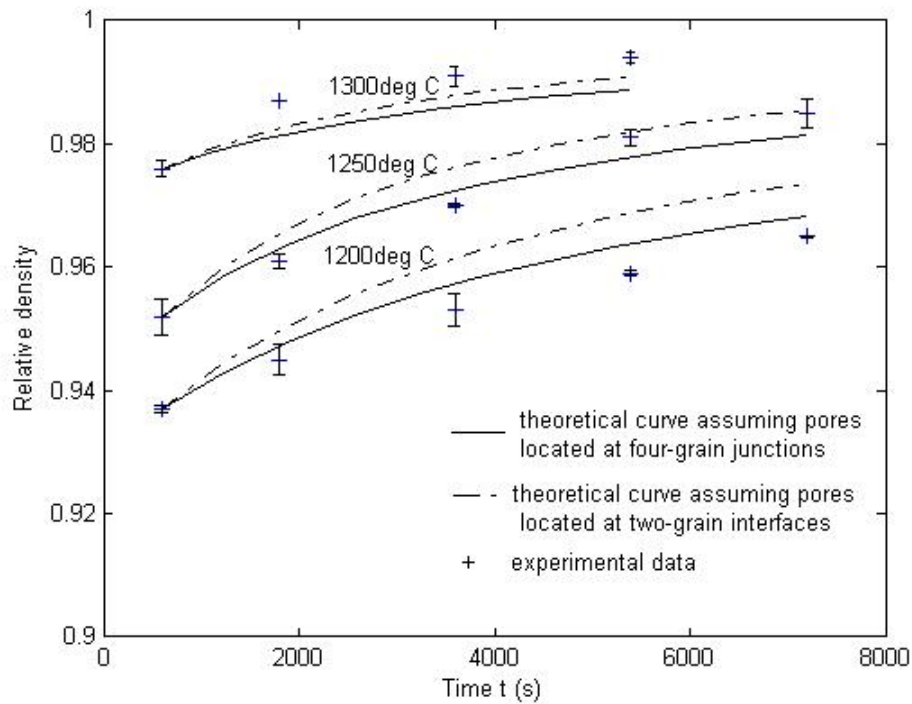
The theoretical curves computed on the premise that all the pores are located at the four-grain junctions or two-grain interfaces are compared with the experimental results as shown in Figure 6.8. When all the pores are assumed as lenticular pores at the two-grain interface, the predicted densities are higher than the values calculated with the assumption that all the pores occupies the four-grain junctions for all the microsize structures. It is to be noted that the effect of separated pores on densification was not considered here.



(a) Microsize structures of $\phi 100 \mu\text{m}$ (Eq. 6-12 used in the curve assuming pores at four grain junctions and Eq. 6-21 used in the curve assuming pores at two-grain interface)



(b) Microsize structures of $\phi 80 \mu\text{m}$ (Eq. 6-13 used in the curve assuming pores at four-grain junctions and Eq. 6-22 used in the curve assuming pores at two-grain interface)



(c) Microsize structures of $\phi 60 \mu\text{m}$ (Eq. 6-14 used in the curve assuming pores at four-grain junctions and Eq. 6-23 used in the curve assuming pores at two-grain interface)

Figure 6.8 Microsize structures: comparison of experimental density-time results with theoretical curves based on different pore locations on boundaries

(b) Considering separated pores and pores located at two-grain interface

To consider the effects of separated pores on densification, Helle *et al.* [137] has assumed that only a fraction of pores on the boundaries, f_p , continue to shrink by diffusional densifying processes after pore separation. A densification rate reduced to $f_p \dot{\rho}$ was proposed in their model. It is assumed that the fraction of pores on the grain boundaries is proportional to the area of grain boundary per unit volume. A stable grain

size as determined by Zener pinning was used to predict f_p as single crystal powder was studied in their work. However, in this research, polycrystalline powder was used and thus grain size prediction based on Brook's model [25] was employed instead. As the pores start to pinch off and isolated pores appear at the beginning of the final stage, all the pores are assumed to be on the grain boundaries at the end of the intermediate stage, that is $\rho = 0.92$ according to Ashby [98]. If the average grain size at $\rho = 0.92$ is $\bar{G}$ and the grain size to be studied is G , it is assumed that $f_p = \frac{\bar{G}}{G}$ for $G \geq \bar{G}$. For $G < \bar{G}$, $f_p = 1$. In this study, $\bar{G} = 13.68 \mu\text{m}$ is used and this is deduced from the microsize structures of $\phi 100 \mu\text{m}$. The grain size of the microsize structures of $\phi 100 \mu\text{m}$ is used here since a relative density close to 0.92 could be found on such microsize structures within the temperatures studied. It is to be noted that f_p is not considered proportional to the overall densification rate as in Helle's model. Instead, it is proportional to the stress item coming from the work done by surface energies. This is because the existence of f_p will not affect the surface areas of the grains but it will affect the pore surface as well as the volume per grain. Thus, including f_p into Equations 6-21 to 6-23, the densification rate for the various microsize structures is shown below:

(i) Microsize structures of $\phi 100 \mu\text{m}$:

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-34039}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{\frac{1}{2}}} \times \left[\frac{0.96 + 10.83 f_p (1-\rho)^{\frac{2}{3}}}{\rho} \times 10^6 + \frac{2.24 + \frac{25.34 f_p \left(1 - \frac{1}{3} \rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{\frac{1}{4}}} \right]$$

Eq. 6-24

(ii) Microsize structures of $\phi 80 \mu\text{m}$:

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-35482}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{\frac{1}{2}}} \times \left[\frac{0.84 + 9.46 f_p (1-\rho)^{\frac{2}{3}}}{\rho} \times 10^6 + \frac{2.24 + \frac{25.34 f_p \left(1 - \frac{1}{3} \rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{\frac{1}{4}}} \right]$$

Eq. 6-25

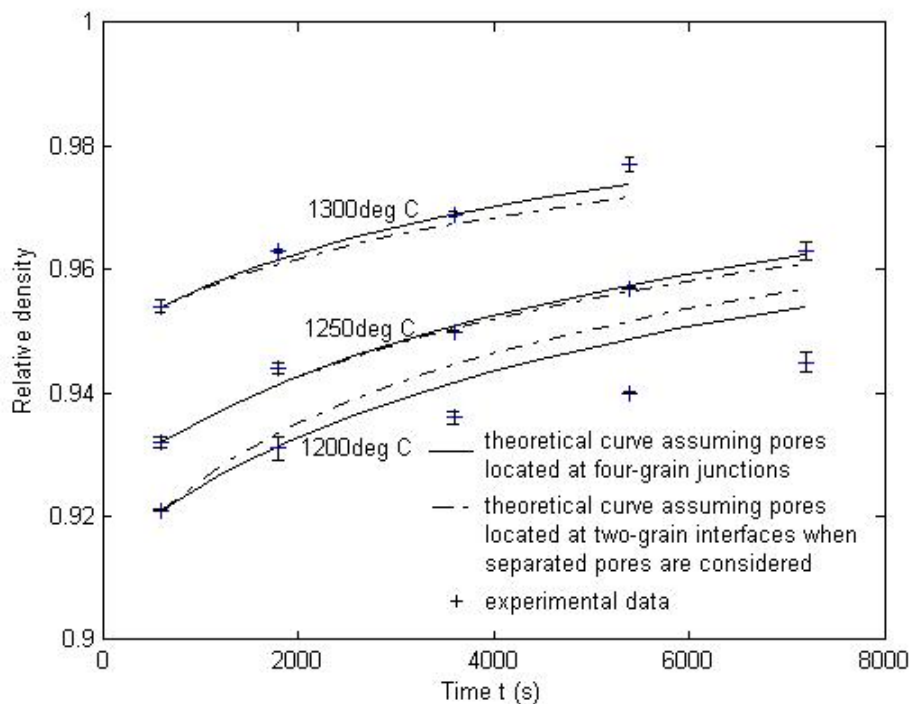
(iii) Microsize structures of $\phi 60 \mu\text{m}$:

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-41135}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]} \times \left[\frac{1.02 + 11.57 f_p (1-\rho)^{\frac{2}{3}}}{\rho} \times 10^6 + \frac{2.24 + \frac{25.34 f_p \left(1 - \frac{1}{3} \rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]^{\frac{1}{2}}} \right]$$

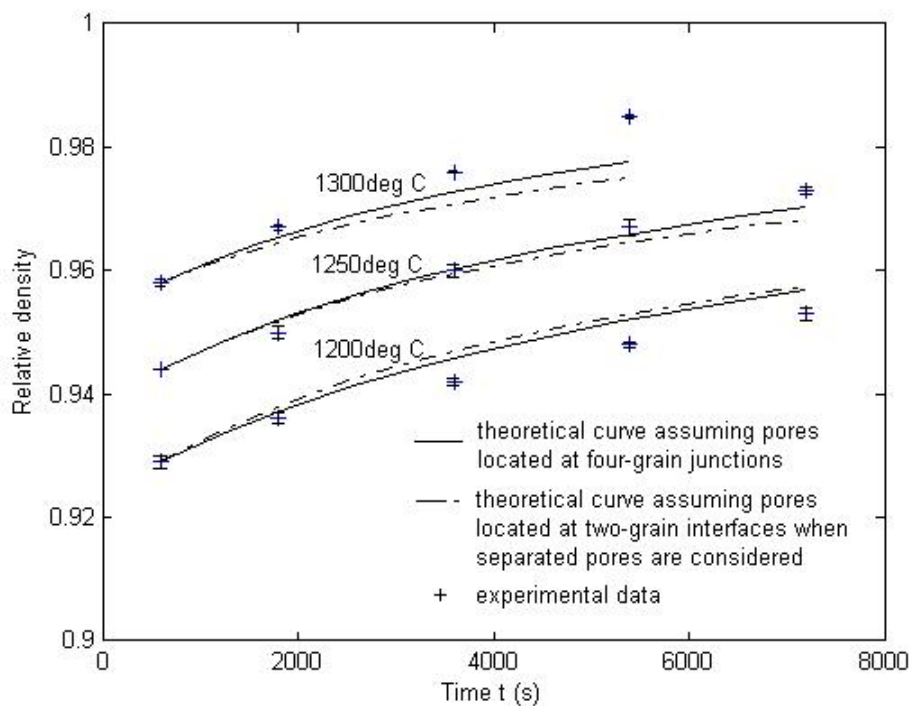
Eq. 6-26

Figure 6.9 depicts the theoretical curves computed when different pores location are considered as well as the experimental density-time results for various microsize structures. Even though a simplified assumption that all the pores are located at four-grain junctions is used, it yields densities similar to that computed when pores are

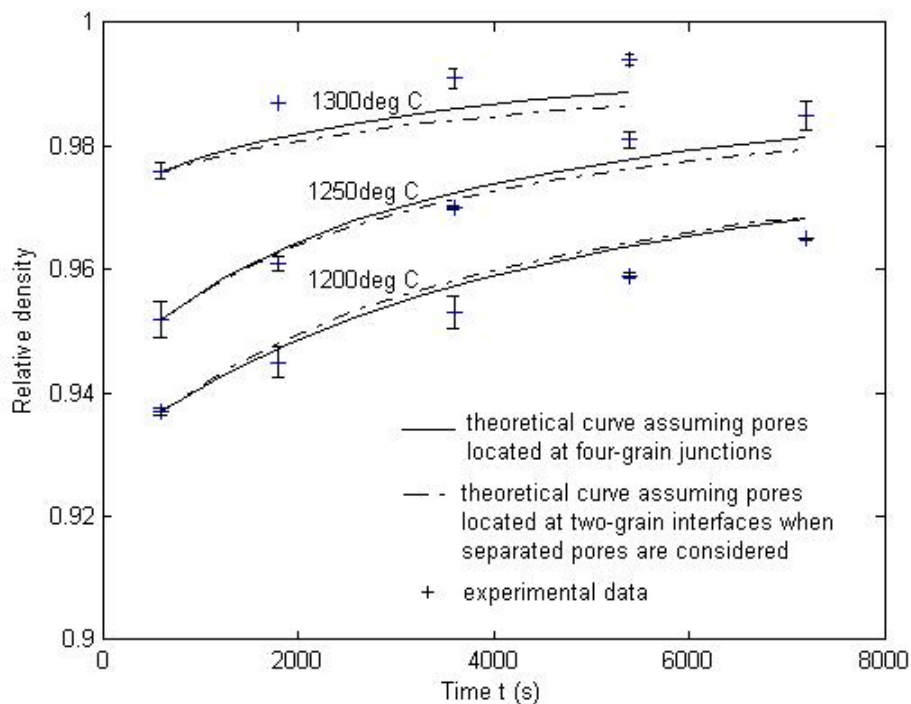
located on two-grain interface and separated pores are considered. This may be due to the increase in sintering stress arising from pores located at the two-grain interfaces complementing the decrease in sintering stress due to separated pores. Further, the controlling mechanism of densification on various microsize structures is lattice diffusion. This is the only mechanism for material transport to the separated pores. Thus, even though lattice diffusion is relatively slow, some separated pores could still be eliminated, unlike Helle's premise [137] that only the pores on boundaries would shrink. Consequently, the simplified assumption of pores located at the four-grain junctions can be used in the model.



(a) Microsize structures of $\phi 100 \mu\text{m}$ (Eq. 6-12 used in the curve assuming pores at four-grain junctions and Eq. 6-24 used in the curve assuming pores at two-grain interface when separated pores were considered)



(b) Microsize structures of $\phi 80 \mu\text{m}$ (Eq. 6-13 used in the curve assuming pores at four-grain junctions and Eq. 6-25 used in the curve assuming pores at two-grain interface when separated pores were considered)



(c) Microsize structures of $\phi 60 \mu\text{m}$ (Eq. 6-14 used in the curve assuming pores at four-grain junctions and Eq. 6-26 used in the curve assuming pores at two-grain interface when separated pores were considered)

Figure 6.9 Microsize structures: comparison of experimental density-time results with theoretical curves based on different pore locations

6.4.4 Effects of boundary energy on the densification of the microsize structures

If the grain boundary energy is neglected for the final sintering stage, Eq. 4-27 can be written as:

$$\sigma_s d(V_s N_g) = \gamma_s d(A_s N_g) \quad \text{Eq. 6-27}$$

As the grain boundary energy is neglected, the pores are assumed to be spherical closed pores situated on four-grain junctions. The pore volume enclosed per polyhedron, V_s , is $8\pi r_s^3/3$. A_s , the pore surface area enclosed per polyhedron, is $(24/4)(4\pi r_s^2)$. As such, Eq. 6-27 can be rewritten as:

$$\sigma_s d\left(\frac{r_s^3}{\rho G^3}\right) = \gamma_s d\left(\frac{3r_s^2}{\rho G^3}\right) \quad \text{Eq. 6-28}$$

The radius of a spherical pore can be expressed in terms of ρ and G :

$$r_s = G^3 \sqrt[3]{\frac{1-\rho}{16\pi}} \quad \text{Eq. 6-29}$$

Substituting Eqs. 4-11, 6-29 into Eq. 6-28 gives

$$\sigma_s = \frac{11.07\gamma_s(1-\rho)^{2/3}}{k'\rho} + \frac{11.07\gamma_s\left(1-\frac{1}{3}\rho\right)}{G(1-\rho)^{1/3}} \quad \text{Eq. 6-30}$$

Substitute Eq. 6-30 into Eq. 4-21 gives the densification rate for various microsize structures as follows:

(i) Microsize structures of $\phi 100 \mu\text{m}$

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-34039}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{\frac{1}{2}}} \times \left[\frac{9.46(1-\rho)^{\frac{2}{3}}}{\rho} \times 10^6 + \frac{\frac{22.14\left(1-\frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{\frac{1}{4}}} \right]$$

Eq. 6-31

(ii) Microsize structures of $\phi 80 \mu\text{m}$

$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-35482}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{\frac{1}{2}}} \times \left[\frac{8.26(1-\rho)^{\frac{2}{3}}}{\rho} \times 10^6 + \frac{\frac{22.14\left(1-\frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{\frac{1}{4}}} \right]$$

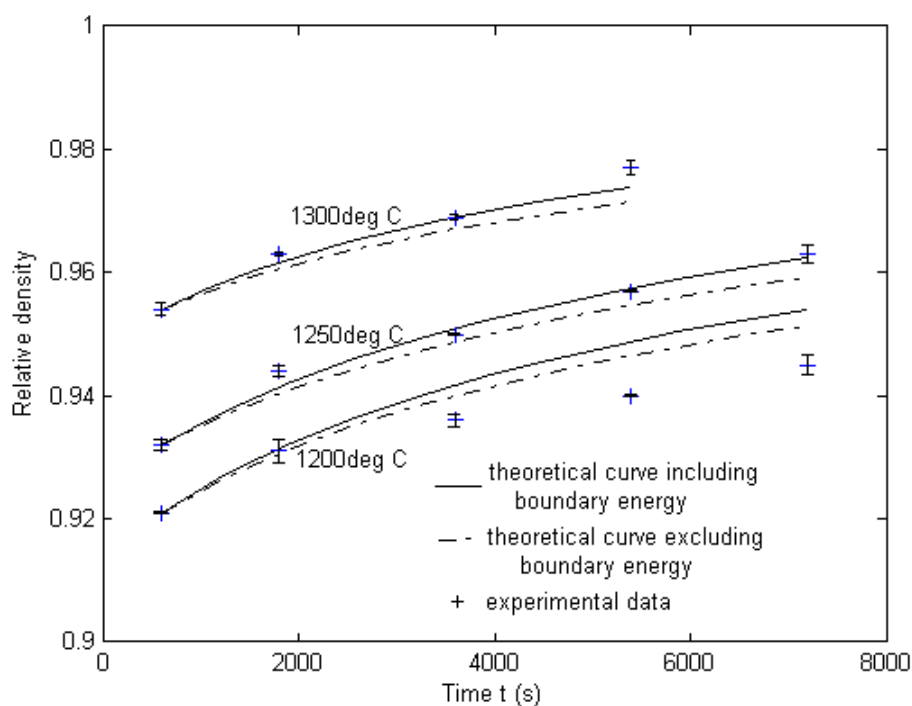
Eq. 6-32

(iii) Microsize structures of $\phi 60 \mu\text{m}$

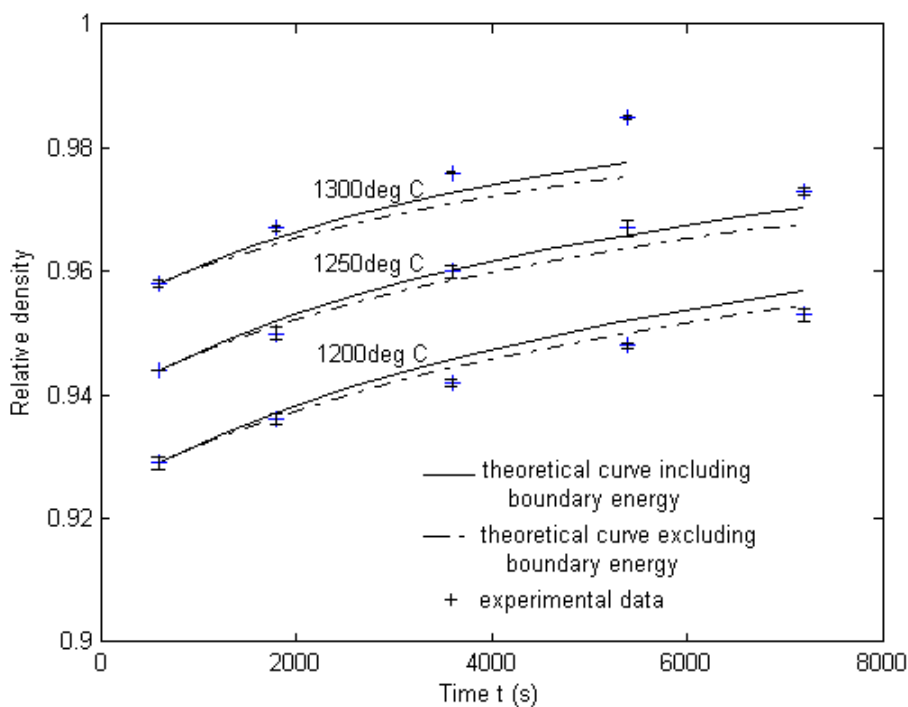
$$\dot{\rho} = \frac{1.44\rho^2 C_1 \exp\left(\frac{-41135}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{T \left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]} \times \left[\frac{10.11(1-\rho)^{\frac{2}{3}}}{\rho} \times 10^6 + \frac{\frac{22.14\left(1-\frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]^{\frac{1}{2}}} \right]$$

Eq. 6-33

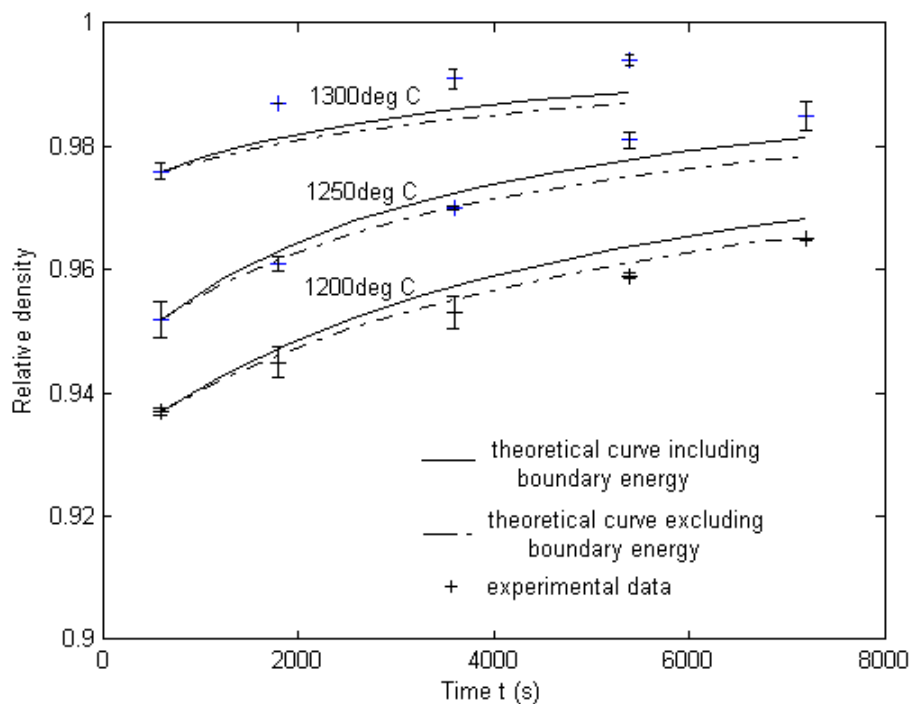
The theoretical curves including and excluding grain boundary energies and the experimental results of various microsize structures are shown in Figure 6.10. It can be seen that when the work done by grain boundary energy is included, the predicted densities are higher for all the microsize structures studied. The higher predicted densities are generally closer to the experimental results.



(a) Microsize structures of $\phi 100 \mu\text{m}$ (Eq. 6-12 used in the curve including boundary energy and Eq. 6-31 used in the curve excluding boundary energy)



(b) Microsize structures of $\phi 80 \mu\text{m}$ (Eq. 6-13 used in the curve including boundary energy and Eq. 6-32 used in the curve excluding boundary energy)



(c) Microsize structures of $\phi 60 \mu\text{m}$ (Eq. 6-14 used in the curve including boundary energy and Eq. 6-33 used in the curve excluding boundary energy)

Figure 6.10 Microsize structures: comparison of experimental density-time results with theoretical curves including and excluding grain boundary energies

6.4.5 Correction factor for the model

As discussed in Section 6.4.2, the model based on the sintering stress Eq. 4-32 overestimates the densities slightly at the lower temperature of 1200 °C and underestimates the densities at the higher temperature of 1300 °C for various microsize structures. This may be attributed to the internal gas pressure that is neglected in the theoretical model. As larger surface-to-volume ratio of the microsize structures makes it

easier for the gas to egress, the gas entrapped in the pores was not considered for simplification. In reality, however, there might still be a fraction of gas left on the microsize structures after pore closure. As gas diffusivity is thermally active, the amount of entrapped gas varies with temperature, more remaining at lower temperatures and less at higher temperatures. In this work, the material constant fitted from a median temperature of the 1250 °C was used for modeling from 1200 °C to 1300 °C. That is to say, a median amount of entrapped gas was considered during the modeling. As a result of this, there lies a discrepancy between the assumed and actual amount of entrapped gas on the microsize structures for various temperatures. At 1200 °C, which is lower than 1250 °C, insufficient internal gas pressure is included in the model and vice versa at 1300 °C, which is higher than 1250 °C. Given that the internal gas pressure acts opposite to the sintering stress, in comparison with the experimental results, the model would predict a higher value at a lower temperature and a lower value at a higher temperature.

As the amount of entrapped gas on the microsize structures varies with sintering parameters, Eq. 4-34 used for the sub-structure cannot be used here. Instead, a correction factor is introduced to incorporate the effects of varying entrapped gas on the densification of various microsize structures. A correction factor proportional to grain size, $\frac{G}{z}$, is proposed. It is related to grain size as the dense layer in the microsize structures, an indicator for gas diffusion, also increases spatially with sintering temperature and time. Here, z is a constant. For debound parts where grain size is akin

to particle size, the correction factor should be 1. Therefore, $z = D$ is used for the correction factor where D is particle size here.

Based on the constitutive model discussed in section 6.3.4, the material constant C_1 in Eqs. 6-12 to 6.14 is replaced by C_3 , which is a material constant when the correction factor is incorporated. For various microsize structures, C_3 is fitted from densification-time data at 1250 °C and used for all the subsequent computations.

$C_3 = 1.90 \times 10^{-9} \text{ s}^{-1} \text{ N}^{-1} \text{ m}^4 \text{ K}$ for microsize structures of $\phi 100 \text{ }\mu\text{m}$

$C_3 = 6.21 \times 10^{-9} \text{ s}^{-1} \text{ N}^{-1} \text{ m}^4 \text{ K}$ for microsize structures of $\phi 80 \text{ }\mu\text{m}$

$C_3 = 3.95 \times 10^{-7} \text{ s}^{-1} \text{ N}^{-1} \text{ m}^4 \text{ K}$ for microsize structures of $\phi 60 \text{ }\mu\text{m}$.

The densification rate of the microsize structure of $\phi 100 \text{ }\mu\text{m}$ is given by:

$$\dot{\rho} = \frac{1.44 \rho^2 C_3 \exp\left(\frac{-34039}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{TD \left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{1/4}} \times \left[\frac{0.96 + 7.82(1-\rho)^{2/3}}{\rho} \times 10^6 + \frac{2.24 + \frac{18.29 \left(1 - \frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.11}{T} \times 10^{-8} t \exp\left(\frac{-39812}{T}\right) + G_o^4 \right]^{1/4}} \right]$$

Eq. 6-34

For the microsize structure of $\phi 80 \text{ }\mu\text{m}$:

$$\dot{\rho} = \frac{1.44 \rho^2 C_3 \exp\left(\frac{-35482}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{TD \left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{1/4}} \times \left[\frac{0.84 + 6.83(1-\rho)^{2/3}}{\rho} \times 10^6 + \frac{2.24 + \frac{18.29 \left(1 - \frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{1.22}{T} \times 10^{-9} t \exp\left(\frac{-36204}{T}\right) + G_o^4 \right]^{1/4}} \right]$$

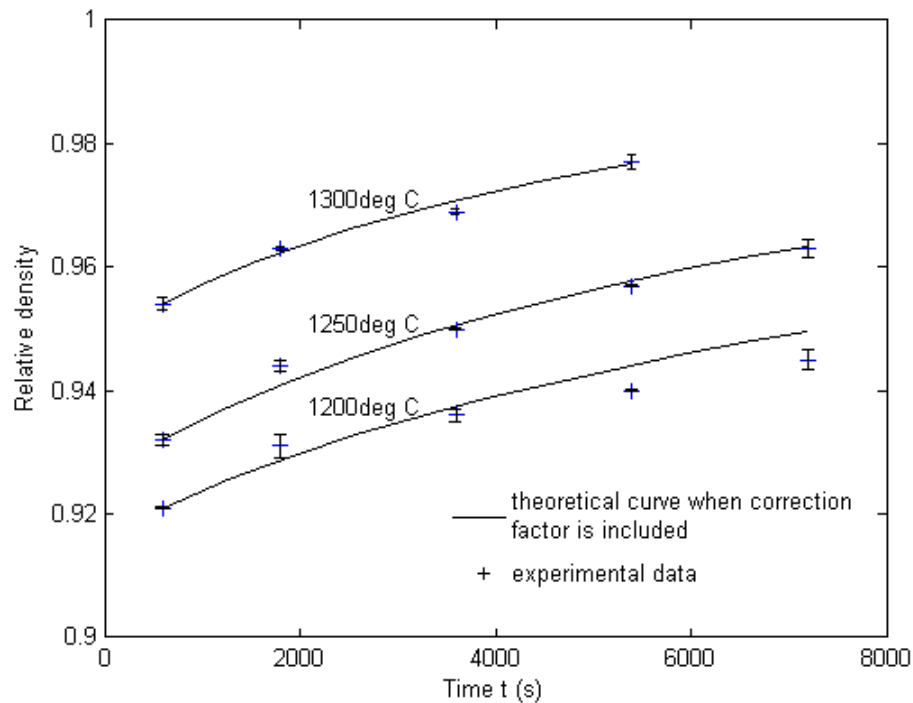
Eq. 6-35

For the microsize structure of $\phi 60 \mu\text{m}$:

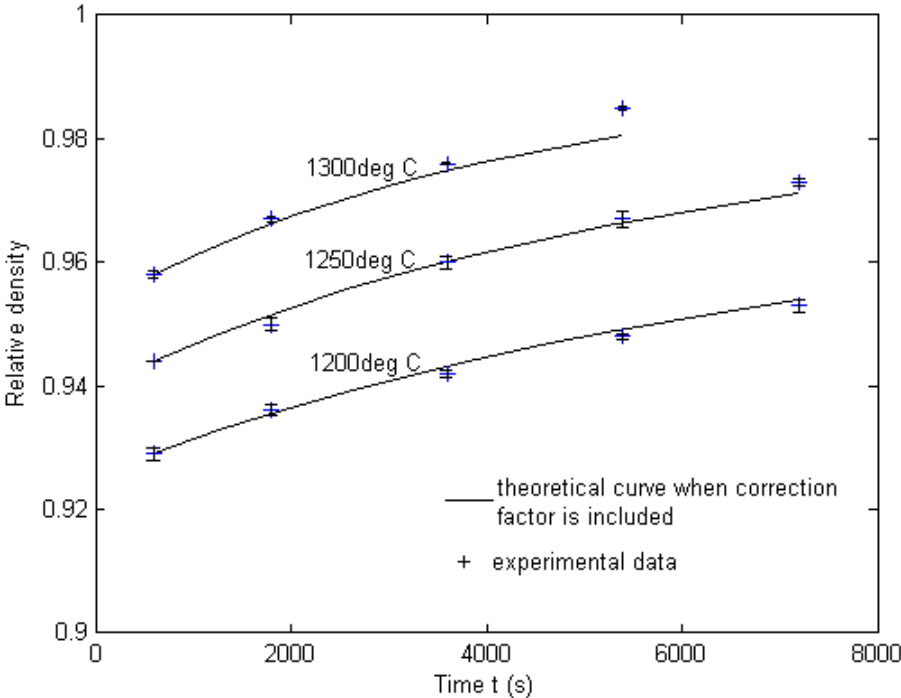
$$\dot{\rho} = \frac{1.44\rho^2 C_3 \exp\left(\frac{-41135}{T}\right) \times \left(\frac{1-\rho}{\rho-0.69}\right)}{TD \left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]^{\frac{1}{2}}} \times \left[\frac{1.02 + 8.35(1-\rho)^{\frac{2}{3}}}{\rho} \times 10^6 + \frac{2.24 + \frac{18.29\left(1 - \frac{1}{3}\rho\right)}{\sqrt[3]{1-\rho}}}{\left[\frac{0.04}{T} t \exp\left(\frac{-30190}{T}\right) + G_o^2 \right]^{\frac{1}{2}}} \right]$$

Eq. 6-36

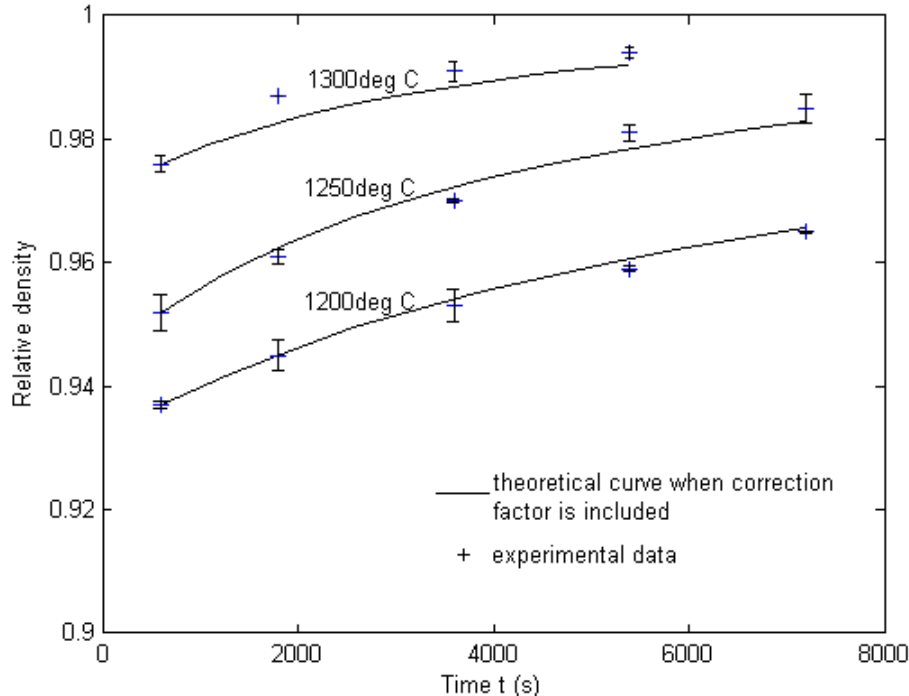
Figure 6.11 compares the theoretical curves computed after including the correction factor in the model with experimental results of various microsize structures. It can be seen that the experimental results agree reasonably well with the theoretical values.



(a) Microsize structure of $\phi 100 \mu\text{m}$ (theoretical curve based on Eq. 6-34)



(b) Microsize structure of $\phi 80 \mu\text{m}$ (theoretical curve based on Eq. 6-35)



(c) Microsize structure of $\phi 60 \mu\text{m}$ (theoretical curve based on Eq. 6-36)

Figure 6.11 Microsize structures: comparison of experimental density-time results with theoretical curves computed with correction factor included in the model

6.5 Conclusions

a) Based on the experiments, surface diffusion controlled pore drag is assumed for grain growth of the sub-structure and microsize structures of $\phi 100\ \mu\text{m}$ and $\phi 80\ \mu\text{m}$ while boundary diffusion is assumed for grain growth of the microsize structures of $\phi 60\ \mu\text{m}$. The calculated activation energies for the sub-structure and various microsize structures during grain growth are listed in Table 6.3.

b) Based on the experiments, boundary diffusion is assumed for the sub-structure during densification when lattice diffusion is assumed for various microsize structures. The calculated activation energies for the sub-structure and various microsize structures during densification are listed in Table 6.6.

c) A new sintering stress expression for the final sintering stage is established by taking into account the variation in grain number. A model for the grain growth and densification of microstructured parts with microsize structures of $\phi 100\ \mu\text{m}$, $\phi 80\ \mu\text{m}$ and $\phi 60\ \mu\text{m}$ is established. For various microsize structures, the theoretical curves slightly overestimate densities at a low temperature of $1200\ ^\circ\text{C}$, in particular for the microsize structures of $\phi 100\ \mu\text{m}$. At a high temperature of $1300\ ^\circ\text{C}$, the model slightly underestimates the densities for smaller microsize structures, i.e. the microsize structures of $\phi 80\ \mu\text{m}$ and $\phi 60\ \mu\text{m}$.

d) The treatment of all pores located at the four-grain junctions in the model gives reasonable fit with the experimental results even though there are separated pores and pores located at two-grain interfaces. Including the work done by grain boundary energy gives higher predicted densities for all the microsize structures studied, which are generally closer to the experimental results. The theoretical curves computed after including the correction factor agree reasonably well with experimental results of various microsize structures.

Chapter 7 Conclusions and Future Work

To investigate the effects of size of microstructured parts on the grain growth and densification, an in-house feedstock that incorporated 316L stainless steel powder of 2.37 μm size and a binder system comprising of PAN-250S and LDPE was used. A circular disc of $\phi 16$ mm and 1.5 mm thick with an array of 24 x 24 (i.e., a total of 576) microsize structures ($\phi 100$ μm x height 200 μm , $\phi 80$ μm x height 196 μm or $\phi 60$ μm x height 191 μm) was molded. The microstructured parts were debound and then sintered under a variety of sintering schedules for the study.

Experimental results show that both grain size and density of the sub-structure of microstructured parts were lower than those of various microsize structures after sintering. The microsize structures of $\phi 100$ μm , $\phi 80$ μm and $\phi 60$ μm were at the final sintering stage while the sub-structure was at the intermediate sintering stage for 1200 $^{\circ}\text{C}$, 1250 $^{\circ}\text{C}$ and 1300 $^{\circ}\text{C}$. It indicates that the size reduction into micrometer regime increased densification. Among the various microsize structures, densification was promoted over grain growth for the microsize structures of $\phi 60$ μm . The presence of oxides on the debound parts and the ensuing internal gas pressure was attributed to different sintering behavior between the sub-structure and various microsize structures.

Sintering kinetics investigation reveals that the controlling mechanism for grain growth or densification varied for the sub-structure and microsize structures. For grain growth, surface diffusion controlled pore drag was assumed for the sub-structure and microsize structures of $\phi 100\text{ }\mu\text{m}$ and $\phi 80\text{ }\mu\text{m}$ while boundary diffusion was assumed for the microsize structures of $\phi 60\text{ }\mu\text{m}$. This might be due to that the microsize structures of $\phi 60\text{ }\mu\text{m}$ has higher density and thus less pore drag is superimposed on the grain boundary to restrain its movement. For densification, boundary diffusion was assumed for the sub-structure when lattice diffusion was assumed for various microsize structures. It corresponds to the scale effect of sintering mechanisms where the relative contribution of grain boundary over lattice diffusion is enhanced with a reduction in scale since the grain size of the sub-structure is smaller than that of the microsize structures. The calculated activation energies for the sub-structure and microsize structures during grain growth and densification are listed in Tables 6.3 and 6.6.

A constitutive model was established to compute densification for the microstructured parts, from the sub-structure to various microsize structures. To take into account the variation in grain number for the final sintering stage, a new sintering stress expression was developed. The constitutive model comprises the following:

1) Grain growth based on Brook's equations

(i) Grain growth under surface diffusion controlled pore drag is given by:

$$G^4 - G_0^4 = \frac{K_1}{T} t \exp\left(\frac{-Q_s}{RT}\right)$$

(ii) Boundary diffusion controlled grain growth is given by:

$$G^2 - G_0^2 = \frac{K_3}{T} t \exp\left(\frac{-Q_b}{RT}\right)$$

2) Sintering stress

(i) For intermediate sintering stage, the sintering stress is given by:

$$\sigma_s = \frac{5.15\gamma_s}{(1-\rho)^{1/2} G}$$

(ii) For final sintering stage, the sintering stress is given by:

$$\sigma_s = \frac{3.35\gamma_b}{k'\rho} + \frac{3.35\gamma_b}{G} + \left(\frac{1}{12\lambda}\right)^{2/3} \frac{12(\beta\gamma_s - \alpha\gamma_b)\left(1 - \frac{1}{3}\rho\right)}{G(1-\rho)^{1/3}} + \left(\frac{1-\rho}{12\lambda}\right)^{2/3} \frac{12(\beta\gamma_s - \alpha\gamma_b)}{k'\rho}$$

3) Internal gas pressure

Assuming ideal gas behavior, if the gas cannot diffuse through the part, the internal gas pressure can be expressed as follows:

$$P_i = \frac{P_{cl}(1-\rho_{cl})\rho T}{T_{cl}(1-\rho)\rho_{cl}}$$

4) Densification

(i) The densification rate for lattice diffusion controlled creep is given by:

$$\dot{\rho} = 9\rho^2 \frac{C_1 \exp\left(\frac{-Q_L}{RT}\right)}{TG^2} \times f\sigma_s$$

(ii) The densification rate for grain boundary diffusion controlled creep is given by:

$$\dot{\rho} = 9\rho^2 \frac{C_2 \exp\left(\frac{-Q_b}{RT}\right)}{TG^3} \times f\sigma_s$$

A comparison of the experimental results of the sub-structure and various microsize structures with the computation based on the constitutive model shows that the model approximately agreed with the experimental results of various microstructured parts. Despite separated pores and pores located at two-grain interfaces, the treatment of all pores located at the four-grain junctions in the model gave reasonable fit with the experimental results. Including the work done by grain boundary energy gave higher predicted densities for all the microsize structures studied, which were generally closer to the experimental results. The theoretical curves computed after including the correction factor agreed reasonably well with experimental results of various microsize structures.

Based on the constitutive model for computing the sintering behavior of various 316L stainless steel microstructured parts, the following is a suggested list of research areas to be focused on in the future:

a) Thermal debinding is an intricate combination of liquid and gas migration, pyrolysis of binder, evaporation and heat transfer in porous media. During debinding, polymer is heated thermally, melted into liquid, and decomposed into vapor. If the diffusion flux of degradation products from the center of the body towards the surface and their evaporation are not fast enough, the concentration of the degradation products in the binder may reach a limit state. This would result in the generation of gases inside the body. Due to polymer content change, temperature change and gas pressure, stress and strain are caused during thermal debinding.

Modeling on the heat and mass transport of polymer removal from a μ PIM part by thermal debinding and the subsequent stress and deformation of the part can be carried out. Based on heat and mass transfer in porous media and elasticity theory, modeling of thermal debinding provides potential to optimize the process. In addition, the knowledge into density field, stress field and geometry of debound parts fabricated by μ PIM would be useful. They can be imported into the constitutive model as inputs of initial density field, initial stress field and initial geometry of the part for sintering. Debinding under other gas atmospheres could be conducted to examine if pore elimination is facilitated during sintering.

b) For the constitutive modeling of sintering in μ PIM, the well-established finite element (FE) method can be used to model the sintering of a microstructured part. In such a model, a debound microstructured part is treated as a continuum solid that undergoes time dependent deformation (creep) during sintering. Two internal state variables, density and grain size, are often used to characterize the microstructure of the material system. These state variables are functions of time and location.

The basic input data required by the continuum FE analysis in such a model include:

- 1) Sintering constitutive law and its parameters
- 2) Grain growth law and its parameters
- 3) Initial average particle size of the powder used
- 4) Initial density field of the debound part
- 5) Initial stress field of the debound part
- 6) Initial geometry of the debound part
- 7) Sintering temperature
- 8) Boundary conditions

Material properties of the powder used are characterized by 1) to 3) on the input list. Some of the parameters are intrinsic material properties, e.g. the specific surface and grain boundary energies, and the diffusion coefficients. With such a model, the analysis can predict the time history of stress and strain fields, density and grain size fields, shape and dimension of the microstructured parts fabricated by μ PIM. To compare the

theoretical calculations with the experimental results, density distributions of microsize structures can be obtained indirectly from the relationship between hardness and relative density.

c) An observation in the research is that microsize structures of $\phi 100\ \mu\text{m}$, $\phi 80\ \mu\text{m}$ and $\phi 60\ \mu\text{m}$ are in the final sintering stage while the sub-structure is in the intermediate sintering stage for the various temperatures studied. It would be useful to conduct experiments for different material systems to examine whether or not similar phenomenon occurs for the various microstructured parts.

In this research, the established constitutive model was compared to experimental results of various microsize structures that were based on lattice-diffusion controlled densification. Experiments for microsize structures made of other material systems which densify by grain boundary diffusion can be carried out to verify if the model is applicable to microstructured parts under boundary diffusion controlled densification. The feasibility of applying the model for grain growth under lattice diffusion or evaporation/condensation-controlled pore drag can also be investigated.

d) For microstructured parts, the smaller the microsize structure, the lesser the number of grains in the structure. Hence, anisotropy effects that were previously neglected in macroscopic specimen can no longer be omitted for microsize structures at the micro level. The preparation of the feedstock for subsequent injection molding, debinding and sintering in μ PIM is important, especially for nanopowder. When smaller particle size is used, more delicate microsize structures as well as higher aspect ratio can be replicated.

Proper feedstock preparation is to be investigated to avoid the presence of large pores that originate from the injection molded parts due to powder agglomeration. Such porosity acts as the most likely source of large isolated pore clusters that may affect sintering. In addition, for metal powder, it is essential to avoid any oxidation during handling since submicron powder tends to be pyrophoric.

It would be useful to apply our constitutive model for the material system to optimize sintering. As particle size decreases, powder becomes more thermodynamically unstable due to larger surface area. Hence, strict control of sintering parameters such as time and temperatures is important because sintering is kinetically enhanced due to an increase in the sintering driving force.

e) Particle size distribution is an important factor that exerts influence on packing density, feedstock viscosity and sintering shrinkage of the final part in μ PIM. In the constitutive model, for simplicity, average particle size was considered for the powder employed. However, the particle size distribution of the powder may affect the sintering behavior of the microstructured parts.

It would be useful to study the effect of particle size distribution on the sintering behavior of various microsize structures. The grain sizes and densities obtained for the microsize structures when various particle size distributions are used can be compared for microstructural control.

f) Atmosphere control is important during sintering of 316L stainless steel microstructured parts. This is because the material is sensitive to the oxidation potential of the sintering atmosphere, where oxide formation is aggravated since smaller particles are employed in μ PIM. The atmosphere used in sintering may change the densification rate, limiting density or grain size. In this research, hydrogen atmosphere is used since it is the most reducing atmosphere, which is more effective in oxide removal.

Apart from hydrogen, vacuum can also be used for sintering of 316L stainless steel powder. Vacuum sintering can be conducted and the difference in the sintering behavior of microstructured parts under different sintering atmospheres can be compared. The effects of internal gas pressure on the densification of the sub-structure and various

microsize structures can be examined through the comparison of grain size and density of microstructured parts obtained under hydrogen and vacuum sintering. It would be also of interest to examine if the dense layers observed on various microsize structures under hydrogen sintering would occur in vacuum sintering.

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Appendix A Thermal Characteristics of Binder Components and Feedstock

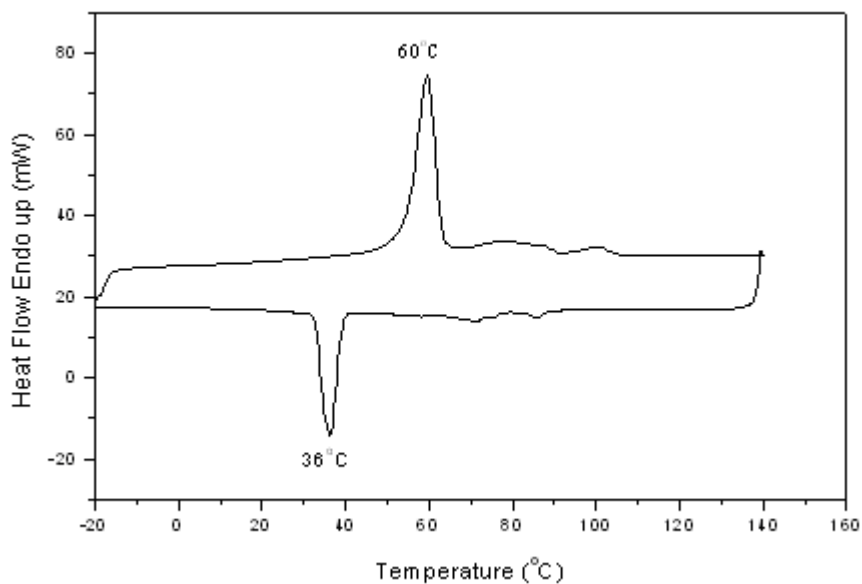


Figure A-1 DSC curve of PAN-250S

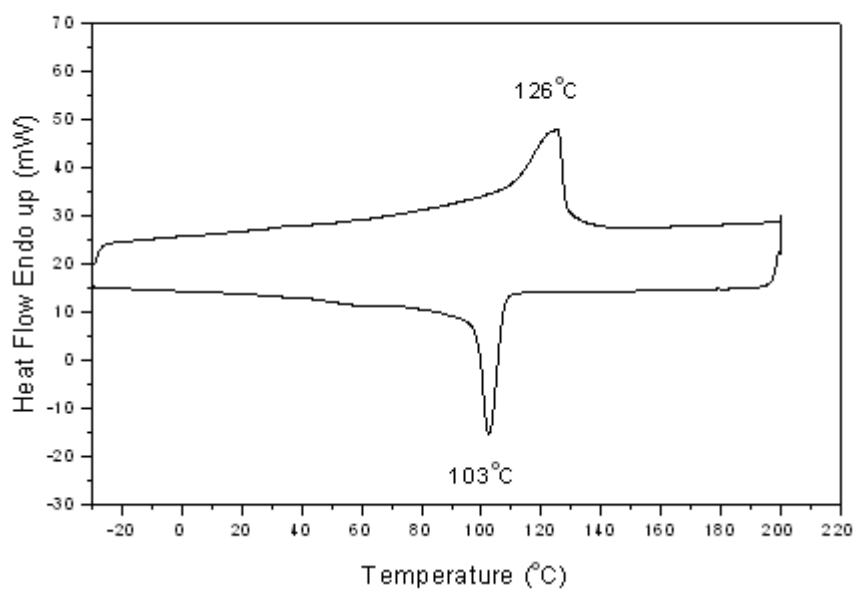


Figure A-2 DSC curve of LDPE

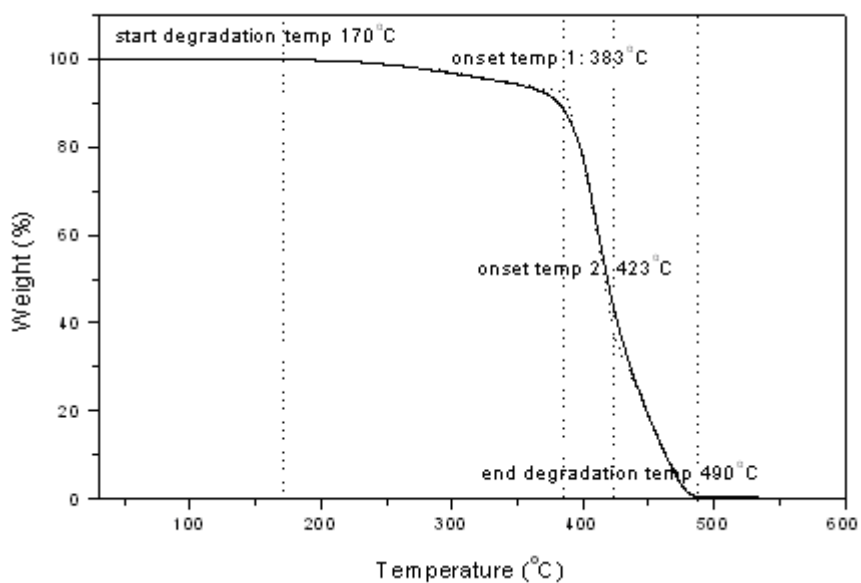


Figure A-3 TGA curve of PAN-250S

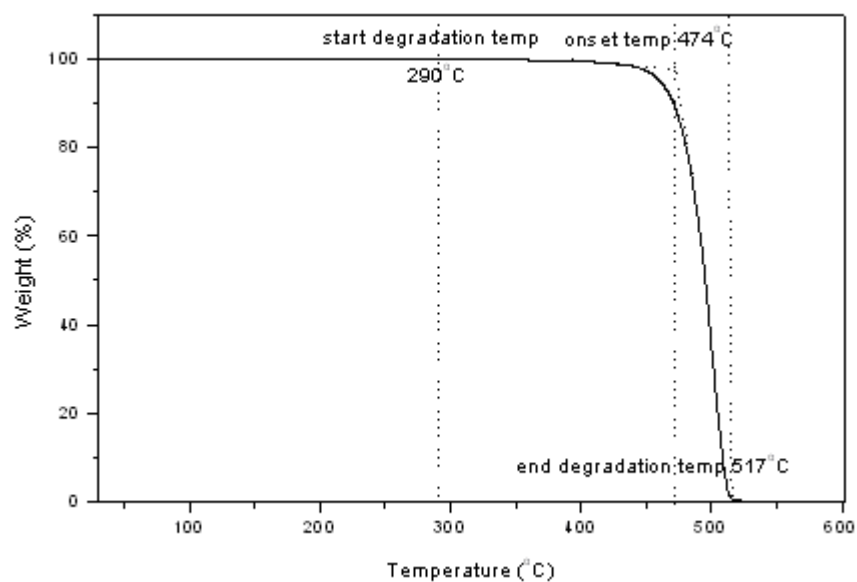


Figure A-4 TGA curve of LDPE

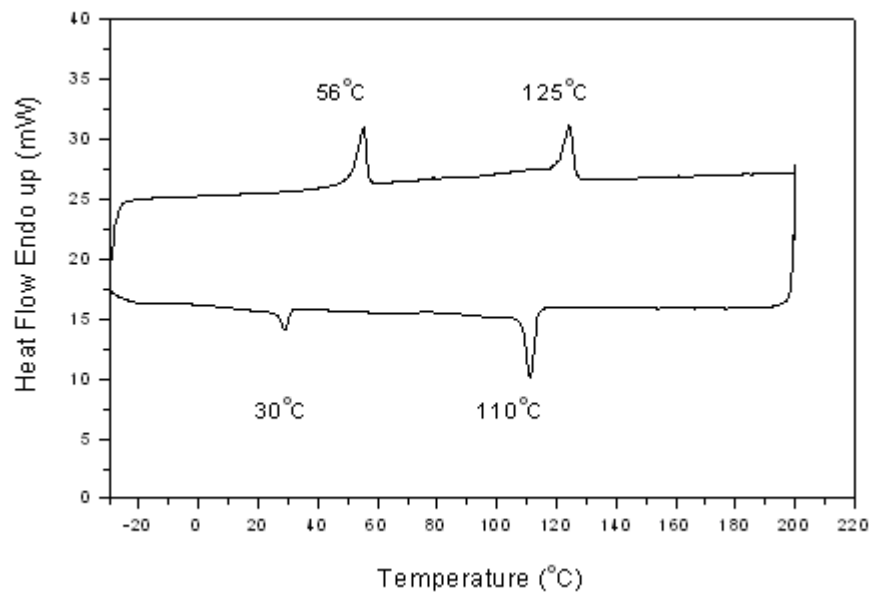


Figure A-5 DSC curve of feedstock

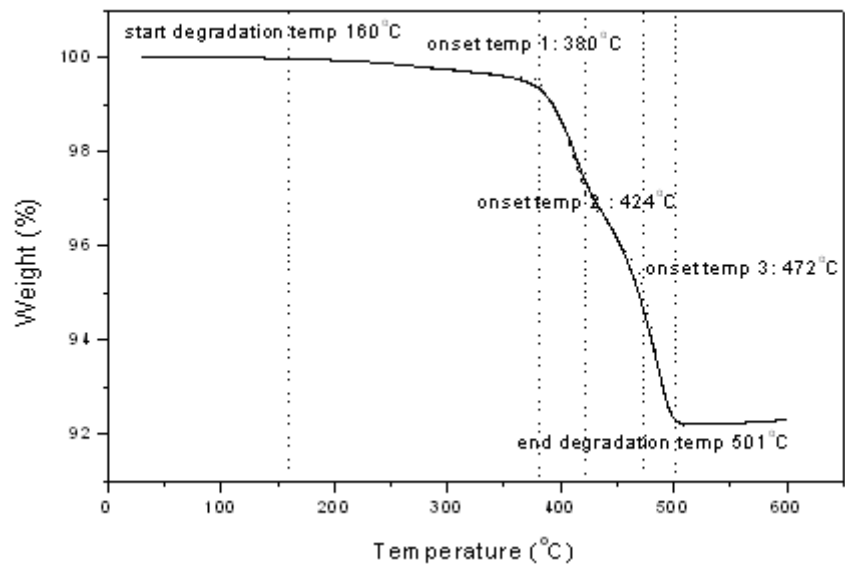


Figure A-6 TGA curve of feedstock

Appendix B Experimental Data of Relative Density

Table B-1 Relative density of sub-structure

Temperature (°C)	Time (min)	Specimen 1		Specimen 2		Mean ^b	Replication variation ^c
		Mean	Variation ^a	Mean	Variation ^a		
1200	10	0.824	0.004	0.820	0.003	0.822	0.003
1200	30	0.838	0.002	0.841	0.003	0.839	0.002
1200	60	0.867	0.004	0.864	0.005	0.865	0.002
1200	90	0.872	0.003	0.872	0.003	0.872	0
1200	120	0.875	0.003	0.875	0.002	0.875	0
1250	10	0.842	0.004	0.840	0.002	0.841	0.001
1250	30	0.864	0.008	0.858	0.009	0.861	0.004
1250	60	0.870	0.004	0.871	0.003	0.871	0.001
1250	90	0.876	0.002	0.874	0.003	0.875	0.001
1250	120	0.877	0.004	0.877	0.004	0.877	0
1300	10	0.880	0.003	0.877	0.003	0.879	0.002
1300	30	0.884	0.002	0.887	0.003	0.885	0.002
1300	60	0.888	0.004	0.886	0.003	0.887	0.001
1300	90	0.878	0.003	0.879	0.005	0.878	0.001

^a Variation was determined from the standard deviation calculated among six readings of each specimen.

^b Mean was used for graph plotting and analysis in this research.

^c Replication variation was determined from the standard deviation calculated between the means derived from each specimen.

Table B-2 Relative density of microsize structures of $\phi 100\ \mu\text{m}$

Temperature (°C)	Time (min)	Specimen 1		Specimen 2		Mean ^b	Replication variation ^c
		Mean	Variation ^a	Mean	Variation ^a		
1200	10	0.921	0.001	0.921	0.001	0.921	0
1200	30	0.932	0.003	0.930	0.002	0.931	0.001
1200	60	0.937	0.001	0.935	0.002	0.936	0.001
1200	90	0.940	0.002	0.940	0.002	0.940	0
1200	120	0.944	0.002	0.946	0.002	0.945	0.001
1250	10	0.931	0.003	0.932	0.002	0.932	0.001
1250	30	0.944	0.003	0.945	0.002	0.944	0.001
1250	60	0.950	0.001	0.950	0.001	0.950	0
1250	90	0.957	0.001	0.957	0.001	0.957	0
1250	120	0.962	0.002	0.964	0.002	0.963	0.001
1300	10	0.954	0.004	0.953	0.002	0.954	0.001
1300	30	0.963	0.002	0.964	0.003	0.963	0.001
1300	60	0.969	0.002	0.969	0.002	0.969	0
1300	90	0.978	0.002	0.976	0.002	0.977	0.001

^a Variation was determined from the standard deviation calculated among six readings of each specimen.

^b Mean was used for graph plotting and analysis in this research.

^c Replication variation was determined from the standard deviation calculated between the means derived from each specimen.

Table B-3 Relative density of microsize structures of $\phi 80 \mu\text{m}$

Temperature (°C)	Time (min)	Specimen 1		Specimen 2		Mean ^b	Replication variation ^c
		Mean	Variation ^a	Mean	Variation ^a		
1200	10	0.930	0.003	0.928	0.002	0.929	0.001
1200	30	0.937	0.003	0.935	0.002	0.936	0.001
1200	60	0.942	0.002	0.941	0.001	0.942	0.001
1200	90	0.948	0.002	0.948	0.002	0.948	0
1200	120	0.954	0.001	0.953	0.003	0.953	0.001
1250	10	0.944	0.003	0.944	0.002	0.944	0
1250	30	0.951	0.002	0.949	0.002	0.950	0.001
1250	60	0.961	0.002	0.960	0.003	0.960	0.001
1250	90	0.968	0.002	0.966	0.002	0.967	0.001
1250	120	0.973	0.001	0.973	0.001	0.973	0
1300	10	0.958	0.002	0.959	0.002	0.958	0.001
1300	30	0.968	0.001	0.967	0.001	0.967	0.001
1300	60	0.976	0.002	0.976	0.002	0.976	0
1300	90	0.985	0.002	0.986	0.001	0.985	0.001

^a Variation was determined from the standard deviation calculated among six readings of each specimen.

^b Mean was used for graph plotting and analysis in this research.

^c Replication variation was determined from the standard deviation calculated between the means derived from each specimen.

Table B-4 Relative density of microsize structures of $\phi 60\ \mu\text{m}$

Temperature (°C)	Time (min)	Specimen 1		Specimen 2		Mean ^b	Replication variation ^c
		Mean	Variation ^a	Mean	Variation ^a		
1200	10	0.937	0.003	0.936	0.004	0.937	0.001
1200	30	0.947	0.005	0.944	0.002	0.945	0.002
1200	60	0.955	0.004	0.951	0.003	0.953	0.003
1200	90	0.959	0.005	0.959	0.004	0.959	0
1200	120	0.965	0.002	0.965	0.003	0.965	0
1250	10	0.950	0.004	0.954	0.003	0.952	0.003
1250	30	0.962	0.004	0.960	0.005	0.961	0.001
1250	60	0.970	0.005	0.969	0.005	0.970	0.001
1250	90	0.982	0.005	0.980	0.007	0.981	0.001
1250	120	0.987	0.003	0.983	0.002	0.985	0.003
1300	10	0.976	0.004	0.975	0.003	0.976	0.001
1300	30	0.988	0.001	0.987	0.004	0.987	0.001
1300	60	0.990	0.005	0.992	0.002	0.991	0.001
1300	90	0.994	0.002	0.993	0.002	0.994	0.001

^a Variation was determined from the standard deviation calculated among six readings of each specimen.

^b Mean was used for graph plotting and analysis in this research.

^c Replication variation was determined from the standard deviation calculated between the means derived from each specimen.

Appendix C Experimental Data of Grain Size

Table C-1 Grain size of sub-structure

Temperature (°C)	Time (min)	Specimen 1		Specimen 2		Mean ^b (μm)	Replication variation ^c (μm)
		Mean (μm)	Variation ^a (μm)	Mean (μm)	Variation ^a (μm)		
1200	10	5.79	0.6	5.69	0.46	5.74	0.07
1200	30	6.90	0.37	6.78	0.34	6.84	0.08
1200	60	7.67	0.34	7.50	0.27	7.58	0.12
1200	90	8.28	0.67	8.32	0.39	8.30	0.03
1200	120	8.92	0.44	8.72	0.71	8.82	0.14
1250	10	7.67	0.56	7.51	0.24	7.59	0.11
1250	30	8.60	0.64	8.52	0.47	8.56	0.05
1250	60	9.36	0.46	9.25	0.23	9.30	0.07
1250	90	10.11	0.72	9.92	0.61	10.01	0.14
1250	120	10.50	0.61	10.64	0.45	10.57	0.1
1300	10	9.16	0.17	9.10	0.27	9.13	0.05
1300	30	9.92	0.25	10.14	0.25	10.03	0.15
1300	60	11.14	0.37	10.97	0.42	11.06	0.12
1300	90	11.80	0.35	11.96	0.51	11.88	0.12

^a Variation was determined from the standard deviation calculated among six readings of each specimen.

^b Mean was used for graph plotting and analysis in this research.

^c Replication variation was determined from the standard deviation calculated between the means derived from each specimen.

Table C-2 Grain size of microsize structures of $\phi 100\ \mu\text{m}$

Temperature (°C)	Time (min)	Specimen 1		Specimen 2		Mean ^b (μm)	Replication variation ^c (μm)
		Mean (μm)	Variation ^a (μm)	Mean (μm)	Variation ^a (μm)		
1200	10	13.80	0.57	13.56	0.82	13.68	0.17
1200	30	15.19	1.06	15.52	0.26	15.35	0.23
1200	60	16.84	0.85	17.18	1.19	17.01	0.24
1200	90	18.24	0.41	18.06	0.45	18.15	0.13
1200	120	19.45	0.7	19.18	0.44	19.32	0.19
1250	10	17.74	1.08	17.93	0.81	17.83	0.13
1250	30	19.63	0.77	19.58	0.71	19.60	0.03
1250	60	21.15	0.83	20.89	0.89	21.02	0.19
1250	90	22.27	0.91	22.53	0.9	22.40	0.19
1250	120	23.88	0.64	23.74	0.78	23.81	0.1
1300	10	20.80	0.65	21.01	0.55	20.91	0.15
1300	30	23.16	0.79	23.41	1.1	23.28	0.18
1300	60	25.12	0.78	25.32	0.68	25.22	0.14
1300	90	27.41	0.99	27.56	0.8	27.49	0.11

^a Variation was determined from the standard deviation calculated among six readings of each specimen.

^b Mean was used for graph plotting and analysis in this research.

^c Replication variation was determined from the standard deviation calculated between the means derived from each specimen.

Table C-3 Grain size of microsize structures of $\phi 80 \mu\text{m}$

Temperature (°C)	Time (min)	Specimen 1		Specimen 2		Mean ^b (μm)	Replication variation ^c (μm)
		Mean (μm)	Variation ^a (μm)	Mean (μm)	Variation ^a (μm)		
1200	10	15.79	0.95	15.37	0.67	15.58	0.29
1200	30	16.86	1.4	17.00	0.79	16.93	0.1
1200	60	17.87	0.7	18.35	0.79	18.11	0.34
1200	90	19.21	0.96	19.45	0.85	19.33	0.17
1200	120	20.07	0.44	20.37	0.64	20.22	0.21
1250	10	18.62	0.99	18.88	0.96	18.75	0.18
1250	30	20.06	0.56	20.32	0.57	20.19	0.19
1250	60	21.53	0.91	21.86	0.79	21.69	0.24
1250	90	23.17	0.76	23.45	0.69	23.31	0.19
1250	120	24.69	0.85	24.87	0.68	24.78	0.13
1300	10	22.54	0.44	22.40	0.75	22.47	0.09
1300	30	24.32	0.72	24.12	0.67	24.22	0.14
1300	60	26.57	0.95	26.41	1.04	26.49	0.11
1300	90	28.57	0.6	28.77	0.74	28.67	0.15

^a Variation was determined from the standard deviation calculated among six readings of each specimen.

^b Mean was used for graph plotting and analysis in this research.

^c Replication variation was determined from the standard deviation calculated between the means derived from each specimen.

Table C-4 Grain size of microsize structures of $\phi 60 \mu\text{m}$

Temperature (°C)	Time (min)	Specimen 1		Specimen 2		Mean ^b (μm)	Replication variation ^c (μm)
		Mean (μm)	Variation ^a (μm)	Mean (μm)	Variation ^a (μm)		
1200	10	15.69	0.92	16.12	0.88	15.90	0.3
1200	30	17.18	0.77	17.18	0.87	17.18	0
1200	60	18.30	0.73	18.59	0.61	18.44	0.21
1200	90	20.23	0.99	19.91	0.76	20.07	0.23
1200	120	21.50	0.88	21.06	0.68	21.28	0.31
1250	10	18.91	0.56	18.69	0.25	18.80	0.16
1250	30	21.36	1.08	20.98	1.01	21.17	0.27
1250	60	23.77	1.01	23.37	1.06	23.57	0.29
1250	90	26.21	1.14	25.78	0.65	25.99	0.3
1250	120	28.61	1.65	28.27	1.45	28.44	0.24
1300	10	27.27	1.04	26.91	0.84	27.09	0.25
1300	30	31.24	1.69	30.49	0.87	30.87	0.53
1300	60	36.33	0.67	35.39	1.32	35.86	0.67
1300	90	40.74	2.61	40.05	2.78	40.39	0.48

^a Variation was determined from the standard deviation calculated among six readings of each specimen.

^b Mean was used for graph plotting and analysis in this research.

^c Replication variation was determined from the standard deviation calculated between the means derived from each specimen.

Appendix D Coefficients for Pores at Four-Grain Junction and Two-Grain Interface

To describe the geometry of the pores, the equations may be represented in a more convenient way by introducing e :

$$e = \cos \theta = \frac{\gamma_b}{2\gamma_s} \quad \text{Eq. D-1}$$

where θ is the dihedral angle, γ_b is grain boundary energy and γ_s is surface energy.

α , β , λ for pores located at the four-grain junctions and the two-grain interface are expressed as follows [180]:

1) For pores at the four-grain junctions:

$$\alpha = 3 \left\{ 2\phi(1-e^2) - E \left[\left(1-e^2 - \frac{E^2}{4} \right)^{1/2} - \frac{E^2}{\sqrt{8}} \right] \right\} \quad \text{Eq. D-2}$$

$$\beta = 24 \left(\frac{\pi}{3} - e\phi - \delta' \right) \quad \text{Eq. D-3}$$

$$\lambda = 2 \left\{ 4 \left(\frac{\pi}{3} - \delta' \right) + eE \left[\left(1-e^2 - \frac{E^2}{4} \right)^{1/2} - \frac{E^2}{\sqrt{8}} \right] - 2e\phi(3-e^2) \right\} \quad \text{Eq. D-4}$$

Where,

$$E = \frac{4}{3} \left(\frac{3}{2} - 2e^2 \right)^{\frac{1}{2}} - \frac{2}{3}e, \quad \text{Eq. D-5}$$

$$\phi = \arcsin \frac{E}{2(1-e^2)^{\frac{1}{2}}} \text{ and} \quad \text{Eq. D-6}$$

$$\delta' = \arccos \frac{\sqrt{2} - e(3-E^2)^{\frac{1}{2}}}{E(1-e^2)^{\frac{1}{2}}} \quad \text{Eq. D-7}$$

2) For pores at the two-grain interface:

$$\alpha = \pi(1-e^2) \quad \text{Eq. D-8}$$

$$\beta = 4\pi(1-e) \quad \text{Eq. D-9}$$

$$\lambda = \frac{2\pi}{3}(2-3e+e^3) \quad \text{Eq. D-10}$$

Appendix E Comparison of Eqs. 4-21 and 4-22 with Johnson's Model

Johnson [133] has reported a combined-stage sintering model through generalized description of microstructural geometry. Densification through all stages of sintering can be given as follows:

$$\dot{\rho} = \frac{3\rho\gamma_s\Omega}{kT} \left(\frac{\Gamma_L D_L}{G^3} + \frac{\Gamma_B \delta D_B}{G^4} \right) \quad \text{Eq. E-1}$$

where Γ_L and Γ_B relates the driving force, mean diffusion distance and other geometric features of the microstructure for lattice diffusion and grain boundary diffusion, respectively.

If there exists only one dominant diffusion mechanism (either lattice diffusion or grain-boundary diffusion), Eq. E-1 can be simplified as follows [132]:

$$\dot{\rho} = \frac{3\gamma_s\Omega D_0}{k} \frac{\Gamma \rho \exp\left(-\frac{Q}{RT}\right)}{TG^n} \quad \text{Eq. E-2}$$

where Γ relates the driving force, mean diffusion distance and other geometric features of the microstructure during sintering, D_0 is a temperature independent preexponential and Q is the activation energy. $D_0 = (D_L)_0$ and $n = 3$ for lattice diffusion, $D_0 = (\delta D_B)_0$ and $n = 4$ for grain-boundary diffusion.

Appendix E

Eq. 4-21 for lattice diffusion controlled densification and Eq. 4-22 for grain boundary diffusion controlled densification can be combined into one equation as follows:

$$\dot{\rho} = \frac{f(\rho, G) \rho \exp\left(\frac{-Q}{RT}\right)}{TG^n} \quad \text{Eq. E-3}$$

where $f(\rho, G)$ is a function of relative density and grain size. $n=3$ for lattice diffusion, $n=4$ for grain-boundary diffusion.

Eq. E-3 will be the same as Eq. E-2 only if $f(\rho, G)$ is equivalent of $\frac{3\gamma_s \Omega D_0}{k} \Gamma$. It is, however, to be noted that derivation of Eq. E-2 and that of Eq. E-3 are different and thus $f(\rho, G)$ differs from $\frac{3\gamma_s \Omega D_0}{k} \Gamma$. Unlike Eq. E-3, the contribution of grain boundary energy is not considered in Eq. E-2. In addition, Γ , composed of scaling factors related to microstructural geometry, is sensitive to abnormalities in the microstructure arising from wide particle and pore size distributions and other factors [133]. In Eq. E-3, comparatively, the porous part is treated as a continuum solid undergoing time dependent deformation due to sintering stress and the overall material response is assumed isotropic.

Appendix F Curve-Fitting Equations for Grain versus Time

Table F-1 Curve-fitting equations for G (m) versus t (s): $G = at^2 + bt + c$

Sintered part	Sintering temperature (°C)	Coefficients		
		a	b	c
Sub-structure	1200	-4.34×10^{-14}	7.85×10^{-10}	5.38×10^{-6}
	1250	-3.48×10^{-14}	7.06×10^{-10}	7.26×10^{-6}
	1300	-4.25×10^{-14}	8.24×10^{-10}	8.66×10^{-6}
Microsize structures of $\phi 100 \mu\text{m}$	1200	-6.50×10^{-14}	1.33×10^{-9}	1.30×10^{-5}
	1250	-4.37×10^{-14}	1.21×10^{-9}	1.73×10^{-5}
	1300	-8.00×10^{-14}	1.81×10^{-9}	2.00×10^{-5}
Microsize structures of $\phi 80 \mu\text{m}$	1200	-4.38×10^{-14}	1.03×10^{-9}	1.51×10^{-5}
	1250	-2.20×10^{-14}	1.07×10^{-9}	1.82×10^{-5}
	1300	-3.33×10^{-14}	1.48×10^{-9}	2.16×10^{-5}
Microsize structures of $\phi 60 \mu\text{m}$	1200	-1.84×10^{-14}	9.52×10^{-10}	1.54×10^{-5}
	1250	-3.67×10^{-14}	1.71×10^{-9}	1.79×10^{-5}
	1300	-9.15×10^{-14}	3.31×10^{-9}	2.52×10^{-5}

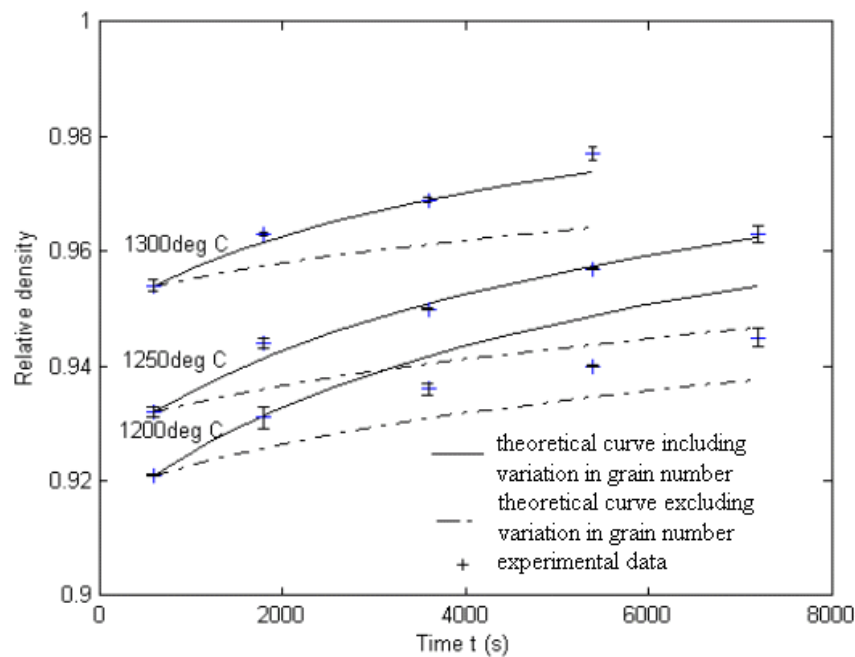
Appendix G Curve-Fitting Equations for Density versus Time

Table G-1 Curve-fitting equations for ρ versus t (s): $\rho = at^2 + bt + c$

Sintered part	Sintering temperature (°C)	Coefficients		
		a	b	c
Sub-structure	1200	-1.57×10^{-9}	2.03×10^{-5}	8.10×10^{-1}
	1250	-1.23×10^{-9}	1.45×10^{-5}	8.35×10^{-1}
Microsize structures of $\phi 100 \mu\text{m}$	1200	-3.63×10^{-10}	6.15×10^{-6}	9.19×10^{-1}
	1250	-3.94×10^{-10}	7.45×10^{-6}	9.29×10^{-1}
	1300	-3.26×10^{-10}	6.54×10^{-6}	9.51×10^{-1}
Microsize structures of $\phi 80 \mu\text{m}$	1200	-2.08×10^{-10}	5.16×10^{-6}	9.26×10^{-1}
	1250	-2.36×10^{-10}	6.28×10^{-6}	9.40×10^{-1}
	1300	-3.12×10^{-10}	7.39×10^{-6}	9.54×10^{-1}
Microsize structures of $\phi 60 \mu\text{m}$	1200	-2.82×10^{-10}	6.32×10^{-6}	9.34×10^{-1}
	1250	-3.84×10^{-10}	8.06×10^{-6}	9.47×10^{-1}
	1300	-9.62×10^{-10}	9.26×10^{-6}	9.72×10^{-1}

Appendix H Comparison of Experimental Results with Theoretical Curves Based on Different Sintering Stress Expressions

Computations of the density-time curves based on Eqs. 6-12 to 6-14 for microsize structures of $\phi 100\ \mu\text{m}$, $\phi 80\ \mu\text{m}$ and $\phi 60\ \mu\text{m}$, where variation in grain number is included, and that based on Raj's research [106], where variation in grain number is excluded, were compared with the experimental results. The results are shown in Figure H-1. When the variation in grain number is considered in the sintering stress, higher densities are predicted in the constitutive model and the predicted densities are closer to the experimental results.



(a) Microsize structures of $\phi 100\ \mu\text{m}$

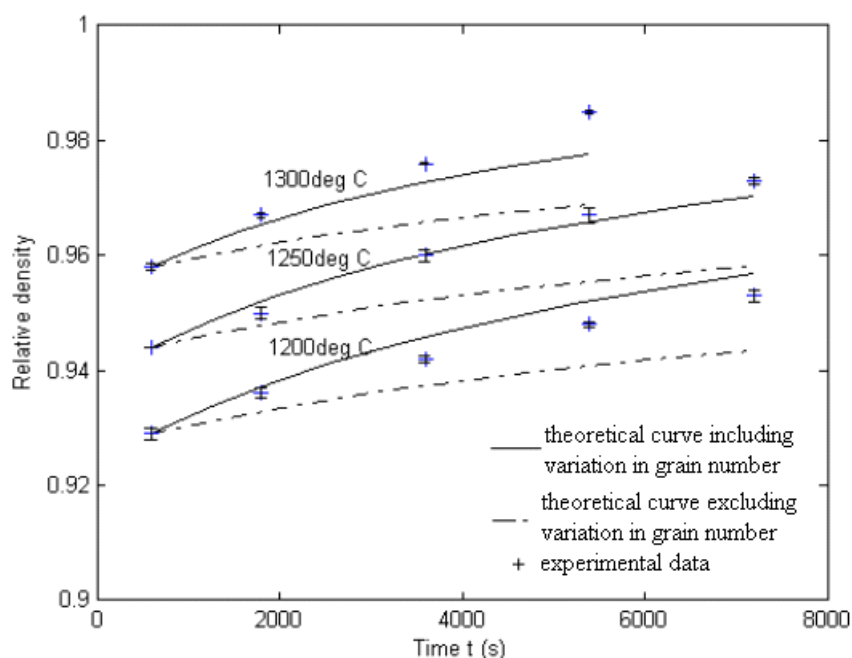
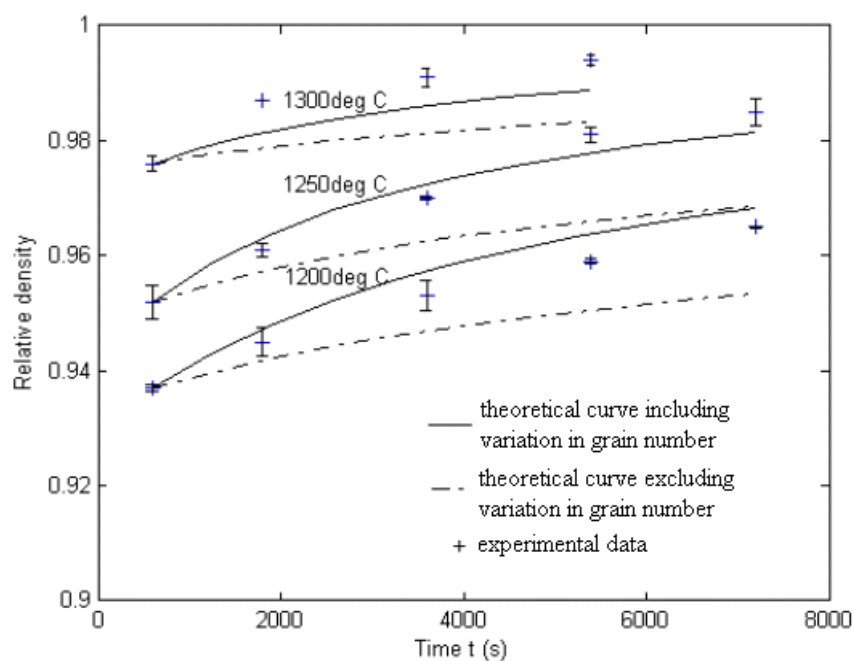
(b) Microsize structures of $\phi 80 \mu\text{m}$ (c) Microsize structures of $\phi 60 \mu\text{m}$

Figure H-1 Microsize structures: comparison of experimental density-time results (for different sintering temperatures) with theoretical curves computed based on different sintering stress expressions