Sintering of an Aluminium Alloy Under Pressurised Conditions

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The University of Queensland in April 2009

School of Engineering
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The paper referenced above was produced from work done for this thesis and has been accepted for publication in Materials Science Forum, as part of the proceedings of the Light Metals Technology
2009 conference to be held on 28th June to 1st July 2009 at Broadbeach, Queensland, Australia. A copy of the paper is included in Appendix A. This paper does not form part of the thesis itself and is not intended to be assessed as a part of it. The paper has been included as an indication that the quality and originality of the research in this thesis is of a level suitable for peer-reviewed publication. The contents of the paper are my own work, and the two co-authors, Prof. Graham Schaffer and Dr. Ji-Yong Yao, were included in recognition of their role as my thesis supervisors.
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Abstract
Increasing concern over the environmental impact of motor vehicles is driving the need for the development of lighter materials to reduce automobile weight and fuel consumption. Sintered aluminium alloys, with their high strength to weight ratios, have potential applications in the automotive industry, but conventional pressed-and-sintered materials have poor mechanical properties due to the presence of residual porosity in the sintered compact. Residual porosity can be eliminated by Hot Isostatic Pressing (HIPing) or combined sinter-HIPing, but these processes are expensive due to the high gas pressures involved, up to several hundred MPa, and also pose a significant safety hazard. There is a limited amount of evidence in the literature suggesting that applied gas pressures as low as a few MPa may be beneficial to the sintering of aluminium alloys, and it is this idea that the present work explores. Compacts of aluminium alloy 2712 (Al-3.8Cu-1Mg-0.7Si-0.1Sn) were prepared from elemental powders and sintered at 590°C for up to 60 minutes in a horizontal tube furnace under constant flowing nitrogen or argon at pressures up to 600 kPa. Archimedes’ method was used to measure the density of sintered compacts, and the amount of open and closed porosity. Increasing the nitrogen pressure at the start of the isothermal holding stage to 160 kPa increased the sintering rate compared to standard atmospheric pressure sintering. Increasing the nitrogen pressure further, up to 600 kPa, had no additional benefit. The sintering rate was increased further by applying a 600 kPa nitrogen pressure during both heating and isothermal holding. The elevated nitrogen pressure had a negligible effect on the maximum sintered density achieved, and sintering in argon at elevated pressures had no measurable effect on the sintered density or sintering rate. It was shown that the elevated pressure aids in the closure of pores open to the specimen surface, contrary to HIPing and sinter-HIPing, where the pores must be isolated prior to the application of pressure. It was also shown that at 600 kPa nitrogen pressure, the sintered density was independent of the presence of tin in the alloy. The improvements to sintering seem to be related to the formation of aluminium nitride.

Keywords
aluminium, sintering, powder metallurgy, nitrogen, pressure

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1 Introduction

Sintered aluminium alloys have many potential applications in the automotive industry, but the widespread use of conventional pressed-and-sintered materials is limited by the poor fatigue properties due to residual porosity in the sintered compact. It is possible to remove these pores via Hot Isostatic Pressing (HIPing), which involves the simultaneous application of elevated temperature and pressure, where the pressure is applied via a fluid, usually a gas. HIPing is expensive, however, due to the high pressures, temperatures and long process times. Specimen geometries are also limited, due to the necessary encapsulation of the powder mass.

An alternative to HIPing is the sinter-HIP (simultaneous sintering and hot isostatic pressing) process whereby the material is sintered to a state of closed porosity, negating the need for encapsulation, and then subjected to the elevated pressure. The advantage of this technique is that the costs are lower than in HIPing, but the properties are better than those resulting from conventional sintering. This process is routinely used with ceramics and hard metals but has not, as yet, been applied to aluminium alloy systems.

Both HIP and sinter-HIP require the application of high gas pressures, up to several hundred MPa in the case of conventional HIP. There is some research in the literature that suggests much lower isostatic pressures, in the order of a few MPa, may have a beneficial effect on aluminium sintering behaviour. Sintering at a lower gas pressure has the potential to reduce processing costs, as there is no need for furnaces to withstand large pressures, and improvement in safety as the lower pressures are less of a hazard.

The aim of this work is to identify the process conditions that enable pressure assisted sintering of a commercial aluminium alloy in nitrogen at pressures in the range of a few atmospheres. From this, the aim is then to understand the process of pressure assisted sintering for this alloy in these conditions, with the ultimate aim of producing fully dense material.

Chapter 2 of this report gives a review of the literature on the powder metallurgy process, sintering theory, and the current state of aluminium alloy sintering, as well as providing a context for the current work. Chapter 3 describes the experimental program used during the course of this work. Chapter 4 presents the results of the experimental program, which are then discussed in Chapter 5. The main conclusions of the work, and suggestions for further work that could be done are presented in Chapters 6 and 7, respectively.
2 Literature Review

2.1 Introduction

There has been increasing pressure on the automotive industry to increase fuel efficiency due to increasing environmental concerns, which has led to an effort by automotive manufacturers to reduce vehicle weight [1, 2]. Aluminium has a density of 2.7 g/cm$^3$ [3], about one third that of steel, which is the principal material used in the automotive industry. This low density makes it an attractive replacement material for applications where minimising weight is important.

Aluminium alloys can be classed as either foundry alloys or wrought alloys, each with their own system of alloy classification. The aluminium powder metallurgy alloys have no such designation system, but sometimes use the wrought system, as shown in Table 2.1. In this system each alloy is given a four digit code, where the first digit indicates the principal alloying element. The second digit indicates modifications to alloy or impurity limits. The last two digits identify the alloy or, in the case of the 1xxx series alloys, the purity of the aluminium [3].

<table>
<thead>
<tr>
<th>4 digit series</th>
<th>Principal alloying element(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1xxx</td>
<td>99.00% Al minimum</td>
</tr>
<tr>
<td>2xxx</td>
<td>Cu</td>
</tr>
<tr>
<td>3xxx</td>
<td>Mn</td>
</tr>
<tr>
<td>4xxx</td>
<td>Si</td>
</tr>
<tr>
<td>5xxx</td>
<td>Mg</td>
</tr>
<tr>
<td>6xxx</td>
<td>Mg and Si</td>
</tr>
<tr>
<td>7xxx</td>
<td>Zn</td>
</tr>
<tr>
<td>8xxx</td>
<td>others</td>
</tr>
</tbody>
</table>

2.2 Powder Metallurgy

2.2.1 Introduction

The subject of powder metallurgy encompasses a number of processes, from powder production and characterisation, to the consolidation of the powder to form a functional part. Metal powders can be used in applications where the powder itself is the end product, for example in paints, varnishes and printing inks, explosives (both civil and military), food additives and pharmaceutical additives [5,
This report, however, is concerned with powder metallurgy as it pertains to the production of load bearing aluminium alloy components through press-and-sinter processing.

The sintering process has been practiced from as early as 4000 B.C., in the fabrication of clay pottery and bricks in open-pit fires to add strength. Sintering of metals has been done as far back as 3000 B.C. by the Egyptians. The Incas made sintered gold-platinum jewellery while the Delhi column in India, which has been dated to about 300 A.D., was forged from iron powder [7]. Modern applications of sintering began as a means of shaping metals that could not be readily melted, as in the production of tungsten light bulb filaments in 1913 [5].

Press-and-sinter powder metallurgical techniques can allow net-shape manufacturing of fine-grained, segregation free materials with a uniform microstructure. Powder metallurgy parts can also have a high dimensional accuracy through solid state sintering and good process control. It is of particular use for materials and phase combinations that would otherwise be impossible to process using traditional casting techniques [8]. Powder metallurgy processes can be used to produce geometries that are difficult, or impossible, to make with conventional casting methods. The major limitation to press-and-sinter powder metallurgy is the size of parts that can be produced. This is due to die wall friction imposing an upper limit on the thickness of the green compact, and the press size limiting the surface area. Some geometries are also restricted, such as holes perpendicular to the pressing direction.

2.2.2 Powder Production

Metal powder production methods can be categorised into mechanical methods such as machining and milling, electrolytic, chemical, atomisation or evaporation techniques [9]. Atomisation is the principal production method of powders for powder metallurgy due to the high level of control over the powder properties [6].

Atomisation involves the breaking up of a liquid metal stream into fine droplets followed by rapid solidification. In fluid atomisation the molten stream is broken up by impingement with water or another liquid, or a gas. In centrifugal atomisation the material to be atomised, in the form of a cylindrical electrode, is rotated at speeds up to 15,000 rpm, while one end of it is exposed to an arc and melted. Centrifugal forces cause the melted material to form droplets. Vacuum atomisation involves the exposure of a gas-supersaturated melt to a vacuum, whereby the melt disintegrates into droplets [10].
The powder blends used in sintering can be made from either elemental or pre-alloyed powders. Elemental powders are generally cheaper, are easier to compact due to the lower strength of the pure elements, and allow greater alloy flexibility. Elemental powders also provide an additional driving force for sintering in the form of the chemical potential due to concentration gradients between adjacent particles.

The powder production method affects the final powder properties such as powder size and distribution, shape, compressibility, purity, and flow ability [6]. These properties in turn affect the green strength, ease of handling and sintering behaviour. For example, spherical powders flow more easily than irregularly shaped powders. Fine powders have a large specific surface area, providing a larger driving force for sintering, but do not flow as well as coarse powders. Polysized powders pack to a higher density than monosized powders and can provide higher green densities.

2.2.3 Green Compact Production

The metal powder and any additives, such as binders and lubricants, are blended to a uniform distribution before being compacted in a die at a moderately low pressure (as compared to forging, for example). During compaction, the powder particles plastically deform and mechanically interlock with one another, providing sufficient strength for subsequent handling, although at this stage the compacts can still be quite fragile. It is desirable to have a uniform density distribution through the thickness of the compact. This can be aided by the use of a floating die, in which both the upper and lower punches move relative to the die wall during compaction.

Powder compaction in a floating die involves several steps (Figure 2.1). First, the lower punch is raised to the fill position and metal powder is poured into the die cavity, level with the top of the die. The lower punch is then lowered to the pressing position, and the upper punch is inserted into the die. Both punches move relative to the die wall and compress the powder mass. The upper punch is removed and the lower punch is raised to eject the powder compact from the die cavity.
Lubricants are used to reduce the friction between the powder and the die wall, allowing lower compaction and ejection pressures, more uniform compact density and longer tool life. Lubricant powders can be added to the powder mixture or applied to the die walls. A commonly used lubricant is ethylene bis stearamide. Other lubricants are calcium stearate, lithium stearate and zinc stearate [9]. Binders can be added to increase the strength of the green compact by aiding particle bonding. Binders are commonly a mixture of several waxy polymers, some examples of which are given in Table 2.2. Additives are burned out of the compact during a low temperature “de-waxing” stage prior to sintering.
Table 2.2. Example of binders used in powder metallurgy processing. From [9].

<table>
<thead>
<tr>
<th>Binder application</th>
<th>composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>extrusion</td>
<td>15% ammonium polyacrylate</td>
</tr>
<tr>
<td></td>
<td>15% ammonium stearate</td>
</tr>
<tr>
<td></td>
<td>45% methyl cellulose</td>
</tr>
<tr>
<td></td>
<td>25% glycerine</td>
</tr>
<tr>
<td>injection molding</td>
<td>69% paraffin wax</td>
</tr>
<tr>
<td></td>
<td>20% polypropylene</td>
</tr>
<tr>
<td></td>
<td>10% carnauba wax</td>
</tr>
<tr>
<td></td>
<td>1% stearic acid</td>
</tr>
<tr>
<td>slip casting</td>
<td>93% water</td>
</tr>
<tr>
<td></td>
<td>4% agar</td>
</tr>
<tr>
<td></td>
<td>3% glycerine</td>
</tr>
<tr>
<td>tape casting</td>
<td>80% toluene</td>
</tr>
<tr>
<td></td>
<td>13% polyethylene glycol</td>
</tr>
<tr>
<td></td>
<td>7% polyvinyl alcohol</td>
</tr>
</tbody>
</table>

2.3 Solid State Sintering

Sintering is a thermally activated process for consolidating a particle compact into a solid [7]. The process relies on mass transport mechanisms to effect the coalescence of individual particles, elimination of pores and shrinkage to full density.

The primary driving force for sintering is the minimisation of specific surface area [5, 7], although there is also a chemical driving force when elemental powders are used, due to the concentration gradient across particle interfaces. The pressure drop across a curved surface, or Laplace pressure, \( \Delta P \), is given by the Laplace equation [12]:

\[
\Delta P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \tag{2.1}
\]

where \( \gamma \) is the surface tension and \( R_1 \) and \( R_2 \) are the principal radii of curvature of the surface, as shown in Figure 2.2.
Figure 2.2. The curvature of a point on a surface, given in terms of the two principal radii of curvature at that point, $R_1$ and $R_2$. From [7].

For a convex surface, the radius of curvature lies inside the mass and the Laplace pressure is positive, applying a tensile stress to the surface. For a concave surface, the radius lies outside the mass and the Laplace pressure is negative, applying a compressive stress to the surface. A solid, curved surface will tend towards a flat, stress-free surface during sintering, through the expedient of random atomic motion resulting in net migration of atoms from regions of positive curvature to those of negative curvature.

There are a number of mass transport mechanisms that contribute to sintering. These can be divided into bulk and surface transport mechanisms. Surface transport mechanisms involve migration of atoms from one region of the surface to another. Atoms may diffuse across the surface itself (surface diffusion), through the particle bulk (volume diffusion) or through the vapour phase (evaporation-condensation). Regardless of the diffusion path, surface transport mechanisms do not result in net densification (shrinkage) of the compact as the atoms merely migrate from one region of the surface to another without affecting inter-particle spacing, represented by the length $L_0$ in Figure 2.3. They do, however, result in particle bonding and strengthening of the compact. Densification of the compact necessitates the motion of mass from the particle bulk to the particle surface. Bulk transport mechanisms occur via diffusion along grain boundaries and volume diffusion where the atom source is within the particle bulk, as well as plastic flow. Figure 2.3 shows two idealised particles in contact with each other, illustrating the diffusion mechanisms described above.
In the early stages of the sintering cycle, once the temperature is sufficient for appreciable solid state diffusion to occur, interparticle bonds, or necks, form at particle contact points (see Figure 2.3), and continuous pore channels are formed between the particles. During the intermediate stage, the interparticle necks enlarge and particle contact areas (represented by the diameter X in Figure 2.3) increase, thus decreasing particle surface area. Sharp pore surfaces are smoothed, becoming more rounded in shape. As the particle contacts increase further in size and coalesce, the continuous pore network breaks down into a series of isolated pores, located at grain boundaries. Thus open pores become closed pores as sintering progresses and the closed pores shrink until all the pores are eliminated. The misalignment of atomic lattice planes at particle contact points results in the formation of grain boundaries. As sintering involves the migration and annihilation of vacancies at surfaces, grain boundaries play an important role in solid state sintering by acting as vacancy sinks. Vacancies need only migrate a relatively short distance to a grain boundary rather than a longer distance to a free surface to be annihilated. During sintering, the high energy grain boundaries are removed by grain growth where smaller grains (with high surface curvature) are consumed by the growth of large grains (with lower surface curvature). Grain boundary diffusion then becomes less dominant as sintering progresses.
2.4 Liquid Phase Sintering

Liquid phase sintering refers to a sintering process wherein a liquid phase is present for at least some of the sintering cycle. The presence of a liquid usually enhances sintering, as compared to solid state sintering. Capillary forces of the liquid act on the solid particles to pull them closer (rearrangement) and also enable liquid to flow into pores (pore filling). These concepts are discussed in the sections on Classic Sintering Theory (section 2.4.2) and Pore Filling Theory (Section 2.4.3). In addition, diffusion rates through the liquid are higher than in the solid, increasing the overall sintering kinetics.

The liquid phase forms on initial heating either from a low melting point constituent or regions which have reached a low melting point composition through solid state diffusion, and the liquid phase may be transient or persistent. In a transient liquid sintering process the liquid dissolves back into the solid during sintering as chemical equilibrium is achieved. During persistent liquid sintering, the liquid remains for the entire duration of sintering. Ideally, the additive responsible for the liquid formation should have a low solubility in the base material, to ensure that the liquid stays segregated at particle surfaces where the enhanced diffusion kinetics are most beneficial, and the base material should have a high solubility in the liquid phase.

2.4.1 Wetting

The degree to which a liquid wets a particular surface is an important parameter in liquid phase sintering and is measured by the wetting or contact angle, $\theta$, the angle between the solid surface and the tangent to the liquid surface at the solid-liquid-vapour triple interface (Figure 2.4) at equilibrium.

Figure 2.4. The wetting angle of a liquid on a solid surface, $\theta$, arises from a balance of the interfacial energies. $\gamma_{SL}$ is the solid-liquid interfacial energy, $\gamma_{LV}$ is the liquid vapour interfacial energy, and $\gamma_{SV}$ is the solid vapour surface energy.
The wetting angle arises from the balance of interfacial energies of the three phases. Balancing the interfacial energies in the horizontal direction gives:

\[ \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \]  

**Equation 2.2**

Where \( \gamma_{SV} \) is the solid-vapour interfacial energy, \( \gamma_{SL} \) is the solid-liquid interfacial energy, and \( \gamma_{LV} \) is the liquid-vapour interfacial energy.

If the interfacial energies of a particular system are known, Equation 2.2 can be used to calculate the equilibrium wetting angle. For chemically pure phases this may be fairly straightforward, but is more difficult in multi-component systems. In powder alloy systems, for example, segregation of elements to particle surfaces will change the surface composition from the bulk composition, altering the interfacial energies. Similarly, chemical reactions between the sintering atmosphere and the solid or liquid phases can produce reaction products at interfaces that will change the surface chemistry. There is some evidence [13] that suggests a range of contact angles can be produced for a given solid-liquid-vapour system and the contact angle can be altered by changing the pressure at the triple interface, leading to the prediction that the wetting angle increases with pressure.

Wetting of the particle surfaces by the liquid phase is important for effective sintering. A low contact angle promotes spreading of the liquid over the solid (Figure 2.5a) and leads to an attractive capillary force between solid particles joined by a capillary bridge (Figure 2.5b), while a high contact angle leads to a repulsive capillary force that acts to push solid particles apart. A liquid that wets the particle surface will cover a greater surface area, increasing diffusion kinetics, as well as inducing capillary flow [14] and pore filling (Section 2.4.3).
Figure 2.5. The effect of contact angle of a liquid on a flat solid (a) and a liquid between two solid particles (b). A low contact angle provides good liquid wetting leading to attraction capillary force between the two particles while a high contact angle gives poor wetting and leads to a repulsive capillary force between the particles. Adapted from [7].

In systems where the contact angle is greater than zero, the liquid does not completely wet the solid surface and there is an equilibrium particle separation distance between particles joined by a liquid bridge [7, 15-17] (Figure 2.6). Particles separated by a distance greater than this will experience an attractive capillary force, and particles with a separation smaller than this will experience a repulsive capillary force. So long as the particles are not constrained then the capillary force will act to move the particles to the equilibrium separation distance. The equilibrium separation distance increases with the contact angle, liquid volume fraction, and decreases with differences in particle size.

Figure 2.6. Liquid copper on tungsten spheres (~200 µm diameter) for a wetting angle of (a) 8° and (b) 85°. For contact angles greater than zero, there is a nonzero equilibrium separation distance between particles connected via a liquid bridge. From [17].

The dihedral angle is another parameter important to liquid phase sintering. The dihedral angle, φ, is formed between two solid grains in contact with a liquid (Figure 2.7a), and is related to the interfacial energies according to:
Where $\gamma_{SS}$ is the solid-solid or grain boundary energy, and $\gamma_{SL}$ is the solid-liquid interfacial energy.

Equation 2.3

$$\gamma_{SS} = 2\gamma_{SL} \cos \frac{\phi}{2}$$

Effectively, the dihedral angle is indicative of the ability of the liquid phase to penetrate grain boundaries. Equation 2.3 shows that for a dihedral angle of zero, the ratio of $\gamma_{SS}$ to $\gamma_{SL}$ is equal to 2. That is, it is more energetically favourable for two solid-liquid interfaces to be present rather than a single solid-solid interface (grain boundary) and the liquid can completely penetrate grain boundaries to form a continuous liquid film between the grains.

As the dihedral angle increases, it becomes less energetically favourable for the liquid to penetrate grain boundaries. The liquid distribution then becomes increasingly discontinuous and the grains can bond together to form a solid skeleton. The shape of liquid filled pores will be dependent on the dihedral angle, becoming more convex with increasing dihedral angle (Figure 2.7b). The corresponding three dimensional liquid distribution is shown schematically in Figure 2.8.
The Laplace equation (Equation 2.1), as discussed in Section 2.3 in regards to a solid surface, also holds true for a liquid surface. For a spherical pore in a liquid, or a hemispherical liquid-gas interface in a circular capillary, the two radii of curvature are equal. If the pressure of the gas phase is denoted by $P_{\text{GAS}}$, and the hydrostatic pressure of the liquid is denoted by $P_{\text{LIQUID}}$, Equation 2.1 then becomes:

$$P_{\text{GAS}} = P_{\text{LIQUID}} + \frac{2\gamma}{R} \quad \text{Equation 2.4}$$

where the $2\gamma/R$ term is the capillary pressure. Equation 2.4 defines an equilibrium condition between the pressure in the pore, the hydrostatic pressure and the liquid meniscus radius. Note that for a spherical bubble of gas in a liquid, the pressure of the gas is greater than the hydrostatic pressure of the liquid, and the value of the radius $R$ is positive.

Equation 2.4 can be rearranged to give the radius of curvature as a function of the pressures:

$$R = \frac{2\gamma}{P_{\text{GAS}} - P_{\text{LIQUID}}} \quad \text{Equation 2.5}$$

Thus, a large difference in pressures between the liquid and gas corresponds to a small pore radius, and the radius increases as the difference in the two pressures approaches zero.

There are two theories that dominate current understanding of liquid-phase sintering. The classic theory proposed by Kingery [18] describes three stages to sintering: particle rearrangement, solution-reprecipitation or contact flattening, and final stage coalescence. The more recent pore filling theory, proposed by Lee and Kang [19] centres on the idea of grain-growth induced pore filling by the liquid phase.

### 2.4.2 Classic Sintering Theory

During the heating stage prior to liquid formation, solid state sintering mechanisms occur. After the onset of liquid formation, and provided there is sufficient volume of liquid formed, capillary forces
draw the liquid into small pores and grain boundaries, covering the particle surfaces in a liquid film. The capillary forces act to rearrange the solid particles to a higher packing density, drawing particles closer together until they touch, effectively reducing the volume of pore spaces. This is called primary rearrangement. Secondary rearrangement can also occur where liquid penetrates grain boundaries within the initial powder particles themselves, resulting in particle fragmentation, and effectively reducing the grain size. Rearrangement can be inhibited by interparticle contacts formed via solid state sintering during the heating stage or if there is insufficient liquid volume to cover the solid particles with a liquid film. Poor wetting of the liquid on the solid particles can also be detrimental to rearrangement as the capillary pressure of the liquid can act to repel particles and produce swelling instead of shrinkage (see Section 2.4.1.).

Once the compact has achieved maximum packing density, there will be no driving force for rearrangement, and diffusion mechanisms become dominant. To describe this intermediate stage of sintering, Kingery used a two sphere model (Figure 2.9). The two spherical solid particles are in contact, held together by the capillary force of a liquid present at the contact area. The capillary pressure exerts a compressive stress at the contact points of the two particles, which increases the chemical potential of atoms at the contacts relative to other regions of the particle away from the contact area. The increased chemical potential provides a driving force for material to dissolve into the liquid and reprecipitate at regions of lower chemical potential, away from the contact area. As material is continuously transported away from the contact area, the contact area increases and flattens, and the particles continuously change shape to become more anhedral until there is a complete elimination of pores.

![Figure 2.9. Kingery’s two sphere model of two solid particles connected by a liquid bridge.](image)

Kingery suggested that the final stage of sintering occurs when the liquid phase mechanisms have become exhausted and solid state sintering becomes dominant. The densification kinetics therefore rapidly diminish to the slower kinetics expected in solid state sintering.
Kingery’s theory predicts a continuous reduction in pore size over time during sintering, regardless of the initial pore size. This is not the case in real sintering, however, as smaller pores tend to be eliminated first, while large pores remain stable for longer times, and may remain in the sintered part. The theory also assumes that there is a continuous liquid film on the particle surfaces. Essentially this means a dihedral angle of zero. For a compact with a dihedral angle greater than zero, the liquid phase will be unable to penetrate the grain boundaries at particle contacts and a solid skeleton will form, preventing rearrangement from occurring as well as limiting diffusion to solid state mechanisms through the particle contacts and the process kinetics should be effectively the same as in solid state sintering. This is not the case in real systems, where it is common for the dihedral angle to be greater than zero, and therefore no liquid film is present at the particles contacts. Yet in these systems the presence of a liquid can improve sintering kinetics. The theory also assumes no grain growth, with the densification provided by change in grain shape only. In real systems grain growth contributes to grain shape change, as smaller particles are eliminated at the expense of larger ones by Ostwald ripening. It is expected, then, that grain growth plays a role in densification.

Kingery’s theory proposes that the increased chemical potential that initiates solution-reprecipitation arises from the compressive stress at the particle contacts, the assumption being that the particles are touching. Yet sintering shrinkage can still be achieved in real systems where the liquid does not completely wet the solid surface and there is an equilibrium particle separation distance (Section 2.4.1).

2.4.3 Pore Filling Theory

The pore filling theory proposed by Lee and Kang [19] was developed from a series of observations of sintering in the Mo-Ni, W-Ni and W-Ni-Fe systems [20-26]. Pore filling is induced by grain growth during sintering, which creates an imbalance in liquid pressures between the liquid present at the specimen surface, and the liquid present at the interior surface of a pore (Figure 2.10).
Figure 2.10. Schematic of the pore filling process. (a) The liquid meniscus radius, $\rho_1$, is equal at the specimen surface and the pore interior. The liquid meniscus radius is lower than the pore radius and the pore remains liquid free. (b) As the grains grow, the liquid meniscus radius increases to a critical value, $\rho_2$, equal to the pore radius and the liquid can then wet the pore interior. (c) Once the pore surface is wet, liquid can spontaneously flow in to fill the pore. From [19].

Assuming that the gas pressure in the pore is equal to the gas pressure outside the compact, then the liquid meniscus radii at the two sites must also be equal due to the uniform hydrostatic pressure of the liquid, in accordance with Equation 2.4. Liquid will not wet the interior surface of a pore unless the liquid meniscus radius exceeds the pore radius. So initially only small pores, with radii lower than the meniscus radius will be wet by the liquid, while larger pores remain liquid free (Figure 2.10(a)). The liquid meniscus radius increases with grain size, and so will increase during sintering due to grain growth. So, for a large pore that is initially not wet by the liquid, the meniscus radius will eventually increase to equal the pore size and the liquid will wet the interior pore surface (Figure 2.10(b)). At this stage, further grain growth will increase the meniscus radius at the specimen surface, but the meniscus radius at the pore is constrained by the pore size and cannot increase further. The meniscus radii at the pore and the surface are then unequal and a pressure imbalance in the liquid is introduced, which induces liquid flow into the pore (Figure 2.10(c)), forming a liquid pool. Once a pore is filled with liquid, the grains around the pore can then change shape and grow to fill the pore space.

Pore filling is inhibited by excess gas pressure inside the pores. The excess gas pressure can be due to the presence of insoluble gases produced from reactions that take place during sintering or can be the sintering gas itself. Figure 2.11 shows a schematic of a compact surface and a pore filled with an insoluble gas.
Figure 2.11. Schematic showing an excess gas pressure inside a pore close to the compact surface. $\rho_s$ is the meniscus radius at the compact surface, $\rho_p$ is the meniscus radius at the pore, $\Delta P_p$ is the difference in pressures in the pore and at the compact surface, $r_p$ is the pore radius and $a$ is the particle radius. An excess gas pressure in the pore decreases the meniscus radius at the pore and inhibits pore filling. From [17].

Using Equation 2.4, the pressure of the liquid, $P_L$, at the compact surface can be expressed as:

$$P_L = P_S - \frac{2\gamma}{R_{surface}}$$

Equation 2.6

and at the pore interior by:

$$P_L = P_S + \Delta P - \frac{2\gamma}{R_{pore}}$$

Equation 2.7

where $P_S$ is the pressure of the sintering gas, $\Delta P$ is the difference between the gas pressure in the pore and the sintering gas, $R_{surface}$ is the liquid meniscus radius at the compact surface, and $R_{pore}$ is the liquid meniscus radius at the pore.

Because the liquid pressure is hydrostatic the two liquid pressures are equal and the two above equations can be rearranged to give:

$$\frac{2\gamma}{R_{pore}} = \frac{2\gamma}{R_{surface}} + \Delta P$$

Equation 2.8

Given that $\Delta P$ is positive, it follows that:

$$\frac{2\gamma}{R_{pore}} > \frac{2\gamma}{R_{surface}}$$

Equation 2.9

and therefore $R_{surface} > R_{pore}$, indicating that the liquid meniscus radius at the pore is lower than that at the compact surface. The low liquid meniscus radius at the pore inhibits the liquid from wetting the pore interior and filling the pore.
Similarly, pore filling theory predicts that applying an excess gas pressure at the compact surface, ie. an elevated sintering gas pressure, improves pore filling, provided that the gas inside the pores is able to diffuse out of the compact. The external gas pressure reduces the grain size, and thus the meniscus radius, required for pore filling to occur [27], which effectively increases the critical size below which pores will be filled.

There are some limitations with pore filling theory in its applicability to real systems. Firstly, it is assumed that there is a continuous liquid phase completely connected between the compact surface and the pores. Once the pore has reached the critical size for pore filling, the liquid that flows into the pore is effectively fed by the liquid at the surface. This necessitates that all the pores are open and interconnected such that liquid is able to flow to any pore space in the compact, and this is not always the case in real systems. Some of the pores become isolated during sintering, as the grains grow and close off the interconnected porosity into discrete, closed, pores. Isolated porosity can also be present in the green compact when high green densities are used, as is the case for aluminium, where green densities in excess of 90% are typical. The theory also assumes a dihedral angle of zero, so that there is a continuous liquid film covering the solid particles, and the liquid phase is able to penetrate between particle contacts. In practice, the presence of a liquid phase is seen to enhance sintering in systems where the dihedral angle is expected to be greater than zero, as in the aluminium system.

2.5 The Use of Elevated Gas Pressures in Sintering

Hot isostatic pressing involves the simultaneous application of elevated temperature and pressure to a porous specimen, be it either a powder compact or a solid part with residual porosity, where the pressure is applied via a gas [28]. The high temperature is applied to reduce the flow stress of the material and increase diffusion kinetics, with homologous temperatures typically in the range of ~0.7-0.8. [29, 30]. The temperatures used in HIP are typically lower than those used in conventional sintering [30], and excessive grain growth, which can reduce the mechanical properties, can thus be avoided. The applied pressure adds to the sintering stress inherent in a powder compact [30] to increase densification. The applied pressure is isostatic, meaning that it is transmitted uniformly over the entire part surface as a stress. This is in contrast to the hot pressing process, which is essentially the same process used to produce a green compact, but the die is maintained at an elevated temperature to soften the material and make it easier to compress [31]. The geometry of the part is limited as the stress is applied uniaxially, whereas in HIPing, more complicated geometries can be used.
Typically, HIPing is used on high-melting temperature or difficult to process materials such as ceramics, refractory metals or cemented carbides [5]. Table 2.3 shows typical HIPing temperatures and pressures for various materials.
Table 2.3. Typical HIPing temperatures and pressures. From [30].

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting point $T_m$ ($^\circ$C)</th>
<th>Yield stress at room temperature (MPa)</th>
<th>Hipping temperature ($^\circ$C)</th>
<th>Hipping pressure (MPa)</th>
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<td>100</td>
</tr>
<tr>
<td>Al/Al$_2$O$_3$</td>
<td>-</td>
<td>-</td>
<td>300</td>
<td>350</td>
</tr>
<tr>
<td>Cu and its alloys</td>
<td>1083 (Cu)</td>
<td>60 to 960</td>
<td>800 to 960</td>
<td>100</td>
</tr>
<tr>
<td>Be and its alloys</td>
<td>1289 (Be)</td>
<td>240</td>
<td>900</td>
<td>103</td>
</tr>
<tr>
<td>Niomonic and superalloys</td>
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<td>1100 to 1280</td>
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<td>-</td>
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<td>200</td>
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<td>1200</td>
<td>100</td>
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<td>100</td>
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<td>-</td>
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<td>150</td>
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<tr>
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<td>-</td>
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<tr>
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<td>2867</td>
<td>6000</td>
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<td>100</td>
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* Low alloy steels (water quenched and tempered)

Several densification mechanisms for HIPing have been proposed [7, 29-37] including plastic flow, viscous flow, power-law creep, diffusional creep, dislocation creep, particle rearrangement and diffusional particle deformation, in addition to conventional sintering mechanisms. Typically the dominant mechanisms are plastic flow, which occurs instantaneously as the applied pressure exceeds the flow stress, and time dependent creep [29, 30].
When the HIP process is applied to a powder system, it is important to differentiate between open and closed pores in the powder compact, as open pores (those connected to the compact surface) cannot be closed by the gas pressure. To overcome this, the powder compact is encapsulated in a gas-tight metal or glass container, called a can, effectively turning open pores into closed pores (see Figure 2.12) At elevated temperatures, the can material softens enough to be deformed by the gas pressure. The can is later removed from the HIPped compact by machining or chemical dissolution.

Figure 2.12. Encapsulation of a powder compact to enable elimination of surface porosity. (a) Before encapsulation. (b) After encapsulation. From [30].

An alternative to conventional HIP is Sinter-HIP, a combination of conventional sintering and HIPing, done simultaneously in a single process [28, 31, 38]. The sinter-HIP process is sometimes referred to as Pressure Assisted Sintering or Overpressure Sintering, and the terms are largely interchangeable. A particular exception to this is where the term Overpressure Sintering is used to describe a process for manufacturing superconductor wire [39, 40] that is not, strictly speaking, sinter-HIP, as the superconductor material is containerised and so is essentially the same as standard HIP. There are several advantages of sinter-HIP over HIP. Firstly, sinter-HIP negates the need for containerisation (and subsequent container removal) by sintering to a state of closed porosity prior to the application of pressure. This occurs in the range of 91-95% of the theoretical density [7, 8, 31, 41]. The lack of a can then allows more complicated geometries to be processed. An additional benefit of pre-sintering to such a high density is that the shrinkage during the HIP stage of sinter-HIP is relatively small and the dimensional control is often better than in conventional HIP [42]. Finally, the isostatic pressures used in sinter-HIPing are typically in the range of 5 to 15 MPa [31], about one-tenth of the pressures used in conventional HIP [43]. Compared to the conventional HIP process, sinter-HIP furnaces are cheaper, have a lower running cost and shorter production time [43]. Sinter-HIP has been used extensively on cemented carbides (also called hard metals) [28, 31,
41, 43-48], silicon nitride ceramics [30, 31, 42, 49-55], and to a lesser extent Al$_2$O$_3$ based ceramics [30, 31, 48, 56]. There is less prior work on sinter-HIP of metallic systems, but some work has been done on steel [31, 42, 46], tungsten heavy alloys [48, 57], magnetic alloys [31, 46], and titanium alloys [29, 31, 58]. There appears to be no prior work on sinter-HIP of aluminium alloys.

Although no work has been done on sinter-HIP of aluminium, there has been some work on the effect of moderate gas pressures on thermal processing of aluminium powder. Studies on the direct nitridation of aluminium powder compacts [59, 60] have shown that nitrogen pressures of 0.5-7 MPa can significantly increase the conversion of aluminium to aluminium nitride. The temperature at which the nitride began to form decreased with increasing nitrogen pressure, and the crystal size of the synthesised AlN increased with the nitrogen pressure, although the authors were unable to identify and explain the mechanisms involved. Nitrogen is known to play an important role in aluminium sintering, and is discussed in Section 2.6.3.

2.6 Powder Metallurgy of Aluminium

2.6.1 Green Compact

Aluminium is highly compressible, with typical green densities above 90% of theoretical density [42]. Cold welding to the die walls can cause spalling, decreasing tool life, and accumulated material can cause the die to seize, as well as adversely affecting the surface finish of the green compact. The use of a lubricant is therefore necessary. The lubricant can be dissolved in a carrier solvent and applied to the die walls at regular intervals, or admixed with the metal powder itself. In the latter case, the wax must be burned out of the compact at an intermediate temperature prior to sintering, as residual wax can inhibit sintering.

2.6.2 The Oxide Layer

Aluminium, like most metals, is always covered by a stable oxide layer, Al$_2$O$_3$. Sintering is inhibited due to the low diffusion rates through the layer, and poor wetting of liquid aluminium on alumina [61]. The surface tension then acts to push the particles apart and leads to swelling of the compact [62].

Most metals are sintered under a reducing atmosphere to aid in the removal of metal oxide and prevent further oxidation. This is problematic in aluminium systems, however, due to the thermodynamic stability of Al$_2$O$_3$. Figure 2.13 shows the partial pressure of oxygen in equilibrium with several metal/metal oxide systems as a function of temperature. At partial pressures above the curve, the oxide is stable, while below the curve the metal is stable. The oxygen partial pressures
required for the reduction of $\text{Al}_2\text{O}_3$ to aluminium metal are unobtainably low through conventional means. However, as the temperature increases during sintering, the oxide layer grows, consuming oxygen from the atmosphere. The gas flow deep in the pore network is slower than at the surface, and if oxygen can be consumed by this self-gettering faster than it can be replenished by fresh gas entering the furnace, then the local oxygen partial pressure can be significantly reduced [63, 64] and enable the formation of, for example, AlN.

![Figure 2.13. Oxygen partial pressures required for the reduction of several metal/metal oxide systems. From [7].](image)

**2.6.3 The Sintering Atmosphere**

Sintering atmospheres include air, inert gases such as argon and helium, hydrogen, dissociated ammonia, nitrogen, natural gas and vacuum [7]. The role of the atmosphere in aluminium sintering is typically to provide an inert environment to limit oxidation. Recent studies have shown that far from being inert, the atmosphere plays an active role in aluminium sintering. Nitrogen is widely accepted as the most efficacious atmosphere [63-66] and sintering shrinkage has been related to aluminium nitride formation [64], although the mechanisms are not fully understood. Furthermore, nitride formation has been shown to be improved by increasing the nitrogen pressure (see Section 2.5). It has been suggested that the formation of AlN inside pores aids in pore filling by reducing the gas pressure, which disrupts the balance of meniscus forces between the pore interior and the compact surface, inducing liquid flow into the pore [65]. It has also been suggested that since the wetting angle of AlN is substantially lower than that of $\text{Al}_2\text{O}_3$, the nitride formation improves wetting behaviour [67], although more recent work has shown that the liquid distribution of sintered Al-Cu alloys is similar under nitrogen and argon atmospheres and as such the presence of a nitride layer does not improve wetting [65, 66].
Argon inhibits sintering by maintaining a gas pressure in the pore system, due to the negligible solubility of argon in aluminium. The gas pressure inside the pores makes a negative contribution to the sintering stress, and inhibits liquid filling of pores.

Hydrogen additions of up to 5% to nitrogen or argon atmospheres have been shown to severely decrease sintering shrinkage [64, 65]. It was suggested [65] that the hydrogen forms aluminium hydride gas, which reduces the partial pressure of hydrogen in the pores, creating a concentration gradient between the pore interior and the external atmosphere. Hydrogen is soluble in liquid aluminium and can therefore diffuse into the pores to maintain a gas pressure and inhibit shrinkage in the same manner as argon.

2.6.4 Alloys

Traditionally, the aluminium alloys used in powder metallurgy are the same or similar to those used in wrought applications. More recently it has been recognised that the alloys must be tailored for sintering. Typical alloys used in powder metallurgy are based on the 2xxx and 6xxx series wrought alloys. Alcoa’s alloys 201B and 601AB are based on the wrought alloys 2014 (Al-4.4Cu-0.5Mg-0.8Si) and 6061 (Al-1Mg-0.6Si-0.25Cu), respectively [6]. Alloy AMB 2712 has a composition of Al-3.8Cu-1Mg-0.7Si-0.1Sn.

2.6.5 Magnesium

Small additions of magnesium (less than 1.5 wt%) have been shown to improve the sintering of aluminium by reacting with the oxide layer [64, 67-71]. It was suggested that this disruption of the oxide layer exposes metallic aluminium that the liquid phase can readily react with, improving the wetting behaviour and enabling sintering to proceed. A possible equation describing the reduction reaction is:

$$3Mg + 4Al_2O_3 \rightarrow 3Al_2MgO_4 + 2Al$$

Equation 2.10

Magnesium has also been shown to increase AlN formation in powder compacts sintered in a nitrogen atmosphere [67], also suggesting that the magnesium exposes aluminium metal that is then able to react with the nitrogen. Experiments on synthesising AlN via direct nitridation of molten Al alloys have also shown that magnesium additions increase the conversion of Al to AlN [72, 73].

Dilatometric studies [62, 66] suggest that the liquid that forms on heating to the sintering temperature does not initially wet the aluminium particles, and the capillary pressure forces the
particles apart, resulting in a net expansion. It is only after some incubation time when the magnesium has reacted with the oxide layer that the liquid can then wet the particles and the capillary pressure becomes attractive and the compact shrinks.

2.6.6 Tin

Tin has been shown to slow the formation of aluminium nitride on an aluminium surface [74-76]. It would seem, then, that the tin negates the beneficial effect of nitride formation (see Section 2.6.3.) on sintering shrinkage and be detrimental to sintering, yet trace additions of tin have been shown to markedly improve the sintering of Al-Cu alloys sintered in nitrogen [66, 77, 78]. It has been suggested that, in Al-Cu alloys, tin atoms preferentially bind to vacancies in the aluminium, reducing Cu diffusion into the solid phase and allowing more of the copper rich liquid to persist for longer times [78]. Although more recently, positron annihilation spectroscopy was used to show that tin does not alter the vacancy concentration in Al-Cu-Mg-Si alloys [66].

It has been suggested that as the surface tension of liquid tin is about 50-60% that of liquid aluminium [79], the tin will segregate to the surface of the liquid phase, reducing the surface tension of the overall liquid [66]. Additionally, the tin is expected to inhibit nitride formation on the liquid aluminium just as with solid aluminium, improving liquid wetting. While tin improves the wetting behaviour of the liquid, its lower surface tension should also reduce the capillary pressure, according to Equation 2.4. Tin may then be beneficial or detrimental to sintering, depending on which effect is dominant. In an argon atmosphere tin has been shown to retard shrinkage [66]. This may then be due to the low surface tension of the tin reducing the capillary pressure (Equation 2.4).

2.7 Summary of the Literature

Increasing concern for the environment is placing pressure on the automotive industry to produce lighter cars as a means of improving fuel efficiency, but the same time the production costs. The low density of aluminium makes its alloys a possible replacement material for the steel that is currently used. Press-and-sinter powder metallurgy is an attractive option for producing complicated, net-shape aluminium components, but the mechanical properties are limited by the presence of residual porosity. This porosity can be removed by subjecting the components to a high pressure/high temperature treatment such as HIP, which is expensive due to the combination of process conditions involved. The sinter-HIP process uses significantly lower pressures and is therefore less expensive than conventional HIP.
There is no prior work on the effect of elevated pressures on the sintering of aluminium alloys. The aim of this work is to explore this effect. Specifically, relatively low pressures in the range of only a few hundred kPa will be used to explore the feasibility of applying the sinter-HIP process to a commercial aluminium alloy.

Based on earlier work, there is an expectation that elevated nitrogen pressures can enhance the formation of aluminium nitride, which has been correlated with higher sintered densities. The outcome may be a low cost method to improve the mechanical properties of sintered aluminium alloys. This may then enable greater use of these alloys in automotive applications.
3 Experimental Method

3.1 Specimen Preparation

The powder mixtures were prepared from elemental powders weighed to an accuracy of 0.1 mg on an A&D model GR-200 analytical balance. The powder mixtures were stored in plastic containers, with each batch weighing between 20 g and 100 g. The powders were weighed on pieces of aluminium foil, with a fresh piece used for each element, to minimise contamination. The main alloy used was the commercial alloy 2712, which has a composition (in wt%) of Al-3.8Cu-1Mg-0.7Si-0.1Sn. For some experiments the amount of magnesium or tin was varied to explore the effect of these elements. In such experiments, the magnesium content was increased from 1% to either 3 or 4%, or the tin content reduced from 0.1% to zero. An addition of 1.5 wt% Acrawax® atomised powder, an ethylene bis stearamide lubricant, was made to all powder mixtures.

The powder alloy mixtures, in their plastic containers, were blended in a Turbula type T2C shaker-mixer for approximately 30 minutes. The blended powders were uniaxially compacted in a 10 mm diameter cylindrical floating steel die with a manually operated Carver model M hydraulic press. Compaction pressures of 100±2 and 200±2 MPa were used. Each powder compact had a mass of ~2 g, weighed to the nearest 0.1 g, and a height of ~10 mm, measured to the nearest 0.1 mm using a Mitutoyo digital micrometer with 0.001mm gradations. The density of the green compact was thus calculated:

$$\rho_g = \frac{4 m}{\pi h d^2}$$

Equation 3.1

Where $\rho_g$ is the green density in g/cm$^3$, $m$ is the compact mass in grams, $h$ is the compact height in centimetres, and $d$ is the compact diameter in centimetres. When calculating the green density, only the mass of metal in the specimen was used, by weighing the compact and subtracting 1.5% to take into account the mass of Acrawax in the compact.

3.2 Sintering

For the preliminary feasibility experiments, four compacts were sintered in each experiment. Three of these were used to determine the sintered density, while the fourth was used for metallography. The compacts were placed in a stainless steel boat, with approximate dimensions 120 x 45 mm and

---

1 Acrawax is a trademark of Lonza Group Ltd.
a wall height of approximately 30 mm, with a 10 mm spacing between each compact, as shown in Figure 3.1.

![Figure 3.1. Top view of the specimen boat used in the preliminary experiments, showing the arrangement of the green compacts.](image)

After the preliminary experiments it was considered that the walls of the boat may affect the flow of the sintering atmosphere over the compacts, and the two upstream compacts may affect the flow of gas to the two downstream ones. The specimen used for metallography may not then have been representative of all four compacts.

To avoid this possibility all subsequent experiments were done using a flat steel plate, instead of a boat, with approximate dimensions of 200 x 55 mm, using only two compacts at a time. Both specimens were then used for sintered density measurement and one or both were used for metallographical examination.

![Figure 3.2. Top view of the specimen plate used for the bulk of the experiments, showing the arrangement of the green compacts.](image)

The furnace used was a stainless steel horizontal tube furnace with an inner diameter of 63 mm, wall thickness of 5.5 mm and a hot zone length of 60 mm. A schematic of the furnace is given in Figure 3.3. The specimen plate was placed such that the specimens were in the centre of the
furnace hot zone. A K-type thermocouple was positioned just above the centre of the specimen plate to monitor the specimen temperature. The control thermocouple, also a K-type, was located outside the furnace tube at the windings, and was connected to a Eurotherm model 2416 P.I.D. set-point controller.

With the specimens inside the furnace, a stainless steel end-plate was bolted on to the open end of the furnace tube, with a seal provided by a rubber o-ring. Prior to starting the sintering program, the furnace was purged at room temperature with nitrogen or argon gas with a flow rate of ~3 l/min for 30-60 minutes, and the gas flowed continuously through the experiment. The sintering was done using bottled high purity nitrogen or argon, with purities of >99.9% and >99.9995% respectively.

![Figure 3.3. Schematic of the pressure furnace.](image)

The elevated pressure in the furnace was controlled by means of a spring valve connected in series with the manual exhaust valve. The spring valve was set to the desired pressure, between 160 and 600 kPa, and the exhaust valve closed while nitrogen or argon gas was flowing into the furnace. When the gas pressure built up to the set pressure, the spring valve opened and the pressure was maintained at the set value. This maintained an elevated gas pressure inside the furnace while still having continuous gas flow. It took approximately one minute for the furnace to achieve the set pressure from the time the exhaust valve was closed. The gas flow rate through the furnace was kept at a constant 3 l/min, regardless of the gas pressure used.

The same thermal treatment was used in all experiments (Figure 3.4). The temperature was increased to 590°C at 5°C/min, with a 30 minute isothermal segment at 300°C to burn off the Acrawax lubricant. The temperature was maintained at 590°C for various times up to 60 minutes, at
which point the pressure was released (for elevated pressure experiments) and the specimens removed from the furnace and allowed to air cool to room temperature.

Due to the thermal characteristics of the furnace, the temperature program had to be optimised to enable constant temperature control (Figure 3.4(b)). This was largely due to the significant thermal lag caused by the increased wall thickness of the custom built furnace tube.

![Graph](image1.png)

**Figure 3.4.** (a) Typical temperature trace of an experiment with a 60 minute isothermal hold at the sintering temperature; (b) Detail of the temperature trace, showing how the set temperature was optimised to produce a constant measured temperature of 590±1°C.
For most of the elevated pressure experiments, the gas pressure was increased at the start of the 590°C isothermal hold. For comparison, some experiments were conducted where the gas pressure was increased at the start of the experiment, when the furnace was at room temperature, and maintained for the entire thermal treatment.

### 3.3 Sintered Density and Porosity Measurement

The density of the sintered compacts was calculated according to ASTM standard B328-96, but using H-Galden ZT180, a hydrofluoropolyether produced by Solvay Solexis, instead of water, on a A&D model GR-200 analytical balance in conjunction with an A&D model AD-1653 specific gravity measuring kit. A schematic of the apparatus is given in Figure 3.5.

![Figure 3.5. Schematic of the sintered density measurement apparatus.](image)

The weight of the compact in dry air was recorded as \( W_{\text{AIR}} \). The compact was then immersed in oil (Mobil DTE 25) under vacuum for 30 minutes, and then at atmospheric pressure for a further 10 minutes to ensure complete pore penetration with oil. The weight of the oil-impregnated compact was then recorded as \( W_{\text{OIL}} \). The impregnated compact was then suspended on a stage immersed in a vessel of H-Galden such that the stage was connected to a balance via a scaffold. The weight of the oil-impregnated compact in H-Galden was then recorded as \( W_{\text{HG}} \). The density of the H-Galden, \( \rho_{\text{HG}} \), was determined as a function of its temperature as measured to the nearest degree Celsius, by linear interpolation of data from technical literature.

The sintered density of the compact, \( \rho_s \), is then given by:

\[
\rho_s = \frac{\rho_{\text{HG}} \cdot W_{\text{AIR}}}{W_{\text{OIL}} - W_{\text{HG}}}
\]

Equation 3.2

Where \( \rho_s \) is given in g/cm\(^3\).
The theoretical maximum density of an alloy, $\rho_t$, can be estimated by:

$$\rho_t = \frac{\sum_{i=1}^{n} \rho_i \cdot \text{wt}\% i}{\sum_{i=1}^{n} M_i}$$

\text{Equation 3.3}

where $\rho_i$ is the density of element $i$ in g/cm$^3$, wt%i is the weight percent of element $i$ in the alloy, $M_i$ is the molar mass of element $i$ in g/mol, and $n$ is the total number of elements in the alloy.

The sintered density can be more usefully expressed in terms of the theoretical maximum density of the alloy, by combining Equation 3.2 and Equation 3.3 to give:

$$\rho_s = \frac{\rho_t \times 100}{\rho_s}$$

\text{Equation 3.4}

The percentage of porosity, $P_{\text{TOTAL}}$, in the compact can then be given by:

$$P_{\text{TOTAL}}(\%) = 100 - \rho_s(\%)$$

\text{Equation 3.5}

The percentage of open porosity, $P_{\text{OPEN}}$, and closed porosity, $P_{\text{CLOSED}}$, can also be calculated:

$$P_{\text{OPEN}}(\%) = \frac{\rho_{HG}(W_{\text{OIL}} - W_{\text{AIR}})}{\rho_{\text{OIL}}(W_{\text{OIL}} - W_{\text{HG}})} \times 100$$

\text{Equation 3.6}

$$P_{\text{CLOSED}}(\%) = P_{\text{TOTAL}}(\%) - P_{\text{OPEN}}(\%)$$

\text{Equation 3.7}

where $\rho_{HG}$ is the density of the H-Galden given in g/cm$^3$.

### 3.4 Metallography

Compacts were immersed in Epofix, a two-part epoxy resin, in a plastic mold and left to cure overnight. After being removed from the mold, the compacts were ground using 500 grit SiC paper using water as a lubricant. The compacts were then polished with 9 $\mu$m and then 3 $\mu$m diamond suspension. The final polishing stage used a 0.04 $\mu$m silica suspension. Compacts were rinsed with ethanol and dried with hot air between each stage. Digital optical micrographs were taken using an Olympus AX70 optical microscope with a Diagnostic Instruments SPOT model 1.4.0 digital camera. Specimens were left unetched. Electron micrographs were taken in a Philips XL30 SEM. Specimens analysed in the SEM were first platinum sputter coated.
The equilibrium liquid volume fraction for this alloy, calculated using Thermocalc thermodynamic software, at 590°C and 1 atm pressure is 18.8%. An unavoidable consequence of the microstructural changes during solidification of such a large volume of liquid is that the solidified microstructures shown in electron micrographs are expected to differ somewhat from their corresponding high temperature microstructures. This problem is exacerbated due to the slow cooling rate of specimens upon removal from the furnace, an unavoidable consequence of the large times required (several minutes) to remove specimens from the furnace.

3.5 Pore Size Distribution

When drawing conclusions from data obtained from image analyses, it is important that the images used in the analysis are representative of the microstructure, particularly when the microstructures are inhomogeneous, as in this work. As an example, the two electron micrographs shown in Figure 3.6 were taken from different parts of the same specimen. The difference in pore distribution is evident, and clearly illustrates the non-uniform nature of the sintered microstructure.
Figure 3.6. Backscattered electron micrographs taken from different parts of the same specimen. The bright phase is solidified copper-rich liquid and the matrix phase is aluminium solid solution. The non-uniformity of the specimen is evident by the differences in the amount, size, and morphology of pores in the two micrographs.
This problem can be addressed in several ways. One approach is to take a large number of randomly located micrographs, although this does not completely rule out the possibility of bias in the images analysed. In particular it tends to bias towards regions of the specimen away from the edge, which is particularly bad for analysing sintered microstructures as the porosity at the specimen surfaces can be different to the bulk material. Another strategy is to perform the analysis over the entire sample. This ensures that all parts of the specimen, the bulk material and all the edges, are represented in the analysis. This was problematic however, due to limitation in computer processing power imposing a maximum size of the digital image used by the analysis software, so a compromise had to be made. A series of four digital optical micrographs were taken down the side of a polished metallographic section of a compact, such that the four micrographs could be digitally joined or “stitched” together to give a single larger micrograph, an example of which is shown in Figure 3.7. This micrograph showed an area of the compact section extending to approximately 3 mm into the specimen, that is, about one third of the entire specimen section. It was this image that was used to calculate the pore size distribution.
Figure 3.7. Typical optical micrograph of sintered compact used for pore size distribution measurements.

Pore size distributions were constructed from the optical micrographs using ImageJ, a public domain image processing and analysis software package produced by the National Institute of Health, USA. As the pore size was calculated from a two dimensional section, the measured pore sizes are expected to be slightly underestimated [80]. For convenience, the pore cross sectional area, $A_{\text{PORE}}$, as measured from the micrographs, was expressed as the diameter, $D_{\text{PORE}}$, of a circle of equal area according to the following equation:

$$D_{\text{PORE}} = 2\sqrt[2]{\frac{A_{\text{PORE}}}{\pi}}$$  \hspace{1cm} \text{Equation 3.8}

### 3.6 Experimental Uncertainty

Powder compacts are non-equilibrium, and at small scales, non-uniform. A certain amount of microstructural homogenisation is expected to occur during the sintering process as the material tends towards equilibrium. Yet it is the exploration of the microstructure during the progression
from a highly non-equilibrium state that is of interest, and as such there is the potential for experimental uncertainty to become significant. The situation is compounded by the large number of process and material variables that affect sintering behaviour, small variations of which may have significant impact on experimental results (Table 3.1).

Table 3.1. Some important variables that affect sintering behaviour.

<table>
<thead>
<tr>
<th>Independent variables</th>
<th>Dependent variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>powder shape</td>
<td>heating rate</td>
</tr>
<tr>
<td>powder size distribution</td>
<td>sintering temperature</td>
</tr>
<tr>
<td>bulk contamination</td>
<td>sintering time</td>
</tr>
<tr>
<td>surface contamination</td>
<td>cooling rate</td>
</tr>
<tr>
<td>bulk alloy composition</td>
<td>atmosphere type</td>
</tr>
<tr>
<td>blended powder homogeneity</td>
<td>atmosphere moisture content</td>
</tr>
<tr>
<td>compaction pressure</td>
<td>atmosphere flow rate</td>
</tr>
<tr>
<td>compaction speed</td>
<td>atmosphere pressure</td>
</tr>
<tr>
<td>specimen geometry</td>
<td>furnace geometry</td>
</tr>
<tr>
<td>lubricant type</td>
<td>furnace material</td>
</tr>
<tr>
<td>lubricant content</td>
<td>crucible material</td>
</tr>
</tbody>
</table>

In an effort to control as many of these variables as possible, experiments were conducted under “identical” conditions (except where indicated in the results section). Despite this, there will always be some experimental uncertainty, so for each set of experimental conditions, repeat experiments were conducted to take into account this uncertainty. To estimate the systematic uncertainty, the results of three experiments conducted over a period of ten months under identical conditions (60 minutes at 590ºC, under nitrogen at 100 kPa) were compared (Table 3.2).

Table 3.2. Systematic variability in specimens sintered under identical conditions.

<table>
<thead>
<tr>
<th>Density (% of theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green compacts</td>
</tr>
<tr>
<td>90.5 ± 0.63 %</td>
</tr>
<tr>
<td>Sintered compacts</td>
</tr>
<tr>
<td>96.7 ± 0.72 %</td>
</tr>
</tbody>
</table>

So systematic uncertainty in the order of up to ~1.5% can be expected. This variability takes into account small differences in process parameters between experiments conducted under ostensibly identical conditions, as well as the effect of any changes over time due to drifting of system parameters. System parameters that may drift could include the thermoelectric properties of a
thermocouple as its composition degrades over time, or the chemical environment in the furnace itself as chemical reaction products accumulate on the furnace walls, for example. A certain amount of this variability is conceivably due to “human error”. That is, variability in powder blend composition and specimen preparation that can produce differences between batches of specimens prepared under identical conditions. To estimate the batch to batch variability due to specimen preparation, twelve compacts of alloy 2712 (with 1.5 wt% Acrawax) were prepared from four separately prepared powder batches, and were sintered under identical conditions in four separate furnace runs conducted on different days, and their densities compared (Table 3.3).

### Table 3.3. Batch to batch variability of compacts prepared and sintered under identical conditions.

<table>
<thead>
<tr>
<th></th>
<th>Density (% of theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green compacts</td>
<td>90.1 ± 0.86 %</td>
</tr>
<tr>
<td>Sintered compacts</td>
<td>97.4 ± 0.28%</td>
</tr>
</tbody>
</table>

Despite a variability in green density of nearly ~1.7%, the variability in sintered density was ~0.6%. Clearly, then, the batch to batch variability is relatively small compared to the systematic variability, and is well controlled.
4 Results

4.1 The Effect of Nitrogen Pressure During Isothermal Holding

4.1.1 Green Compact Pressed at 100 MPa

The green density of specimens compacted at 100 MPa was 84.1±1.0 %. A backscattered electron micrograph of the corresponding green microstructure is given in Figure 4.1.

Figure 4.1. Backscattered electron micrograph showing the green microstructure of a compact pressed at 100 MPa. The predominant grey particles are aluminium. Representative alloying element particles are labelled.

The predominant grey particles in Figure 4.1 are aluminium, and the dark grey particles are magnesium. The magnesium particles have reacted with the water used in the metallographic preparation, and so appear rough and fractured. The bright, dendritic particles are copper, while the smaller, rounded, bright particles are tin. Silicon particles are difficult to differentiate from the aluminium, because the atomic number contrast between the two elements is low. The silicon particles can also be identified by their smaller size and angular shape.
4.1.2 Sintered Density at 100 kPa and 600 kPa Nitrogen Pressures During Isothermal Holding, for Green Compact Pressed at 100 MPa

The green compact was sintered at 590ºC in nitrogen, at a heating rate of 5ºC/minute. The initial nitrogen pressure was 100 kPa. The nitrogen pressure during isothermal holding was either maintained at 100 kPa, or increased to 600 kPa. Results are shown in Figure 4.2 for a 100 MPa compaction pressure.

Figure 4.2 shows that for a 100 MPa compaction pressure, and nitrogen at 100 kPa, the density increased from 84.1 to 97.4% after an isothermal hold of 40 minutes. The densification rate initially increased over time until 15 minutes, after which the rate decayed. The density was effectively the same, for the first 15 minutes, for the two different nitrogen pressures. At some time between 15 and 20 minutes, the density under the two different regimes diverged, with the 600 kPa nitrogen pressure resulting in a lower density than 100 kPa nitrogen. There was net shrinkage at both pressures.
4.1.3 Porosity Characterisation for 100 kPa and 600 kPa Nitrogen Pressures During Isothermal Holding, for Green Compact Pressed at 100 MPa

The results presented in section 4.1.2 showed how the sintered density changed during isothermal holding at different pressures. This section examines how the amount of open and closed porosity changed during isothermal holding. Open pores are those that are connected to the specimen surface, and closed pores are discrete pores isolated from the specimen surface. Figure 4.3 shows the amount of open and closed porosity as a function of the isothermal hold time for a 100 kPa nitrogen pressure. Figure 4.4 shows the same information for a 600 kPa nitrogen pressure.

Figure 4.3. Development of open and closed porosity for 100 kPa nitrogen pressure during isothermal holding at 590°C. The green compact was pressed at 100 MPa. Initially nearly all of the porosity was open and over time the amount of open porosity decreased. The closed porosity reached a maximum at 15 minutes and then decreased over the remaining time.

Figure 4.3 shows that at the 100 kPa nitrogen pressure there was 16% total porosity at the start of the isothermal hold. Most of this porosity, 14%, was open. The amount of open porosity decreased to about 1% after 20 minutes and stayed relatively constant for the remainder of the isothermal hold. The closed porosity, initially at 1.5% at the start of the isothermal hold, increased to 4.7% after 15 minutes and gradually decreased to 2% over the next 15 minutes, remaining constant for the remainder of the experiment.
The porosity at a 600 kPa nitrogen pressure, as shown in Figure 4.4, follows the same general trends as at 100 kPa nitrogen pressure (Figure 4.3). The porosity at the start of isothermal holding was identical under both regimes, as this was measured before the nitrogen pressure was increased to 600 kPa. At the start of isothermal holding nearly all of the porosity was open. The open porosity rapidly decreased to 0.5-1% after 15 minutes and remained constant for the remainder of the isothermal hold. This minimum value was slightly lower than the minimum achieved under a 100 kPa nitrogen pressure, as shown in Figure 4.3, and was reached in a shorter time. The closed porosity, initially at 1.5%, increased to 11% at 10 minutes and then decreased to 3.4% over the next 20 minutes.

Even though the density, and thus the total porosity under 100 kPa and 600 kPa nitrogen pressures were very similar through most of the isothermal hold (Figure 4.2), there were significant differences in the proportion of open and closed porosities in each case. This is most pronounced at 10 minutes into the isothermal hold, as shown in Table 4.1.
4.1.4 Green Compact Pressed at 200 MPa

The green density of specimens compacted at 200 MPa was 90.5±0.6 %. A backscattered electron micrograph of the corresponding green microstructure is given in Figure 4.5.

The green microstructure is similar to that for 100 MPa compaction pressure (Figure 4.5), aside from the amount of porosity. The predominant grey particles are aluminium, while the irregular bright particles are copper and the small rounded bright particles are tin. Magnesium is dark grey and the small angular silicon particles are a slightly lighter grey than the aluminium.

---

Table 4.1. Open and closed porosity after 10 minute isothermal hold, for 100 MPa compaction pressure

<table>
<thead>
<tr>
<th>Nitrogen pressure during isothermal hold (kPa)</th>
<th>Open porosity (%)</th>
<th>Closed porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>9.6</td>
<td>2.6</td>
</tr>
<tr>
<td>600</td>
<td>1.7</td>
<td>10.8</td>
</tr>
</tbody>
</table>

---

![Figure 4.5](image)
4.1.5 Sintered Density at 100 kPa and 600 kPa Nitrogen Pressures During Isothermal Holding, for Green Compact Pressed at 200 MPa

Green compacts were pressed at 200 MPa and sintered under the same conditions as those pressed at 100 MPa. Results are shown in Figure 4.6.

![Figure 4.6. Sintered density of alloy 2712 as a function of isothermal hold time at 590°C, sintered in nitrogen. Green compacts were pressed at 200 MPa. Open circles show the density with nitrogen at 100 kPa. Filled circles show the density with 600 kPa nitrogen pressure applied upon reaching the isothermal holding temperature. Increasing the nitrogen pressure during isothermal holding decreased the time to maximum density, and slightly increased the maximum achievable density.](image)

When the nitrogen pressure was 100 kPa the density, initially at 88.7%, increased to 96.8% by 16 minutes into the isothermal hold and stayed fairly constant for the remainder of the isothermal hold of 60 minutes. When the nitrogen pressure was increased to 600 kPa, the density increased to over 97% in the first 10 minutes, and further to 97.5% over the next 10 minutes. The density stayed relatively constant for the remainder of the isothermal hold. A net shrinkage was achieved in both nitrogen pressures. Increasing the nitrogen pressure from 100 kPa to 600 kPa during isothermal holding increased the sintering rate during this stage. The maximum density achieved was also increased slightly.

It was at 10 minutes into the isothermal hold that the densities under each nitrogen pressure were at their most divergent. Backscattered electron micrographs showing typical microstructures at this time are given in Figure 4.7.
Figure 4.7. Backscattered electron micrographs showing microstructures of compacts sintered in nitrogen. Green compacts were pressed at 200 MPa. (a) 10 minute isothermal hold at 100 kPa nitrogen pressure; (b) 10 minute isothermal hold at 600 kPa nitrogen pressure. The predominant grey phase is aluminium solid solution, the bright phase is solidified liquid, and the black regions are pores. Aside from the amount of porosity, the two microstructures are similar.
The two microstructures shown in Figure 4.7 appear to have similar liquid distributions, and there don’t appear to be any significant differences in grain size and shape. This appears consistent with the sintered density data: 95% and 97% for a 100 kPa nitrogen pressure and 600 kPa nitrogen pressure respectively (see Figure 4.6).

4.1.6 Porosity Characterisation at 100 kPa and 600 kPa Nitrogen Pressures During Isothermal Holding, for Green Compact Pressed at 200 MPa

Figure 4.8 shows the amount of open and closed porosity as a function of the isothermal hold time for a 100 kPa nitrogen pressure. Figure 4.9 shows the same information for a 600 kPa nitrogen pressure.

Figure 4.8 shows that for a 100 kPa nitrogen pressure there was 7% open porosity at the beginning of the isothermal hold. This decreased rapidly to a limiting value slightly lower than 1% and stayed constant for the remainder of the isothermal hold. The closed porosity was initially about 4.5% and decreased to between 2.0% and 2.5% by 16 minutes into the isothermal hold.
Figure 4.9. Development of the open and closed porosity for 600 kPa nitrogen pressure during isothermal holding at 590°C. The green compact was pressed at 200 MPa. The open porosity, initially higher than the closed porosity, rapidly decreased to a limiting value. The closed porosity gradually decreased to a limiting value.

At 600 kPa nitrogen pressure (Figure 4.9) the behaviour of the open porosity was effectively the same as for a 100 kPa nitrogen pressure (see Figure 4.8). The open porosity was initially at 7% and deceased to a limiting value between 0.5% and 1% by 10 minutes into the isothermal hold. This was almost identical to the behaviour of the open porosity in 100 kPa nitrogen. The closed porosity, initially at about 4.5%, gradually decreased to a limiting value between 1.6% and 2% by about 20 minutes into the isothermal hold. This follows the same trend as for a 100 kPa pressure, but with a slightly lower limiting value.

4.1.7 Pore Size Distribution at 100 kPa and 600 kPa Nitrogen Pressures During Isothermal Holding, for Green Compact Pressed at 200 MPa

Where the results presented in section 4.1.6 were concerned with the amount of porosity, this section examines the size of the pores, with no distinction between open and closed pores. Figure 4.10 shows the pore size distribution after 10 minutes isothermal holding at 590°C, for both 100 kPa nitrogen pressure and 600 kPa nitrogen pressure. The pore size distribution for an unsintered, or green, specimen is also shown for comparison.
For the three sets of conditions used (green specimen, 100 kPa nitrogen pressure, 600 kPa nitrogen pressure), the number frequency of pores in each size fraction decreased exponentially with increasing pore size, over the range of pore sizes measured. Sintering for an isothermal hold of 10 minutes at 100 kPa nitrogen pressure resulted in a significant decrease in the absolute number of pores in all size fractions, compared to the green state. Increasing the nitrogen pressure to 600 kPa for the isothermal hold decreased the number of pores in all size fractions even further. There is significant experimental scatter in the data for the lowest size fraction, most likely because these low sizes approach the resolution limit of the image analysis technique used.

### 4.1.8 Sintered Density at Various Nitrogen Pressures During 10 minute Isothermal Hold, for Green Compact Pressed at 200 MPa

In previous sections, results were presented for nitrogen pressures of 100 kPa and 600 kPa applied during different lengths of isothermal holding time. In this section, results are presented for various nitrogen pressures between 100 kPa and 600 kPa applied during an isothermal holding time of 10 minutes. Compacts were sintered under the same conditions as in previous sections. The results of these experiments are shown in Figure 4.11.
Figure 4.11. Sintered density of alloy 2712 after a 10 minute isothermal hold. The green compact was pressed at 200 MPa. The nitrogen pressure was increased from 100 kPa upon reaching the isothermal hold temperature. Increasing the nitrogen pressure from 100 kPa to 160 kPa increased the density sharply, but further increases in nitrogen pressure up to 600 kPa had a negligible effect on density.

Figure 4.11 shows that when the nitrogen pressure was raised to 160 kPa during the isothermal hold the density increased from 95% to 97%. Increasing the nitrogen pressure further had a negligible effect on the density.

4.1.9 Porosity Characterisation at Various Nitrogen Pressures During 10 Minute Isothermal Hold, for Green Compact Pressed at 200 MPa

Figure 4.12 shows the amount of open and closed porosity as a function of nitrogen pressure applied during a 10 minute isothermal hold.

The open porosity had already reached a minimum limiting value of between 0.5% and 0.8% by 10 minutes into the isothermal hold regardless of the nitrogen pressure (Figure 4.12). The amount of closed porosity, initially at about 5%, was reduced rapidly with increasing nitrogen pressure. A nitrogen pressure of 160 kPa was sufficient to reduce the closed porosity to a minimum limiting value of 2.5%. Further increases in nitrogen pressure up to 600 kPa had negligible effect on the closed porosity.
Figure 4.12. Development of the open and closed porosity for various nitrogen pressures, where the nitrogen pressure was increased from 100 kPa at the start of isothermal holding. The green compact was pressed at 200 MPa. Increasing the nitrogen pressure from 100 kPa to 160 kPa decreased the amount of closed porosity, while further increases had no effect. The amount of open porosity was independent of the nitrogen pressure.

4.2 The Effect of Nitrogen Pressure During Heating and Isothermal Holding

In this section results are presented from experiments where a nitrogen pressure of 600 kPa was applied during both the heating and isothermal stages of the sintering cycle. This is distinct from the results shown in section 4.1 where the nitrogen pressure was elevated from 100 kPa to 600 kPa only for the duration of the isothermal hold.

4.2.1 Sintered Density at a 600 kPa Nitrogen Pressure During Heating and Isothermal Holding

Green compacts were pressed at 200 MPa and sintered under the same conditions as in previous sections, with the exception that the nitrogen pressure was maintained at a constant 600 kPa during both heating and isothermal holding. Results are shown in Figure 4.13
Figure 4.13. Sintered density as a function of isothermal hold time at 590°C. Green compacts were pressed at 200 MPa. The nitrogen pressure was 600 kPa during both heating and isothermal holding. The density increased linearly from 95% to 97% after 10 minutes of isothermal holding.

When the nitrogen pressure was kept at 600 kPa for both the heating and isothermal holding stages of the sintering cycle, the density had reached over 95% by the start of the isothermal hold (Figure 4.13), so a net shrinkage had been achieved by the start of isothermal holding. This value is significantly higher than when the pressure was applied during the isothermal stage only (Figure 4.6), where the density was only ~89% at the start of the isothermal hold, although by 10 minutes into the isothermal hold, the density in both cases had reached the same maximum value of ~97%. It is evident then that applying the pressure over both the heating and isothermal stages improves the sintering rate by a greater amount than applying the elevated pressure during the isothermal stage only.

Figure 4.14 shows backscattered electron micrographs of microstructures corresponding to the start of the isothermal hold and a 10 minute isothermal hold.

In Figure 4.14 the grey phase is aluminium solid solution, the bright phase in the grain boundaries is solidified liquid and the black regions are pores. The microstructures in Figure 4.14 are essentially identical except for the apparently lower amount of porosity in Figure 4.14b. The microstructure in Figure 4.14b is essentially identical to that in Figure 4.7b, where the 600 kPa pressure was applied during the isothermal stage only.
Figure 4.14. Backscattered electron micrographs showing sintered microstructures of compacts sintered at a 600 kPa nitrogen pressure applied during heating and isothermal holding. (a) Start of isothermal holding; (b) 10 minutes isothermal holding. The predominant grey phase is aluminium solid solution, the bright phase is solidified liquid, and the black regions are pores. The microstructures are essentially identical.
4.2.2 Porosity Characterisation at a 600 kPa Nitrogen Pressure During Heating and Isothermal Holding

Figure 4.15 shows how the amount of open and closed porosity varied over a 10 minute isothermal hold where the nitrogen pressure was maintained at 600 kPa through both the heating and isothermal holding stages.

![Graph showing porosity variation](image)

Figure 4.15. Development of the open and closed porosity for a 600 kPa nitrogen pressure applied during both heating and isothermal holding. Green compacts were pressed at 200 MPa. The amount of open porosity was constant throughout the isothermal hold, while the closed porosity decreased fairly linearly from 4% to 2%.

The amount of open porosity was constant throughout the isothermal hold, at a limiting value slightly less than 1%. By the time the temperature reached the isothermal hold temperature, all the open porosity had been effectively closed. At the start of isothermal holding there was 4% closed porosity, which reduced to 2% after 10 minutes.

4.3 The Effect of Argon Pressure During Isothermal Holding

4.3.1 Sintered Density at 100 kPa and 600 kPa Argon Pressures During Isothermal Holding

Compacts were pressed at 200 MPa and sintered under the same conditions as previous sections, except argon was used instead of nitrogen. Figure 4.16 shows the sintered density as a function of the isothermal holding time.
Figure 4.16. Sintered density of alloy 2712 as a function of isothermal hold time at 590ºC, sintered in argon. 200 MPa compaction pressure. Open circles show the density at 100 kPa argon pressure. Filled circles show the density with the argon pressure increased to 600 kPa upon reaching the isothermal hold. There was a net expansion during sintering until 60 minutes into the isothermal hold, where the sintered density was equal to the green density. Increasing the argon pressure during isothermal holding had negligible effect on sintered density.

With argon at 100 kPa, the density increased continuously from 88.3% to 90.5% over the isothermal stage of the sintering cycle. When the argon pressure was increased to 600 kPa, the density curve was almost identical to the 100 kPa curve. Increasing the argon pressure during isothermal holding had a negligible effect on the density.

There was a net expansion when sintering under argon, meaning that the sintered density was lower than the green density. It was only after an isothermal hold of 60 minutes that the density increased to equal the green density.

A comparison of the sintered density in argon (Figure 4.16) with that under nitrogen (Figure 4.6), shows that nitrogen is more efficacious. There was no net shrinkage in argon, regardless of pressure, while in nitrogen there was significant shrinkage, up to ~7%. The density was insensitive to pressure in argon, whereas in nitrogen increasing the pressure increased the sintering rate.

Figure 4.17 shows backscattered electron micrographs of specimens sintered under argon for a 10 minute isothermal hold at both 100 kPa and 600 kPa argon pressures.
Figure 4.17. Backscattered electron micrographs showing sintered microstructures of compacts sintered in argon. Green compacts were pressed at 200 MPa. (a) 10 minute isothermal hold at 100 kPa argon pressure. (b) 10 minute isothermal hold at 600 kPa argon pressure. The predominant grey phase is aluminium solid solution, the bright phase is solidified liquid and the dark regions are pores. Some solidified liquid can be seen inside some of the pores. The microstructures are essentially the same.
Figure 4.17 shows that there is negligible difference between the microstructures for 100 kPa and 600 kPa argon pressure. This is in agreement with the density data shown in Figure 4.16, where the densities under the two different argon pressures was the same.

### 4.3.2 Porosity Characterisation at 100 kPa and 600 kPa Argon Pressures During Isothermal Holding

Figure 4.18 shows the amount of open and closed porosity as a function of the isothermal hold time for a 100 kPa argon pressure. Figure 4.19 shows the same information for a 600 kPa argon pressure.

![Graph showing porosity development](image)

Figure 4.18. Development of the open and closed porosity for 100 kPa argon pressure during isothermal holding at 590°C. Green compacts were pressed at 200 MPa. The open porosity decreased continuously over time. The closed porosity decreased slightly in the first 10 minutes and then increased constantly over time. The total porosity decreased by ~2% over 60 minutes.

In argon, the open porosity was 6.5% at the start of the isothermal hold and decreased to 3.5% over 60 minutes. The closed porosity decreased slightly in the first 10 minutes from 5.2% to 4.5% and then increased continuously over the rest of the isothermal hold to 6.0%. The decrease in the amount of open porosity was slightly greater than the increase in closed porosity, such that there was only a small change in total porosity. The total porosity decreased constantly from about 11.7% to 9.5%.
At 600 kPa argon pressure (Figure 4.19), the open porosity decreased constantly from 6.5% at the start of the isothermal hold to 3.5% over 60 minutes. Conversely, the closed porosity increased from 5% to 6.3% at a constant rate. The reduction in open porosity was slightly greater than the increase in closed porosity, so that there was a net reduction in total porosity of about 2%. The data for total porosity at 600 kPa argon pressure (Figure 4.19) is almost identical to that under 100 kPa (Figure 4.18), however there were slight differences in the open and closed porosity curves for the two different argon pressures.

4.4 The Effect of Magnesium on the Sintering of Al-3.8Cu-xMg-0.7Si-0.1Sn Alloys in Nitrogen at Elevated Gas Pressures.

4.4.1 Sintered Density at 100 kPa and 600 kPa Nitrogen Pressures Applied During Isothermal Holding

Green compacts of alloy Al-3.8Cu-xMg-0.7Si-0.1Sn were pressed at 200 MPa and sintered for 10 minutes in nitrogen under the same conditions as in previous sections. The magnesium content was either 1, 3, or 4 wt%. The density measurements are shown in Figure 4.20.
Figure 4.20. Sintered density of Al-3.8Cu-xMg-0.7Si-0.1 for a 10 minute isothermal hold at 590°C, sintered in nitrogen. 200 MPa compaction pressure. Open circles show the density for 100 kPa nitrogen pressure. Filled circles show the density with the nitrogen pressure increased to 600 kPa upon reaching the isothermal hold. Under both nitrogen pressures, increasing the magnesium content from 1% to 3% resulted in an increase in density. Increasing the magnesium content further to 4% had no additional effect.

Figure 4.20 shows that for a 100 kPa nitrogen pressure, increasing the magnesium content from 1% to 3% increased the density from 95% to 97%. Similarly in 600 kPa nitrogen, increasing the magnesium from 1% to 3% increased the density from 97% to 98%. Further increases in the magnesium content up to 4% had no further effect on the density for either nitrogen pressure.

### 4.4.2 Porosity Characterisation at 100 kPa and 600 kPa Nitrogen Pressures During Isothermal Holding

Figure 4.21 shows the amount of open and closed porosity as a function of the magnesium content for a 10 minute isothermal hold time at 100 kPa nitrogen pressure. Figure 4.22 shows the same information for a 600 kPa nitrogen pressure during isothermal holding.

For a 10 minute isothermal hold at 100 kPa nitrogen pressure the open porosity was insensitive to the magnesium content, remaining at a constant value of 0.8-0.9%. The closed porosity, however, decreased from 4% to 2% as the magnesium content was increased from 1% to 3%. Increasing the magnesium content further to 4% had no further effect on the porosity.
Figure 4.21. Development of open and closed porosity of alloys of varying magnesium content for a 10 minute isothermal hold at 590°C and 100 kPa nitrogen pressure. Green compacts were pressed at 200 MPa. The magnesium content had no effect on open porosity. Increasing the magnesium content from 1% to 3% decreased the amount of closed porosity, but increasing the magnesium content further had no effect.

Figure 4.22. Development of open and closed porosity of alloys of varying magnesium content for a 10 minute isothermal hold at 590°C and 600 kPa nitrogen pressure. Green compacts were pressed at 200 MPa. The magnesium content had no effect on open porosity. Increasing the magnesium content from 1% to 3% decreased the amount of closed porosity, but increasing the magnesium content further had no effect.

Figure 4.22 shows that for a 10 minute isothermal hold at 600 kPa nitrogen pressure the magnesium content had no effect on the amount of open porosity. The open porosity stayed at a constant value.
of 0.5%. This value is lower than that under 100 kPa nitrogen (see Figure 4.21). Increasing the magnesium content from 1% to 3% decreased the amount of closed porosity from 2.5% to 1.5%.

### 4.4.3 Spatial Distribution of Magnesium at 100 kPa and 600 kPa Nitrogen Pressures During Isothermal Holding

The spatial distribution of magnesium across a sectioned sintered specimen was measured using energy dispersive x-ray spectroscopy. Compacts of alloy 2712 were pressed at 200 MPa and sintered using the same procedure as in previous sections, for an isothermal holding time of 10 or 60 minutes and a nitrogen pressure of 100 kPa or 600 kPa during isothermal holding.

![Magnesium content measured at various points across a 10mm specimen section](image)

Figure 4.23. Magnesium content measured at various points across a 10mm specimen section, determined using EDS. The nominal magnesium content of the alloy was 1wt%. Specimens were sintered in nitrogen at 590 °C for an isothermal hold of 10 minutes or 60 minutes. The nitrogen pressure was either 100 kPa or 600 kPa during the isothermal hold. The experimental variability makes it impossible to differentiate the results under the different sets of process conditions.

Figure 4.23 shows that the experimental uncertainty in the EDS measurements was significant. For this reason it is not possible to differentiate the results from each set of process conditions. So the effect of nitrogen pressure on magnesium vapourisation could not be determined using this technique. It is worth noting, however, that the nominal magnesium concentration of the alloy was 1 wt%, yet Figure 4.23 shows the measured concentration in the sintered compact to be significantly less than this.
4.5 The Effect of Tin on the Sintering of Al-3.8Cu-1Mg-0.7Si-xSn in Nitrogen at Elevated Gas Pressures

4.5.1 Sintered Density at 100 kPa and 600 kPa Nitrogen Pressures Applied During Isothermal Holding

Green compacts of alloy Al-3.8Cu-1Mg-0.7Si-xSn were pressed at 200 MPa and sintered for 10 minutes in nitrogen. The pressure was either maintained at 100 kPa for the entire duration of the experiment, or raised to 600 kPa at the start of the isothermal hold. The tin content was either 0 or 0.1 wt%. The density measurements are shown in figure (Figure 4.24)

![Figure 4.24. Sintered density of Al-3.8Cu-1Mg-0.7Si-xSn for a 10 minute isothermal hold at 590°C, sintered in nitrogen. 200 MPa compaction pressure. At 100 kPa nitrogen pressure, increasing the tin content from 0% to 0.1% increased the density by 3.3%. At 600 kPa the density was higher than at 100 kPa, and insensitive to the presence of tin.](image)

At 100 kPa nitrogen pressure, the density was 91.3% when there was no tin in the alloy. When the tin content was increases to 0.1%, the density increased to 94.6%. This is consistent with previous work (see Section 2.6.6) where small tin additions increased the density of Al-Cu alloys sintered in nitrogen. When the nitrogen pressure was increased to 600 kPa at the start of the isothermal hold, the density was ~95.5%, and the density was insensitive to the presence of tin. Increasing the pressure from 100 kPa to 600 kPa increased the sintered density of the tin-containing alloy by ~1%, although this is not considered to be significant due to the experimental uncertainty inherent in the experimental technique (see Section 3.6).
4.6 Summary of Results

The major findings of the experimental work are:

- Increasing the pressure from 100 kPa to 160 kPa increased the sintering rate in nitrogen (Figure 4.6).
- Increasing the pressure further to 600 kPa had no additional benefit (Figure 4.11).
- The highest sintering rate was achieved by increasing the pressure prior to the closure of the pore network (Figure 4.13).
- A pressure of 600 kPa had no effect on sintering behaviour in argon (Figure 4.16).
- Elevated pressure aids in closing open porosity (Figure 4.3 and Figure 4.4).
- At 100 kPa nitrogen pressure, the sintered density was higher when there was tin in the alloy. At 600 kPa nitrogen pressure, the density was independent of the presence or absence of tin (Figure 4.24).
5 Discussion

In this section, potential sintering mechanisms enhanced by the elevated pressure are proposed and their validity discussed with respect to the experimental results presented in Chapter 4.

5.1 Enhanced Pore Closure

At the start of the isothermal hold (Figure 4.3) there was 14.3% open porosity and 1.5% closed porosity. At this time, the liquid phase is still developing, and the newly forming liquid will spread and redistribute about the open pore channels. This liquid may then close off the continuous pore network into a series of discrete, closed pores, as well as inducing particle rearrangement due to capillary forces. This may explain the reduction in open porosity over the first fifteen minutes.

The behaviour of the closed porosity was more complicated. It increased during the early stages of isothermal holding and then decreased. The amount of closed porosity arises from a balance between two competing phenomena. The first is the closure of open porosity, which increases the amount of closed porosity by an equal magnitude. The second is the shrinkage of the compact, which decreases the amount of closed porosity. The closed porosity increased early in the isothermal stage, meaning that the open porosity was closing faster than the closed porosity could be eliminated via shrinkage. Once the amount of open porosity had reduced to a minimum value, at about 15-20 minutes into the isothermal hold, the closed porosity started to decrease.

The amount of open and closed porosity in 600 kPa nitrogen (Figure 4.4) follows the same general trends as in 100 kPa (Figure 4.3). During the first 10 minutes of the isothermal stage, the open porosity closed off and was reduced to effectively zero open porosity. This contrasts with 100 kPa nitrogen where there was still a significant amount of open porosity at 10 minutes, as summarised in Table 4.1. This suggests that the elevated pressure helps close-off open porosity.

While the amount of closed porosity in 600 kPa nitrogen peaked at 10 minutes (Figure 4.4), it may actually have occurred earlier, but there is no data point for an earlier time due to limitations in the experimental technique. The increase in closed porosity may then have been effectively instantaneous, perhaps due to rapid liquid redistribution and particle rearrangement, forcing grains closer together and making capillaries narrower, allowing them to close off into discrete pores earlier.
The sintered density curve for 600 kPa nitrogen is identical to the curve corresponding to 100 kPa nitrogen pressure (Figure 4.2) for the first 15 minutes of the isothermal stage. After this time, the two curves deviate, with the 600 kPa curve having a lower density. At the start of the isothermal hold there was only ~1.5% closed porosity while there was 14.3% open porosity. So the vast majority of the porosity was still open, despite some liquid already forming. Therefore the gas pressure inside the pores that subsequently closed after the gas pressure was increased was 600 kPa. This elevated internal pore pressure may have inhibited pore shrinkage due to the lower pressure difference between the pore interior and the external atmosphere, compared to those pores that were closed prior to application of pressure. By 15 minutes into the isothermal stage, all the open porosity had been effectively eliminated. Given that the curves deviate after fifteen minutes, and there is no open porosity after 15 minutes, it seems that the adverse effect of the high pressure nitrogen on the density is related to the closed porosity.

5.2 Enhanced Nitridation

Okada et al. [59] reported that elevated nitrogen pressure enhanced nitride formation on a pure aluminium powder compact, and Pieczonka et al. [64] reported that sintering shrinkage is related to nitride formation, also using pure aluminium powder. It is therefore probable that the applied pressure is increasing the rate of nitride formation, although it is uncertain as to how this in turn improves sintering. This would explain why the applied pressure has no effect under argon.

If the elevated gas pressure is enhancing nitride formation then it would be expected that the more open pore structure of the low green density specimens would have more nitride forming and a subsequently higher sintered density. While it may be possible that the low compaction pressure specimens do in fact have more nitride forming, the density is not improved (Figure 4.2).

Under argon the elevated gas pressure had no effect on the sintered density, despite the amount of open and closed porosity at the start of isothermal holding, just before the pressure was increased, being almost identical under nitrogen and argon atmospheres. Since elevated gas pressure has no effect in argon, it seems likely that the beneficial effect of elevated pressure is due to something unique to the nitrogen system. It is possible, however, that any benefit of the applied pressure may be negated by argon trapped inside isolated pores, preventing them from completely closing. Upon release of the applied pressure at the end of an experiment, the high pressure gas inside the pores may expand and enlarge the pores again. This could be verified by high pressure dilatometry, where any dimensional change upon release of the gas pressure could be directly observed.
Tin is known to improve the densification behaviour of Al-Cu alloys, and to inhibit the formation of aluminium nitride (Section 2.6.6). It is expected then, that the tin free alloy should have a lower density than the tin-containing alloy (Section 4.5). Figure 4.24 shows that this is true at 100 kPa pressure, consistent with work elsewhere. However at 600 kPa the sintered density is independent of the presence of tin. Assuming that different amounts of nitride form in the tin-free and tin-containing alloys when sintered at 600 kPa, then the nitride cannot have an effect on the sintered density, and the improved sintering response at elevated pressures is due to some other effect.

Another possible explanation is that there are two competing effects: the presence of tin which inhibits nitride formation, and the elevated pressure which is thought to improve nitride formation. The amount of nitride that actually forms will result from a balance between the two effects. The elevated pressure may provide enough of a driving force to drive the nitride formation reaction forward despite the presence of tin. Thermogravimetric analyses have been used in the past to quantify nitride formation, and high pressure thermogravimetric analyses could determine if the tin is having an effect on nitride formation at elevated pressures, and help to explain the role of tin.

5.3 Enhanced Wetting

The wetting angle of liquid Al on Al₂O₃ at 660ºC has been reported as 103±6º [81], and the wetting angle of liquid Al on AlN at 827ºC is reported as 41±2º [82]. It is expected, then, that wetting behaviour will be better in the presence of nitrogen, yet the micrographs of specimens sintered in argon (Figure 4.17) show that the liquid phase wets the matrix material well enough to penetrate grain boundaries and coat the inner surface of some of the pores. It has been shown (Section 2.6.5) that magnesium disrupts the oxide layer via the formation of MgAl₂O₄, exposing aluminium metal which is then readily wet by the liquid metal. The absence of a nitride layer, then, does not preclude good wetting in an alloy containing magnesium. Since the elevated pressure has no beneficial effect under argon it seems that the pressure is not improving liquid wetting.

5.4 Restricted Magnesium Vapourisation

Increasing the magnesium content from 1% to 3% increases the sintered density both with and without an applied gas pressure. Increasing the magnesium content from 3% to 4% did not improve the density further, showing that there is a critical magnesium concentration above which no more benefit can be derived. This is consistent with the critical role magnesium plays in aluminium sintering (Section 2.6.5). Figure 4.20 shows that applying a 600 kPa gas pressure increases the sintered density regardless of the magnesium content, although the applied pressure has more of an effect with low magnesium content. This may be due to the applied gas pressure inhibiting magnesium vapourisation, allowing more of the magnesium to remain in the condensed state to
react with and reduce the oxide layer. Although Figure 4.23 shows that the magnesium content in
the sintered compacts, although lower than the nominal 1 wt% of the initial alloy, seemed to be
independent of the applied pressure. Regardless, if the beneficial effect of elevated pressure was
solely due to magnesium retention in the aluminium matrix, then the effect should also be observed
under argon, which it is not. In addition, the fact that the applied pressure increases the density
regardless of the magnesium content indicates that there is another mechanism active that is
independent of any beneficial effect of the magnesium.

Figure 4.20 also shows that increasing the magnesium content from 1% to 3% improves the sintered
density as much as by applying a 600 kPa gas pressure. Altering the magnesium content may then
be a more practical way of improving the density rather than sintering under pressure.

5.5 Enhanced Pore Filling

Elevated gas pressure enhances both the sintering rate and sintered density under nitrogen (Figure
4.6). Due to the amount of scatter in the experimental data it could be argued that the difference in
final density achieved under the two nitrogen pressures is negligible.

With the application of 600 kPa nitrogen pressure (Figure 4.9), the amount of closed porosity
decreased faster than at 100 kPa (Figure 4.8). There was no noticeable difference in behaviour of
the open porosity in the two regimes, although it may be that there was a difference at times shorter
than 10 minutes, and as such they were not detected. This is contrary to the behaviour observed for
a 100 MPa compaction pressure, where the elevated pressure seems to have aided in reducing the
amount of open porosity and increasing the closed porosity.

According to the pore filling model [26], liquid flow into a pore is controlled by a balance of forces
between the gas pressure outside the specimen and gas pressure inside the pore. If the gas pressure
in the furnace is increased, a pressure imbalance is established between the pore interior and the
compact exterior, inducing liquid flow into pores that would otherwise remain liquid-free. If the
gas pressure is kept constant during the whole sintering cycle, this imbalance is not introduced and
the pore filling occurs more slowly. According to this theory, then, the elevated pressure applied in
this work should aid in the filling of pores, provided that the elevated pressure was applied after
pore closure. The elevated pressure would help to remove only those pores that are already closed.
In the case of 200 MPa compaction pressure, there was about 7% open porosity and 4.5% closed
porosity (Figure 4.9), in which case it would be expected that the elevated pressure would be
somewhat beneficial, as over one third of the total porosity was already closed at the time of
pressure application. Conversely, for a 100 MPa compaction pressure, nearly all of the porosity was open at the time of pressure application (Figure 4.4). In this case it would be expected that the elevated pressure would have a negligible benefit. This is reflected in the experimental results.

There appears to be a step increase in the density when the nitrogen pressure is increased from 100 kPa to 160 kPa (Figure 4.11) for a 10 minute isothermal hold. Further increases in the nitrogen pressure, up to 600 kPa, have no effect on the density. For sintering times of 20 minutes or longer, there is negligible difference in density with pressure (Figure 4.6). If the gas pressure enhanced pore filling, then the density would be expected to increase with the nitrogen pressure. This is clearly not the case, suggesting that the gas pressure is not enhancing pore filling.

Pore filling relies on the pores being closed at the time of pressure application to establish a pressure imbalance between the pore interior and the specimen surface. If the nitrogen pressure is increased before pore closure, as in Section 4.2, then the gas pressure inside the pores, when they do eventually close, will be higher than in atmospheric pressure sintering, but the pressure difference between the pores and the furnace will be zero and the situation is identical to sintering under atmospheric pressure. The elevated pressure should then have no beneficial effect. Yet Figure 4.13 shows accelerated sintering when an elevated pressure was applied to a compact with open pores. This apparent contradiction may be explained by considering that nitrogen is expected to be consumed, to some extent at least, within the pores via nitride formation, thereby reducing the internal pore pressure and creating an excess external gas pressure. In addition, the higher pressure inside the pores, when they close, may increase the rate of nitride formation inside the pore compared to atmospheric pressure sintering, causing the pore to shrink faster than if the pressure was lower.

In pore filling, increasing the external pressure is expected to increase the critical size above which pores will be filled. In that case one would expect that increasing the pressure would reduce the amount of smaller pores, while having no effect on pores larger than some critical value. Figure 4.10 shows, however, that there was a reduction in the number of pores across all size fractions up to 100 µm diameter with an increase of nitrogen pressure from 100 kPa to 600 kPa. This is several possible explanations for this. The increased pressure may have increased the critical pore size to a value above 100 µm, such that all pores were small enough to be filled. Alternatively, the pressure may not have improved pore filling at all, or to such a minor extent that the improvement was insignificant. In this case it seems that pore filling is not a dominant sintering mechanism for this system under the experimental conditions investigated. Finally, the micrographs used for the pore
size analyses may not be representative of the high temperature microstructure, as discussed in Section 3.4.

Pore filling theory predicts that pores fill with liquid sequentially from smaller pores to larger ones, as the liquid meniscus radius increases with time. Yet the micrographs show large and small pores coexisting under a range of experimental conditions. This might be explained by some of the pores, small and large, being isolated from a source of liquid, perhaps because of the high green densities used, and thus unable to fill with liquid. Although pore filling theory is based on a model system with a continuous liquid network extending to the specimen surface. That being the case, it seems that pore filling theory does not accurately describe the system under investigation here, and it might therefore be inappropriate to consider these experimental results in terms of pore filling theory.

5.6 Enhanced Rearrangement

There is an equilibrium separation distance between two solid spheres connected by a liquid bridge with a large wetting angle (Section 2.4.1). The applied gas pressure may decrease the equilibrium interparticle spacing by increasing the pressure drop across the liquid-vapour interface and hence the capillary pressure (or suction), and provide effectively instantaneous compact rearrangement, bringing particle centres closer together, closing some interconnected pore channels, and resulting in an overall shrinkage. While this hypothesis is speculative, there is some evidence that is consistent with it. Specifically, Figure 4.3 and Figure 4.4 show that the beneficial effect of elevated pressure is the closure of open porosity, and that this open porosity closes sometime in the first ten minutes of isothermal holding. Figure 4.13 shows that the density is improved when the pressure is applied before a state of closed porosity, and it seems reasonable that rearrangement would be independent of the amount of open and closed porosity. However, if this pressure induced rearrangement is indeed an active mechanism, it would be expected to have the same beneficial effect regardless of the type of gas used. Yet results (section 4.3) indicate that elevated pressure has no effect under argon. Furthermore, micrographs show that the microstructures under nitrogen and argon are similar, in that both show extensive interparticle bonding and liquid penetration of grain boundaries, showing that the grains are joined not so much by liquid bridges as liquid films, such that the idea of a finite particle separation may not be appropriate, and the grains appear to be constrained such that they cannot move closer together via rearrangement. These observations are made from the solidified microstructures, however, and may not be representative of the actual microstructure and liquid volume fraction present at the sintering temperature. So at the sintering....
temperature the interparticle spacing may be larger than that observed in the solidified microstructures

### 5.7 Plastic Deformation

It is possible that even at such relatively low applied pressures, the material could be undergoing plastic deformation. The yield strength of aluminium alloy 2024-O is reported as 2 MPa at 538ºC [83]. It is conceivable, then, that at 590ºC, the yield strength is in the range of pressures used in this work and the compacts may be undergoing plastic deformation, in regions of closed porosity.

If the pressures used in this work are indeed sufficient to induce plastic deformation, then it would be expected that it would occur in those compacts sintered in argon. As the gas pressure has no effect in argon, it is reasonable to exclude plastic deformation from the possible shrinkage mechanisms, unless of course it is the presence of argon trapped in pores, effectively insoluble in liquid aluminium, that prevents pores from closing under the applied stress.

Out of all the experimental conditions used in this work, the highest sintered rates were achieved by applying a 600 kPa nitrogen pressure during both heating and isothermal holding, i.e. before the compact had reached a state of closed porosity. However, for the typical HIP mechanisms of creep and plastic flow (Section 2.5) to be active, the pores must be isolated from the specimen surface prior to pressure application. This suggests that the mechanisms responsible for the improved sintering in this work are different to those in HIPing.
6 Conclusions

The aim of this work was to explore the feasibility of using elevated pressures to activate the sintering of an aluminium alloy, and to determine favourable processing conditions. This work has shown the process is feasible in a nitrogen atmosphere, with pressures of 600 kPa resulting in an increase in the sintering rate, while pressures as low as 160 kPa were shown to be effective. For the best improvement in sintering rate, the pressure should be applied prior to heating. Of the two green densities used, only the specimens pressed to ~92% showed an improvement. Specimens pressed to ~84% did not respond favourably to pressure. It was also found that at 600 kPa nitrogen pressure, the sintered density became insensitive to the presence of tin in the alloy.

The experimental evidence shows that sintering of an aluminium alloy produced from elemental powder mixtures may be enhanced by the application of moderate nitrogen pressures. This improvement could be due to enhanced formation of aluminium nitride.
7 Suggestions for Further Work

It has been shown that the application of elevated nitrogen pressure is beneficial to the sintering of an aluminium alloy, yet several questions remain unanswered. Further work to address the outstanding issues could include the following:

- Experimental results have shown a discontinuity in the sintered density with increasing gas pressure, under certain experimental conditions. This phenomenon could be explored further with a larger set of experimental conditions. These could include longer sintering times, varying green densities, and using an argon atmosphere.

- High pressure dilatometry could be used to identify the specific sintering mechanisms by identifying which expansion or shrinkage events are affected by the gas pressure. Understanding the mechanism(s) involved could explain why the elevated pressure improved the sintering rate but not the density, and how the pressure helps to close open porosity.

- It has been suggested elsewhere that there is a correlation between sintering shrinkage and the formation of aluminium nitride, and the experimental evidence in this work suggests that nitrogen plays an important role in elevated pressure sintering. This could be pursued further by thermogravimetric analyses at elevated pressures.

- While improving the sintering rate is a beneficial outcome, the purpose was to eliminate the porosity (i.e. increase the density). The density was increased by increasing the magnesium content of the alloy, indicating that the composition used is not optimal for this particular sintering technique. A series of experiments varying the composition could result in an alloy with a more favourable sintering response under elevated pressure conditions. Particular attention needs to be placed on the role of tin, as it limits aluminium nitride formation.
8 References


9 Appendix A

Pressure Assisted Sintering of an Aluminium Alloy

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Keywords: aluminium, sintering, powder metallurgy, gas pressure, heating

Abstract

An aluminium alloy was sintered using a conventional press and sinter process, at various gas pressures, to observe the effect of sintering gas pressure on the densification rate. Compacts of aluminium alloy 2712 (Al-3.8Cu-1Mg-0.75Si-0.15Sn) were prepared from elemental powders and sintered in a horizontal tube furnace under nitrogen or argon at 590°C for up to 60 minutes, and air cooled. The gas flow was adjusted to achieve specific gas pressures in the furnace. It has been found that increasing the nitrogen pressure at the start of the isothermal holding stage to 160kPa increased the densification rate compared to standard atmospheric pressure sintering. Increasing the nitrogen pressure further, up to 600kPa, had no additional benefit. The densification rate was increased significantly by increasing the gas pressure to 600kPa during both heating and isothermal holding. Under argon the elevated pressure did not increase the densification rate. Results seem to suggest that the beneficial effect of the elevated pressure on the rate of densification is related to nitride formation.

Introduction

Liquid phase sintering is a net-shape process for consolidating metal powders [1]. The atmospheric condition in the furnace is critically important for sintering aluminium alloys. Various sintering gases including nitrogen, argon, nitrogen-hydrogen and argon-hydrogen mixtures, and vacuum, have been used and nitrogen has been shown to be efficacious [2-5]. Nitrogen is known to react with aluminium to form AlN and improve sintering densification [4]. Inside a pore, the consumption of nitrogen gas as it forms the nitride can reduce the pressure inside the pore and aid in pore filling by the liquid phase [3]. Argon is effectively insoluble in aluminium and so becomes trapped inside isolated pores and limits densification, while hydrogen effectively stops sintering completely [3,4]. Elevated gas pressures are known to improve sintering response in the hot isostatic pressing (HIP) and combined sinter-HIP processes, using gas pressures up to ~100 MPa [6]. A necessary requirement of the HIP process is that pores must be isolated from the specimen surface to be eliminated during the process. To achieve this, the powder mass may be containerised or alternatively it may be sintered to a state of closed porosity prior to pressure application. This is expected to occur in the range of 91-95% of theoretical density [7,8]. The aim of this work is to determine how gas pressure influences the densification rate of an aluminium alloy sintered using a conventional press and sinter process.

Experimental Method

Elemental powders of Al, Cu, Mg, Si and Sn were blended with 1.5wt% Acranax C, an ethylene bis stearamide lubricant powder, in a Turbula shaker mixer for ~30 minutes. The alloy composition, in weight percent, was Al-3.8Cu-1Mg-0.75Si-0.15Sn. The blended powder was compacted at 200MPa in a 10mm diameter floating cylindrical steel die, to produce green compacts weighing ~2g and with a height of ~10mm. A horizontal tube furnace was modified to enable it to operate at pressures up to 600kPa (Figure 1). Green compacts were placed on a flat steel tray in the furnace hot zone, adjacent to a thermocouple. Compacts were heated to 590°C at 5°C min⁻¹, with a 30
minute isothermal “burn-off” stage at 300°C to remove the lubricant wax. Compacts were subject to an isothermal hold at 590°C for times up to 60 minutes before being removed from the furnace and air cooled. Either nitrogen or argon flowed continuously through the furnace at ~31 mm$^3$. 

![Figure 1. Schematic of the pressure sintering furnace.](image)

The gas pressure inside the furnace was controlled by using a valve to restrict the exhaust gas flow out of the furnace. This enabled an elevated pressure to be maintained while still having continuous gas flow through the furnace. Three different gas pressure regimes were used, and are described in Table 1.

<table>
<thead>
<tr>
<th>Pressure regime</th>
<th>Description</th>
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<tbody>
<tr>
<td>Low pressure regime</td>
<td>100kPa gas pressure for entire thermal treatment</td>
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<tr>
<td>Mixed regime</td>
<td>100kPa gas pressure during heating to 590°C, then 600kPa gas pressure during isothermal hold.</td>
</tr>
<tr>
<td>High pressure regime</td>
<td>600kPa gas pressure for entire thermal treatment</td>
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</tbody>
</table>

To investigate the effect of gas pressures intermediate between 100kPa and 600kPa, some experiments were performed using the mixed regime, but the pressure was increased to between 160, 200 or 300kPa during the isothermal hold, and the length of the isothermal hold was 10 minutes. The sintered density of compacts was calculated using Archimedes’ method using H-Galden ZT180, a hydrofluoropolyether, as the immersion fluid. Sintered densities are expressed as a percentage of the calculated theoretical density for this alloy, 2.790g cm$^{-3}$. The amount of porosity is then equal to the percentage density subtracted from 100.

Results and Discussion

For a nitrogen atmosphere (Fig. 2), under the low pressure and mixed regimes, i.e. when the gas pressure prior to the isothermal hold was 100kPa, the density at the start of the isothermal hold was 88.7%. Under the low pressure regime the density increased to 96.8% by sintering for 16 minutes into the isothermal hold and remained constant. Under the mixed regime, where the gas pressure was increased to 600kPa at the start of the isothermal hold, the density increased to 97% as early as 10 minutes into the isothermal hold and stayed constant. Under the high pressure regime, where the pressure was 600kPa for the entire experiment duration, the density at the start of the isothermal hold was 95%, approximately 6% higher than the other two regimes. The density then increased to 97% by 10 minutes into the isothermal hold. Under all three regimes, a net shrinkage occurred. For an argon atmosphere (Fig. 2), there was no difference in the sintered densities between compacts sintered under the low pressure and mixed regimes. In both regimes the density increased from 88.3% at the start of the isothermal hold, to 90.5% after 60 minutes. Under argon, the compacts experienced a net expansion.
Figure 2. Sintered density under different gas pressure regimes in nitrogen and argon. See text for details.

Figure 3. Density of compacts sintered under the mixed regime for 10 minutes, for various nitrogen pressures used during the 590°C isothermal hold.

The largest improvement in the sintering rate was achieved in nitrogen under the high pressure regime, when the elevated pressure was applied while the pores were still open to the compact surface, contrary to the requirement of the HIP and sinter-HIP process that pores must be isolated from the specimen surface for the gas pressure to improve sintering. This suggests that the mechanism(s) of elevated pressure sintering of the current aluminium alloy differ from those in HIP and sinter-HIP. This, together with the observation that gas pressure had no effect in argon, in turn suggests that the elevated pressure is having some effect on the chemistry of the system to improve the sintering response, by affecting the reaction(s) between the nitrogen gas and the solid and/or liquid phases. By varying the nitrogen pressure used during the isothermal hold under the mixed regime (Fig. 3), it was found that pressures as low as 160kPa were sufficient to observe an improvement in sintering rate. For pressures between 160 and 600kPa the density was an
independent of the gas pressure. From these observations it can be seen how elevated gas pressures have the potential to decrease sintering times.

Summary

Sintering aluminium alloy Al-3.8Cu-1Mg-0.7Si-0.1Sn under continuous flowing nitrogen at gas pressures from 160 to 600 kPa improved the densification rate in the first 10 minutes. The improved densification rate was apparent at pressures as low as 160kPa, while further increases in gas pressure, up to 600kPa, did not improve the densification rate further. Under an argon atmosphere, the densification rate was not affected by increases of gas pressure in the same pressure range. The mechanism(s) by which the nitrogen pressure enhances the sintering response was considered to be related to reaction(s) between nitrogen and aluminium. Sintering under pressurised nitrogen can reduce sintering cycle times, which can reduce the energy requirements and costs associated with furnace operation.

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