Characterising Precipitate Evolution in High Temperature Cast Aluminium Alloys using Synchrotron Radiation

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Abstract

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Characterising Precipitate Evolution in High Temperature Cast Aluminium Alloys using Synchrotron Radiation

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Novel casting alloys that retain their mechanical strength at temperatures up to 300 °C are needed in order to improve automotive engine efficiency. The addition of Zr and V is a promising combination as a means of introducing the thermally stable cubic $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ nano-precipitates. In this project, the evolution of the $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ precipitates in multi-component cast aluminium alloys was characterised in a statistically significant way using small-angle X-ray scattering (SAXS). Unlike established metallurgical techniques, such as transmission electron microscopy (TEM), SAXS measures billions of precipitates in a single experiment.

Two Al-6.8Si (wt.%) alloys were employed. One contained 0.30 wt.% Zr and 0.30 wt.% V and the other 0.37 wt.% Zr and 0.34 wt.% V. The alloys were cast and isothermally aged at 400 °C for times ranging from 3 to 50 h. Synchrotron SAXS was undertaken at the Diamond Light Source (DLS). Direct evaluation methods of SAXS spectrum were employed in order to extract information about the average precipitate size, precipitate size distribution and their evolution with ageing time. These results were compared with the results provided via TEM, both validating the methodology, and demonstrating the benefits and drawbacks of SAXS.

From the SAXS analysis, the Guinier radius, $R_g$, was found to increase with ageing time from around 2 nm at 3 h to approximately 9 nm at 50 h. Precipitate volume fraction also increased from 0.11 vol.% to 0.24 vol.% for the lower solute alloy and from 0.14 vol.% to 0.33 vol.% for the higher solute one. In both alloys, the precipitate number density was observed to continuously decrease with ageing time. For the higher solute alloy, the average precipitate radius from the TEM measurements was found to be consistently smaller than $R_g$.

Such a study is important because it extends the experimental SAXS methodology previously used only in simplified alloys to multi-component cast alloys of industrial importance. Moreover, the findings from this investigation suggest that both alloys quickly enter a stage where the precipitate growth and coarsening overlap, and the precipitate number density continuously decreases with time. Finally, this study underlines the importance of preliminary SAXS data treatment and provides an analytical guide in order to successfully characterize low volume fraction of precipitates in multi-component cast alloys.
Declaration

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Dedicated to those who did not fight for the Victory but for the Glory
Chapter 1: Introduction

Nowadays, more than ever, the development of energy efficient vehicles is required. In order to reduce the environmental impact of everyday transportation, the development of lightweight automotive engines operating at high temperatures is needed. Although aluminium alloys have been replacing steel and cast iron in automotive engines over the last 40 years, their applicability is limited to temperatures below 250 °C. This is attributed to the rapid drop in strength associated with the instability of nano-precipitates which are introduced by age hardening. In that context, if a small amount of transition metals is added, significant improvements in high temperature strength have been observed. In the past, many combinations of transition metals have been proposed in order to develop high temperature aluminium alloys. This work aims to investigate the combination of Zr and V in order to precipitate thermally stable and coarsening resistant precipitates (also referred to as dispersoids). This combination is showing promise but there are still unknown aspects of the precipitate evolution in multi-component cast aluminium alloys. In order to quantitatively characterise the evolution of the Zr/V containing trialuminide precipitates, small-angle X-ray scattering (SAXS) has been employed. SAXS is a bulk material analysis technique that provides statistically significant results by measuring large numbers (billions) of precipitates. The quantitative characterisation of thermally stable precipitates in cast aluminium alloys is considered a key target for developing a future generation of automotive engines.

1.1 Aluminium Alloys and SAXS

In the past, precipitation phenomena have been commonly investigated by traditional means of metallurgical characterisation including electron microscopy and mechanical testing (yield strength measurements). Although these techniques are well proven, in practice it is difficult to obtain statistically valid results from electron microscopy when alloys with low volume fraction (i.e. <0.5 vol.%) and heterogeneously distributed precipitates are investigated. On the other hand, SAXS is a large volume and non-destructive technique that provides statistically significant results by measuring large numbers (billions) of precipitates. SAXS can provide quantitative information on precipitates of nanometre scale including
mean precipitate size, precipitate size distribution (PSD) and volume fraction. Although many successful SAXS investigations can be found in the literature, only a few focus on aluminium alloys containing precipitates of the Al₃M type (where M is a transition metal such as Zr, V, Sc, Ti or combination of those). Furthermore, this technique has not been extensively applied to multi-component cast alloys and to the best of the author’s knowledge the Zr/V combination has not been previously investigated using synchrotron SAXS. In this project, we couple SAXS and transmission electron microscopy (TEM) in order to shed more light on the precipitation evolution of two multi-component cast aluminium alloys with different levels of Zr and V additions.

1.2 Objectives

The main objectives of this work are to:

1. Assess the applicability of synchrotron SAXS to the study of multi-component cast aluminium alloys of industrial importance.
2. Characterise and compare the precipitate evolution in two Al-6.8Si (wt.%) based alloys with low volume fractions of Al₃ZrₓV₁₋ₓ precipitates.
3. Demonstrate the advantages of SAXS over traditional means of characterisation when quantitative results are needed and clearly highlight any specific limitations.
4. Provide an analytical guide for future research.

1.3 Thesis Structure

The present thesis is divided into five chapters and is organized as follows:

Chapter 2 is the literature review which is divided in two main parts. At the beginning of the first part (section 2.1 to 2.6), aluminium is compared to the other light metals and the basic applications of cast aluminium alloys in the automotive industry are presented. Then the retardation of Ostwald ripening is directly linked to the development of high temperature cast aluminium alloys, and the potential benefits that arise from the addition of transition metals in aluminium alloys to form metastable cubic trialuminides are highlighted. At the end of this part, the Al-Zr alloy and the advantages of ternary V additions are critically reviewed.
second part of this chapter (section 2.7) is devoted to SAXS. This section covers the basic theory of X-ray scattering and presents the advantages of synchrotron SAXS compared to traditional means of characterisation. The prerequisites for studying precipitation phenomena in metallic systems are discussed in detail. At the end of this chapter, a list of previous SAXS investigations on aluminium alloys provides a concise guide of the research undertaken in the field.

Chapter 3 is the methodology chapter where the composition and the heat treatments of the investigated alloys are provided. The aims and objectives of an ex situ and an in situ SAXS experiment conducted at Diamond Light Source (DLS) are described. Only the ex situ experimental results are used for this MPhil thesis, but for completeness the in situ methodology is included in case the data are analysed in the future. At the end of this chapter, the TEM and SAXS data analysis is described and the SAXS data calibration method is presented.

Chapter 4 is in a journal paper format and presents the results of the ex situ experiment. In this chapter the precipitate evolution in two multi-component cast aluminium alloys is quantitatively characterised by ex situ synchrotron SAXS. Data analysis is performed using direct evaluation methods on SAXS profiles and the quantitative results are compared with a TEM investigation. The evolution of heterogeneously distributed precipitates was quantified including average precipitate size, size distribution, volume fraction and number density.

Chapter 5 summarises the major conclusions and findings of the ex situ experiment. Based on these findings, further work on the in situ data is proposed.
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Chapter 2: Literature Review

Overview: The first part (sections 2.1 to 2.6) of Chapter 2 focuses on the metallurgical side of the project. First, the advantages of aluminium alloys compared to the other light metals are discussed and applications of cast aluminium alloys in the automotive industry are presented. The fundamental theories of precipitation hardening, Orowan mechanism and Ostwald ripening, are briefly described. These are then followed by a review of the elemental selection criteria for developing high temperature aluminium alloys. Evidence suggests that the addition of transition metals in cast aluminium improves strength at temperatures up to 400 °C. At the end of this part, the most promising additions of transition metals in aluminium alloys with are reviewed.

2.1 Light Metals in the Automotive Industry

Since the inception of the automotive industry and right through to the current age of alternative fuel vehicles, manufacturers have achieved significant advances in fuel efficiency through engineering design and materials selection. During this evolution, one of the major material challenges was the strength to weight ratio, since the latter has a direct impact on fuel efficiency [1]. This has become even more important over the last four decades, due to the stringent regulations over emissions and fuel consumption that modern cars must comply with.

The reason behind the extensive weight of modern cars is the constant trend to become larger, safer and more luxurious. Also, the use of metals such as iron and copper, having high densities, deteriorates the problem. In order to achieve the desirable weight reduction, strength to weight ratio, ductility and stiffness, the use of lighter metals and alloys is required. During the last four decades aluminium, magnesium and titanium have been increasingly employed in the automotive and aerospace industry [2]. These metals are commonly called light metals because of their lower density relative to iron [2]. Their progressive implementation in the automotive industry is having a direct impact on vehicles’ performance, efficiency and emissions.
2.1.1 Advantages of Aluminium

Of these three metals, the choice of aluminium over titanium for automotive structural components is obvious on the basis of weight and cost. This can be clearly understood when considering that the energy consumed in producing pure titanium is almost 70% higher than aluminium and nearly 14 times higher compared to steel [3]. Moreover, aluminium is 60% lighter than titanium. From the aspect of weight reduction, magnesium would be the ideal metal for automotive applications because it is 33% lighter than aluminium [4]. However, compared to aluminium, magnesium has a 25% lower ultimate tensile strength, 40% lower modulus, 35% lower fatigue strength and poor corrosion resistance [4]. In essence, aluminium takes the lead for a like to like replacement of steel in automobiles. A number of physical properties of aluminium, magnesium and titanium are summarised in Table 2.1 [2].

Table 2.1 The light metals physical properties in comparison with iron and copper [2].

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Al</th>
<th>Mg</th>
<th>Ti</th>
<th>Fe</th>
<th>Cu</th>
</tr>
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<tr>
<td>Crystal structure</td>
<td>-</td>
<td>fcc</td>
<td>cph</td>
<td>cph</td>
<td>bcc</td>
<td>fcc</td>
</tr>
<tr>
<td>Density (d)</td>
<td>kg/m³</td>
<td>2700</td>
<td>1740</td>
<td>4510</td>
<td>7870</td>
<td>8960</td>
</tr>
<tr>
<td>Elastic modulus (E)</td>
<td>GPa</td>
<td>70</td>
<td>45</td>
<td>120</td>
<td>211</td>
<td>130</td>
</tr>
<tr>
<td>Thermal conductivity 20-100 °C</td>
<td>Wm⁻¹K⁻¹</td>
<td>238</td>
<td>156</td>
<td>26</td>
<td>78</td>
<td>397</td>
</tr>
<tr>
<td>Coefficient of ther. Exp. 0-100 °C</td>
<td>10⁻⁶ K⁻¹</td>
<td>23.5</td>
<td>26</td>
<td>8.9</td>
<td>12.1</td>
<td>17</td>
</tr>
</tbody>
</table>

2.1.2 Applications of Cast Aluminium Alloys in the Automotive Industry

Aluminium alloys are divided into two major categories: cast and wrought. Cast aluminium alloys have been applied to various industrial applications and their most widespread use can be found in the automotive sector [1]. Aluminium castings are used in a variety of automotive applications including wheels, brake components, suspension and engine parts. In the current review, we will focus on cast aluminium alloys that can potentially be employed in automotive engine components.
For a long time, aluminium castings have been employed instead of cast iron as an engine block material in order to reduce weight. It has been shown that a 10% vehicle weight reduction results in an 8-10% improvement in fuel economy [5]. In addition to the weight reduction, the advantages of cast aluminium engine components include the ability to have thinner and more variable wall dimensions, closer dimensional tolerances and less costly melting-metal costs [4] in comparison with cast iron.

In modern automobiles, almost 100% of pistons, 75% of cylinder heads and 85% of intake manifolds and transmission parts are manufactured from cast aluminium alloys [1]. Some examples of automotive aluminium alloys are those based on Al-Si, Al-Si-Mg, Al-Si-Cu and Al-Si-Cu-Mg. Some alloys are used in the as-cast condition, but most are given a heat treatment to increase strength via precipitation hardening (described in the next section). However, their implementation is restricted to low temperatures only. When conventional cast aluminium alloys are subjected to elevated temperatures, they suffer strength loss that restricts their implementation to temperatures below 250 °C [6]. This is due to the instability of the hardening precipitates at elevated temperatures.

2.2 Fundamentals of Precipitation Hardening

Cast aluminium alloys derive their strength from a phenomenon known as age or precipitation hardening. Age hardening is a phenomenon observed in specific alloy systems which show a marked change in solid solubility with temperature. A dispersion of precipitates is exploited to enhance the strength of a soft parent matrix. The precipitation hardening process typically involves three main steps: solution treatment, quenching and ageing. The precipitation hardening results from the different solubility of elements between high and low temperatures and the objective is the formation of finely dispersed coherent or semi-coherent precipitates that will give rise to strength. In general, precipitation in aluminium alloys is diverse, with precipitates having different shapes (e.g. rods, plates, needles, spheres) and levels of coherency with the matrix (e.g. fully, semi and incoherent). Some examples of industrial aluminium alloys that respond positively to age hardening are the Al-Cu [7], Al-Mg-Si [8-10], Al-Si-Cu-Mg [11, 12].
2.2.1 Principles of Precipitation Hardening

When precipitates develop in a matrix, higher strength is obtained due to their ability to immobilize the moving dislocations during deformation. Several hardening mechanisms exist, which do not simultaneously apply or strongly influence all metallic systems [13]. The amount of strengthening depends on the precipitate size, volume fraction and the nature of interaction between the precipitates and dislocations. There are two main mechanisms that describe the interaction between precipitates and dislocations. These are the precipitate shearing and the dislocation looping.

When precipitate particles are relatively soft and small, it is more likely that moving dislocations will shear them. In this case, alloys are strengthened but no maximum strength values are attained. This phenomenon can be explained by the Friedel effect, a mechanism that describes the interaction between precipitates and dislocations. A schematic representation of the Friedel effect is shown in Figure 2.1. The effectiveness of precipitates to immobilize dislocations increases with their size, as long as they are not sheared by them [14].

![Schematic representation of the Friedel effect](image)

*Figure 2.1 Schematic representation of the Friedel effect [15].*

If precipitates continue to grow, another mechanism is likely to simultaneously take place. This mechanism is called the Orowan mechanism and explains the interaction between dislocations and precipitates at the later ageing stages. When precipitates are large but not spaced closely together, it is more favourable for dislocations to bypass them by bending and bowing. The relationship between the applied stress and dislocation bowing is:

\[ \Delta \tau_{or} = \frac{Gb}{L} \]  

(2.1)
where $\Delta \tau_p$ is the increase in yield stress due to the precipitation looping, $G$ is the shear modulus of the matrix, $b$ is the Burger’s vector of the dislocation and $L$ is the inter-particle distance [16]. As a consequence, expanding loops are formed around precipitates while dislocations continue to move. This occurs in four stages as illustrated in Figure 2.2 [17]. These stages are: approach, sub-critical, critical and escape step.

![Figure 2.2](image)

*Figure 2.2 The four stages of looping formation around particles are the a) approach, b) sub-critical, c) critical and d) escape step [17].*

Theoretically, when the probability of a dislocation to bypass a precipitate equals the probability of shearing it, maximum strength is obtained [18]. This is schematically presented in Figure 2.3. To explain this further, the overall mechanical strength depends on the precipitate size and volume fraction. In Figure 2.3, maximum strength is obtained when curve A and B intersect at point C. We can further increase this point by increasing the precipitate volume fraction or decreasing the size of precipitates that can resist shearing. This will simultaneously raise to a higher level both curves A and B. The critical size ($D_c$) refers to the minimum size of particles that can resist shearing. This size varies with different precipitate phases and depends on the morphology and the crystal structure of the particles [18]. Overall, the mechanical strength will peak when hard precipitates, which can resist shearing, obtain high density and uniformly spread throughout the matrix. In this case, the only way that dislocations can bi-
pass precipitates, is when sections of them pass over or under the precipitates by a process such as cross-slip [18].

![Diagram](image)

*Figure 2.3 Schematic representation of relationship between precipitate radius and strength for a typical precipitation hardened alloy.*

2.2.2 Stability of Age Hardening Precipitates

As discussed in the previous section, the strength of an age hardened alloy is directly related to the precipitate size. For this reason, after the formation of small precipitates, it is essential to restrict further growth. This is an extremely important parameter to consider when designing aluminium alloys for high temperature applications because, at elevated temperatures precipitate growth is difficult to avoid. The phenomenon of precipitate coarsening is often referred to as Ostwald ripening and will be presented here.

Ostwald ripening is a well-known phenomenon that was first observed by Wilhelm Ostwald [19, 20]. During this phenomenon, larger particles grow at the expense of smaller ones that dissolve and in the end vanish. This spontaneous thermodynamic process is driven by the overall reduction in surface energy. Larger particles have lower surface energy due to their lower surface to volume ratio. This results in lower energy per particle and generally to an overall lower energy state. In order to attain the lowest energy state possible, atoms will diffuse through the matrix from particles of smaller radius to those of larger radius. The underlying driving force is the Gibbs Thompson effect *i.e.* the limit of solid solubility is dependent on the particle radius due to particles of smaller radius having a higher free energy.
The rate of atom loss from a particle is either controlled by the rate of transfer across the particle-matrix interface or by diffusion from the particle to the matrix. The theory proposed by Lifshitz, Slyozov and Wagner (LSW) [21] has treated both these cases, and experimental results suggest that the growth of coherent precipitates is diffusion controlled [22, 23]. According to the theory [22], the average precipitate size $\bar{r}$ increases with time $t$ according to:

$$(\bar{r}(t))^3 - (\bar{r}(0))^3 = kt$$ (2.2)

where $\bar{r}(t)$ is the average precipitate radius at time $t$, $\bar{r}(0)$ is the average precipitate radius at the onset of coarsening, $k$ is the coarsening rate constant given by:

$$k = \frac{8\gamma D V_m^2 C_0}{9RT}$$ (2.3)

where $D$ is the diffusivity of the solute, $C_0$ is the solubility limit of that solute in the matrix, $\gamma$ is the interfacial free energy between the matrix and the precipitate, $V_m$ is the molar volume of the precipitate, $R$ is the ideal gas constant and $T$ is the absolute temperature. The coarsening rate constant is typically reported in m$^3$h$^{-1}$.

Many modifications have been proposed for cases where the precipitate is not a pure element and/or not spherical [24]. Moreover, the effect of the precipitate volume fraction and the initial size distribution on the coarsening rate has been extensively studied and many different theories have been proposed [24, 25]. In every case, theory predicts that coherent precipitates should coarsen slower than incoherent precipitates and the coarsening rate can be reduced by reducing the solubility of precipitate atoms in the matrix.

Precipitate coarsening is a deleterious phenomenon for aluminium alloys required to operate at elevated temperatures because it results in the average precipitate radius increasing while the number density concomitantly decreases. Therefore the ageing precipitates are less effective in acting as barriers to dislocation movement and so the strength of the alloy decreases.
2.3 The Limitations of Conventional Cast Aluminium Alloys

Unfortunately, the applicability of conventional cast aluminium alloys [1] is significantly limited to temperatures below 250 °C, due to instability and coarsening of ageing precipitates that leads to reduced strength. Aluminium alloys such as the Al-7Si (wt.%) family are amongst the most common aluminium casting alloys. Figure 2.4 shows the Al-Si equilibrium phase diagram [26]. Various industrial alloys have been developed based on the Al-Si system with different concentrations of Cu, Mg Mn and other elements [27]. Amongst them, two characteristic examples of cast aluminium alloys that are used in high temperature automotive components are those based on Al-Si-Mg and Al-Si-Cu. These commercial alloys are frequently referred to as A356 and A319, respectively.

![Figure 2.4 The Al-Si equilibrium phase diagram](image)

The A356 alloy has a composition of Al-7Si-0.3Mg (wt.%) and is used in transmission cases and engine parts [28]. The small additions of Mg lead to the precipitation of the $\beta''$ $(\text{Mg}_2\text{Si})$ particles. At the peak aged condition these precipitates are needle-shaped and are fully coherent with the matrix. As a result the yield strength of this alloy is more than double that of the binary system containing the same amount of Si. However, when exposed to temperatures above 200 °C the $\beta''$ precipitates coarsen quickly and transform to the equilibrium structures. The coherency loss has a negative impact on the overall strength.
The A319 alloy has been available for many years and its composition lies within the ranges 3-10.5 wt.% Si and 1.5-4.5 wt.% Cu [29]. It has been used in engine crankcases, engine blocks and cylinder heads [30] due to its higher strength compared to A356 or binary alloys. It derives its strength from the small semi-coherent \( \theta' (\text{Al}_2\text{Cu}) \) precipitates that form on the \{100\}_\alpha planes and are nucleated in high volume fractions. However, this alloy cannot retain its strength at temperatures above 250 °C [31] where the plate-shaped precipitates coarsen quickly and lose their coherency with the matrix.

For the reasons described above, new aluminium alloys that retain their strength at demanding operating conditions need to be developed. In order for such alloys to retain their strength at temperatures above 250 °C, the coarsening of the precipitates must be slow and the precipitates themselves must be thermodynamically stable at the operating temperature. In the following section, the criteria that must be considered when designing cast aluminium alloys for high temperature applications are discussed.

### 2.3.1 Element Selection Criteria for High Temperature Regimes

When cast aluminium alloys are designed, precipitates should have a number of characteristics. These characteristics are: high volume fraction, small average size, high level of coherency with the matrix, thermodynamic stability and coarsening resistance at the target temperature. At high temperatures the level of coherency and the resistance to coarsening are two parameters that should be carefully designed.

In order for cast aluminium alloys to retain their strength up to 300 °C, an improved microstructure that contains thermally stable and coarsening resistant precipitates is required [32]. In an attempt to improve strength under such conditions, aluminium alloys have been modified with additions of elements such as Sc, Zr, V and Ti [33-37]. These elements, known as transition metals, give rise to strength through the formation of metastable cubic trialuminide precipitates (such as \( \text{Al}_3\text{Zr} \)) and are thought to resist the deleterious phenomenon of precipitate coarsening at temperatures up to approximately 350 °C [38].
Unlike the commercial A319 and A356 alloys, aluminium alloys that are modified with the addition of transition elements cannot be precipitation hardened with conventional heat treatments (i.e. solution treatment in the $\alpha$-Al phase field, quenching and subsequent ageing at $\sim 180 \, ^{\circ}\mathrm{C}$). This is attributed to the low equilibrium solid solubility of transition elements in aluminium. Moreover, particles composed of transition metals dissolve slowly during solution treatment (i.e. at temperatures between 500 and 600 $^{\circ}\mathrm{C}$). For those reasons, in order to attain a supersaturated solid solution, a high cooling rate should be employed during casting from the melt. In this way, transition elements remain in supersaturated solid solution and precipitates start forming when the alloys are aged directly at elevated temperatures. A consequence of this is that there is a non-uniform solute distribution in the solid due to microsegregation during solidification. Hence elevated temperature ageing will give rise to non-uniform precipitation. Throughout the literature, because of the different way they develop, these particles are frequently referred to as dispersoids. In this thesis for simplicity, we will refer to them as precipitates.

In the following section the transition elements and their advantages when alloying aluminium will be discussed.

2.3.2 The Transition Metals

During the last 30 years, the addition of transition elements in aluminium has been an ongoing research field. Of all the transition elements the most promising additions in aluminium are Sc, Zr, V and Ti [39]. The addition of these elements results in the formation of the Al$_3$M ($M =$ transition metal) precipitates. Precipitates composed of Sc form the thermodynamically stable cubic L1$_2$ crystal structure [40] whilst precipitates composed of Zr, V and Ti attain the metastable cubic L1$_2$ crystal structure [41]. The latter is fully coherent with the aluminium matrix and transforms to the complex tetragonal D0$_{22}$ or D0$_{23}$ crystal structures which are semi-coherent. At high temperature regimes, precipitates composed of these metals have two main advantages. These are:

**Diffusivity** – In order to minimise the coarsening of precipitates and the associated loss of strength, low diffusivity of solute elements at high temperatures...
is required, as seen from eq. 2.3. Element diffusivity controls the Ostwald ripening kinetics, since solute atoms are transferred through the matrix from the dissolving small precipitates to the growing larger ones. The lower the diffusivity of elements composing the L12 precipitates, the more effectively the Ostwald ripening phenomenon is suppressed. Table 2.2 shows the diffusion coefficient of some transition metals. At 400 °C, V has the lowest diffusivity amongst transition metals (4.85×10^{-24} \text{ m}^2\text{s}^{-1}) while Sc has the highest (1.98×10^{-17} \text{ m}^2\text{s}^{-1}) which is more than three orders of magnitude smaller than that of Cu (2.27×10^{-14} \text{ m}^2\text{s}^{-1}) [42] and Mg (6.14×10^{-14} \text{ m}^2\text{s}^{-1}) [43].

\textbf{Table 2.2 The partition } k_o \text{ and diffusion } D \text{ coefficients of Sc, Ti, V and Zr in aluminium.}

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>(k_o)</th>
<th>(D \text{ at } 400 \degree C (\text{m}^2\text{s}^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>21</td>
<td>0.82</td>
<td>1.98×10^{-17}</td>
<td>[44, 45],[46]</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>10.0</td>
<td>7.39×10^{-22}</td>
<td>[41],[47]</td>
</tr>
<tr>
<td>V</td>
<td>23</td>
<td>3.3</td>
<td>4.85×10^{-24}</td>
<td>[44],[46]</td>
</tr>
<tr>
<td>Zr</td>
<td>40</td>
<td>2.5</td>
<td>1.20×10^{-20}</td>
<td>[48],[47]</td>
</tr>
</tbody>
</table>

\textbf{Lattice Matching} - Precipitates will not only resist coarsening when the diffusivity of the composing element is small but also when the precipitate/matrix interface energy is low. Coherency between precipitates and matrix is translated to a low energy interface and thus little driving force for coarsening. The lower the matrix misfit is, the lower the interfacial energy and the higher the coarsening resistance is [34]. The metastable L12 precipitates are highly coherent with the matrix. Table 2.3 shows the lattice parameters of different L12 precipitates and their absolute and relative mismatch with the aluminium matrix. The absolute mismatch \(\delta\) was defined and calculated as follows:

\[
\delta(\%) = \left(\frac{a-a_0}{a_0}\right) \times 100
\]  \hspace{1cm} (2.4)

where \(a_0\) is equal to 4.05 Å for pure Al. Amongst the Al3M precipitates, the Al3Zr phase possesses the smallest relative mismatch (+0.74%) while the Al3V has the largest (-4.44%). The lattice parameters used in the calculation were published values measured at room temperature and thermal expansion at elevated temperatures might slightly affect the results [49, 50].
### Table 2.3 The relative and absolute mismatch between the Al₃M precipitates and the aluminium matrix. The lattice parameters are published data at room temperature.

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>Lattice Parameter (Å)</th>
<th>Mismatch with Al</th>
<th>Absolute mismatch δ</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₃Sc</td>
<td>4.103</td>
<td>+1.31%</td>
<td>1.31%</td>
<td>[51]</td>
</tr>
<tr>
<td>Al₃Ti</td>
<td>3.967</td>
<td>-2.05%</td>
<td>2.05%</td>
<td>[52]</td>
</tr>
<tr>
<td>Al₃V</td>
<td>3.870</td>
<td>-4.44%</td>
<td>4.44%</td>
<td>[53]</td>
</tr>
<tr>
<td>Al₃Zr</td>
<td>4.080</td>
<td>+0.74%</td>
<td>0.74%</td>
<td>[52, 54, 55]</td>
</tr>
</tbody>
</table>

Considering the critical role of element diffusivity and lattice matching, Zr is an excellent candidate for alloying with aluminium. Overall, the Al₃Zr precipitates possess the smallest relative misfit with aluminium and Zr has a small diffusion coefficient compared to other metals. The binary Al-Zr alloy and its characteristics are discussed in the following section.

### 2.4 The Al-Zr Alloy System

#### 2.4.1 Phase Equilibria

The binary Al-Zr alloy system is a well-studied system that attains high strength at elevated temperatures. Zr addition to an aluminium matrix results in the formation of the Al₃Zr phase. According to the binary Al-Zr phase diagram, precipitation of the Al₃Zr phase is only thermodynamically possible when the Zr concentration exceeds 0.01 wt.% at 350 °C and increases to 0.08 wt.% when the temperature is raised to 500 °C. Figure 2.5 shows the Al-Zr equilibrium phase diagram at high temperatures [48]. The maximum solubility of Zr in aluminium is reported to be 0.28 wt.% (0.083 at.%) at 660.8 °C [48].
2.4.2 Solidification of Al-Zr Alloys

The partition coefficient of Zr in aluminium is larger than unity \( k_0 = 2.5 \), Table 2.2) and for this reason when Zr is added in multi-component alloys, it generally segregates in the opposite direction to the major alloy elements (e.g. Cu, Si and Mg) which all have \( k_0 < 1 \). In a detailed study, Robson and Prangnell [56] demonstrated that following solidification, the solid dendrite shows variations in composition from the core (which solidifies first) to the edge which solidifies last. In the same investigation Zr was shown to enrich the dendrite core whilst Cu and Mg additions were lean at the core and tended to enrich the dendrite edges. In another study Robson and Prangnell [57] provided evidence that the precipitation within a grain depends strongly on the distribution of Zr solute and the lowest Zr solute concentration was present at the grain boundaries. Lü et al. [58] showed that the Zr concentration in the dendrite centre is higher than the dendrite edges, regardless if a one or a two-step homogenisation treatment is used. Figure 2.6 shows a characteristic segregation pattern of Al₃Zr precipitates found in an Al-Cu-Zr alloy [59].
2.4.3 Ageing of Al-Zr Alloys

When ageing is conducted at temperatures below 550 °C the Al₃Zr precipitates form with the metastable cubic L1₂ crystal structure [48]. The effectiveness of these precipitates in providing strengthening is strongly related to their size, coarsening resistance, spacing and distribution [56]. As Robson and Prangnell reported [57], the peak nucleation rate of the L1₂ occurs at 450 °C and the peak growth rate at 555 °C. This fits well with their prediction that the most rapid kinetics for precipitation are obtained at 495 °C [57]. In the same study, they reported that after 100 h at 500 °C the Al₃Zr L1₂ phase does not transform to the equilibrium structure. In another investigation, Knipling et al. [60] did not observe the equilibrium structure when ageing an Al-Zr alloy for 1600 h at 425 °C. Sepehrband et al. [32] reported significant improvements in the strength of a cast A319 alloy when adding 0.15 wt.% of Zr and solutionising it at 503 °C for 24 h (Figure 2.7a). However, when the alloy was aged at 195 °C the strength continuously decreased after 6 h and the hardening behaviour remained unaffected (Figure 2.7b). For this reason, this alloy cannot be used in high temperature applications. The higher strength obtained could apparently be attributed to the higher solute content and the grain refining effect of Zr additions and not to the formation of a trialuminide precipitate.
Characterising Precipitate Evolution in High Temperature Cast Aluminium Alloys using Synchrotron Radiation

In the binary Al-Zr alloy, the prolonged ageing of the L1₂ Al₃Zr precipitates for more than 20 h, at temperatures above 550 °C [57], will result in the transformation to the equilibrium semi-coherent D0₂₃ crystal structure, which is stable up to the melting point. Han et al. [61] confirmed that in alloys containing additions of Si, Ti or V, the Al₃Zr phase does not only form the equilibrium D0₂₃ structure but the formation of D0₂₂ structure is also favoured. Both the D0₂₃ and D0₂₂ crystal structures are semi-coherent with the aluminium matrix. Figure 2.8a [62] shows the equilibrium crystal structures in comparison with the metastable L1₂.

2.4.4 The Equilibrium Crystal Structures

The D0₂₂ structure is identified as tetragonal with dimensions \( a₀=0.39 \) nm and \( c=0.90 \) nm. The unit cell dimensions of D0₂₃ have been known for several years and are reported to be \( a₀=0.4014 \) nm and \( c=1.732 \) nm [63]. Thus, as Lityńska et al. [64] confirmed, the lattice parameters of D0₂₂ are very close to \( a₀ \) and \( 2a₀ \) and to \( a₀ \) and \( 4a₀ \) for D0₂₃, where \( a₀ \) is the lattice parameter of aluminium. Therefore, both the equilibrium tetragonal crystal structures match the aluminium lattice rather well [61] but not perfectly. As Lityńska et al. [64] concluded, the substitution of aluminium by Si in the Al₃Zr particles increases the stability of the D0₂₂ structure. Han et al. [61] reported that the D0₂₃ crystal structure has a lower lattice misfit with the matrix and possess a smaller interfacial energy that increases the coarsening resistance of this phase compared to the D0₂₂. For this
reason, when comparing the two equilibrium semi-coherent crystal structures, the D0\textsubscript{23} is preferred.

![Figure 2.8 a) The different crystal structures of the Al\textsubscript{3}Zr precipitates [62] and b) the planar faults seen in an L1\textsubscript{2} Al\textsubscript{3}Zr precipitate which are believed to be the first steps of the transformation to the equilibrium crystal structure [64].]

2.4.5 Effect of Si on the Precipitation Kinetics

The addition of Si to the binary Al-Zr alloy accelerates the precipitation kinetics of the Al\textsubscript{3}Zr phase [64-67]. Hori et al. [65] investigated the behaviour of the Al\textsubscript{3}Zr phase when 0.12 wt.% Si was added by employing TEM and resistivity measurements. They concluded that Si additions provide nucleation sites for the continuous precipitation of the L1\textsubscript{2} crystal structure. This has also been suggested by Ikeda et al. [66] where they concluded that Si additions accelerate the precipitation kinetics more than Fe does. In another study, Lityński et al. [64] aged an Al-Mg-Si-Zr alloy at 540 °C for 30 mins and investigated the precipitates using high-resolution electron microscopy (HREM). Figure 2.8b [64] shows the planar faults detected in the spherical L1\textsubscript{2} precipitates which are believed to be the first step of the transformation to the equilibrium structure. Their observation indicates that the conversion temperature at which precipitates transform to the equilibrium structure is reduced with Si additions. Evidence of this was also provided by Gao et al. [67]. In this study, precipitates transformed to the equilibrium structure when ageing was conducted at 525 °C. The authors also reported that when a small amount of Si (3.9 at.%) substitutes for aluminium in the L1\textsubscript{2} precipitates, the precipitation of the D0\textsubscript{23} particles is accelerated.
2.5 Alloying of $\text{Al}_3\text{Zr}$ Precipitates

The $\text{Al}-\text{Zr}$ system is one of the most interesting aluminium alloys for high temperature applications. For this reason, many studies have investigated the potential benefits of alloying the $\text{Al}_3\text{Zr}$ precipitates with other metals [68] or transition metals that also form the $\text{L}_1_2$ crystal structure [41, 69-71]. This was mainly motivated by the advantages of further reducing the lattice mismatch and attaining a higher volume fraction of precipitates.

For the reasons described above, Sc is one of the most studied additions in the $\text{Al}_3\text{Zr}$ precipitates [35, 72-77]. The new alloy has improved mechanical properties compared to the binary system at temperatures above 400 °C [78]. This is attributed to the core-shell chemical composition that the $\text{Al}_3\text{Zr}_x\text{Sc}_{1-x}$ precipitates have [35, 72-77]. Deschamps et al. [72] investigated the precipitation kinetics in this system and concluded that the composition heterogeneity results from the difference in diffusion coefficient between Sc and Zr. This means that at the early stage of growth, Sc diffuses faster and starts forming precipitates. When the solid solution is depleted in Sc, precipitates grow by Zr diffusion. In another study, Clouet et al. [79] evaluated the chemical heterogeneity of the precipitates and reported that the core consists of pure Sc while in the shell the ratio of Zr and Sc is approximately 1. Robson [77] suggested that although the precipitates will always contain more Sc than Zr, the precipitate composition will reflect the initial distribution of elements in the matrix (i.e. precipitates towards the dendrite edges will contain more Sc than those towards the dendrite centres). Belov et al. [80] studied the effect of composition and cooling rate on hardening the $\text{Al}-\text{Zr}-\text{Sc}$ system. They recommended that the total Zr and Sc concentration in commercial aluminium alloys should not exceed 0.4 wt.% with a ratio of $\text{Zr}/\text{Sc} \geq 2$, in order to completely introduce Sc and Zr into solid solution and fully use the hardening potential of the $\text{Al}_3\text{Zr}_x\text{Sc}_{1-x}$ precipitates.

Despite the advantages of this system, additions of Sc increase the lattice mismatch of the $\text{Al}_3\text{Zr}$ phase which in turn increases the interface energy and hence reduces the coarsening resistance. In addition, compared to the other transitions metals, Sc is a fast diffuser (Table 2.2). Furthermore, the cost of Sc is too high for its implementation in industrial applications. The addition of other
elements in the Al$_3$Zr$_x$Sc$_{1-x}$ precipitates, in order to reduce the amount of Sc used, might result in the alteration of the core-shell to a double core-shell chemical structure. Booth-Morrison et al. [81] investigated the additions of Er in the Al$_3$Zr$_x$Sc$_{1-x}$ precipitates and concluded that the chemical structure of the precipitates depends on the extra element addition and the heat treatment applied. However, the relationship between the chemical structure, the extra element addition and the heat treatment is a matter of dispute [81].

Alloying the Al$_3$Zr phase with Ti additions has been investigated as well [50, 82, 83]. Knipling et al. [60] concluded that Ti additions do not improve the coarsening resistance of the Al$_3$Zr precipitates and the ternary addition of Ti was not observed to retard the strength loss at temperatures from 375 to 600 °C [60, 82]. In another study, Knipling [41] concluded that additions of Ti in the binary Al-Zr alloy are unlikely to remain in solid solution after conventional solidification. This was attributed to the strong tendency for primary Al$_3$Ti precipitation when the maximum solubility is approached. Zhang et al. [83] demonstrated that the primary Al$_3$(Zr,Ti) intermetallics can be significantly refined when ultrasonic melt treatment (UST) is applied. Precipitation of small coherent Ti-rich phases has been reported only for high supersaturated alloys produced by nonequilibrium processes and similar supersaturations cannot be achieved by conventional castings [41].

More recently, V has increasingly received much attention due to the tendency to substitute for Zr in the metastable coherent L1$_2$ precipitates [84]. With V additions the new precipitate formula composition should be written as Al$_3$Zr$_x$V$_{1-x}$. Figure 2.9 shows the phase diagram of the binary Al-V alloy [44]. The maximum solid solubility of V in aluminium is 0.58 wt.% (0.33 at.%) at 662.1 °C. In the following section the advantages of V additions in the Al$_3$Zr precipitates are discussed.
2.5.1 Advantages of V Additions

A significant advantage of substituting V for Zr is that the former possess the lowest diffusion coefficient of all transition metals at 400 °C (Table 2.2), in contrast to Sc which has the highest. This characteristic potentially enhances the coarsening resistance of the Al$_3$Zr precipitates at elevated temperatures, making it an excellent candidate for applications where strength at high temperatures is required.

Moreover, V has the ability to significantly lower the lattice mismatch between the Al$_3$Zr precipitates and the aluminium matrix [85]. While the Al$_3$Zr precipitates have a positive crystallographic mismatch with aluminium (+0.74%), the Al$_3$V phase has a negative (-4.44%). By assuming Vegard’s law and using the lattice parameters of the L1$_2$ precipitates in Table 2.3, a composition of Al$_3$Zr$_{0.85}$V$_{0.15}$ was calculated to almost eliminate the lattice mismatch. This methodology was followed by Lee et al. [34], Han et al. [61] and Chung et al. [86] to calculate the mismatch of the Al$_3$M precipitates with the aluminium matrix but, might not be wholly accurate. Nevertheless, small V additions can greatly affect the ageing behaviour of the Al$_3$Zr precipitates because the improved coherency leads to an improved coarsening resistance at elevated temperatures [87].

Figure 2.9 The equilibrium Al-V phase diagram [46].
Furthermore, the combination of Zr and V results in a higher volume fraction of precipitates compared to the binary Al-Zr alloy. The last advantage of V additions in the Al$_3$Zr precipitates is that the critical cooling rate of the alloy decreases [17]. As Fan [17] reported, a medium critical cooling rate of 35 Ks$^{-1}$ is sufficient enough to retain 0.4 wt.% V and 0.1 Zr wt.% in solid solution. On the other hand, 0.6 wt.% of Zr requires a cooling rate of 95 Ks$^{-1}$, which is unattainable with traditional casting processes [17].

2.5.2 Characterisation of the Al$_3$Zr,V$_{1-x}$ Precipitates

The majority of studies found in the literature on the ternary Al-Zr-V system, investigate alloys that have been prepared by melt-spinning [34, 84-88]. Melt-spinning is employed because the larger achievable supersaturation of solutes leads to higher volume fraction of precipitates and also the rapid solidification minimizes microsegregation. Chen et al. [85, 87] investigated the coarsening behaviour of the L1$_2$ Al$_3$Zr$_x$V$_{1-x}$ precipitates in melt-spun Al-Zr-V alloys by employing TEM. Based on the TEM measurements for the average precipitate radius, the coarsening rate constant was calculated at different temperatures. However, TEM studies can only examine small material volumes which are often restricted to a single grain, thus allowing local investigation of a relatively small number of precipitates [85]. This is considered an inherent drawback of TEM studies when good statistical results are required.

Furthermore, Al-Zr-V alloys which were not rapidly solidified, exhibit a more heterogeneous precipitate distribution compared to melt-spun alloys [89], hence it is difficult to obtain statistically valid results. TEM results reported for arc-melted Al-Zr-V alloys [89], may be subjected to large biases related to the heterogeneous precipitate distribution [60].

2.6 Mechanical Properties of Conventionally Cast Alloys Containing Zr and V Additions

The data presented in this section were provided by Ford Motor Company in a private communication. Ford has investigated the potential of Zr and V additions in developing aluminium alloys for high temperature engine and transmission components by studying their effect on the yield strength.
Figure 2.10 shows the yield strength measurements obtained from two conventionally cast Al-6.8Si (wt.%) alloys with different levels of Zr and V additions. Alloy 2 has higher Zr and V content than Alloy 1. Both alloys were aged at 400 °C prior to testing and at least three measurements were taken at each ageing time. It is clear that there is a change of yield strength with ageing time, and on average, Alloy 2 obtains higher yield strength compared to Alloy 1. This can be attributed to the higher concentration of precipitating elements in Alloy 2 which results in a higher precipitate volume fraction. However, it is interesting that the yield strength measurements in both alloys show significant scatter. The large scatter in the yield strength measurements is probably the result of casting defects, such as porosity or oxides, which have been well demonstrated to have this effect [90, 91].

In the present project, we aim to quantitatively characterise the precipitation evolution of the $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ precipitates in these two conventionally cast aluminium alloys. For this reason, we employed the SAXS technique that provides statistically significant results by examining a bulk material volume. This technique is systematically described in the next section.

2.7 Small-angle X-ray Scattering (SAXS)

Overview: This final section of Chapter 2 is dedicated to small-angle X-ray scattering (SAXS). At the beginning of this section, the general theory of
scattering is briefly presented. Then the focus is shifted to SAXS and the distinct advantages that this bulk technique offers when investigating precipitation phenomena. Synchrotron SAXS and the advantages of ex situ and in situ experiments are also discussed. Furthermore, systematic literature review of previous SAXS investigations on aluminium alloys with detailed experimental information is presented. At the end of Chapter 2, the research contribution of the present work is highlighted.

2.7.1 The Basic Principles of Scattering

Scattering is a bulk material technique that has been extensively employed in materials science for a number of years. The materials studied are diverse because this technique can be either used with X-rays or neutrons. Although this thesis is concerned with X-ray scattering only, the basic theory presented here can also be applied to neutron scattering with slight modifications.

When X-rays encounter a form of matter, a proportion will pass through, some will be absorbed and transformed into other forms of energy and the remainder will be scattered [92]. Diffraction is produced by the interference of waves scattered by an object [93]. X-ray scattering is dominated by the interaction of the incident radiation with electrons. The nuclear contribution in X-ray scattering is neglected since the nuclear scattering energy is $10^6$ times less than the electron scattering energy [94].

2.7.2 The Basic Theory of SAXS

SAXS is a scattering technique that employs X-rays to study the internal structure of matter. This technique is a contrast method which is based on the average electron density difference between regions of the sample.

X-rays are described either as electromagnetic waves or particles called photons. When X-rays strike an object, photons interact with electrons either elastically or inelastically. Inelastic scattering occurs when a photon collides with a loosely bound or free electron and loses a fraction of its energy. The electron is bounced away and the photon deviates through an angle $2\theta$ [95]. The secondary scattered wave has a wavelength larger than the incoming wave (incoherent scattering).
This type of scattering cannot produce interference phenomena and for this reason carries no structural information. Inelastic scattering is also referred to as Compton scattering which is part of the background constant in a SAXS experiment [96].

Elastic scattering occurs when photons collide with strongly bound electrons without energy transfer. Due to the collision, electrons start oscillating at the same frequency as the incoming photons and every illuminated electron emits synchronous secondary waves. These waves are coherent and this type of scattering is called coherent scattering. Coherent waves interfere with each other and the interference can be either constructive (waves in phase), destructive (waves out of phase in 180° multiples) or in between. The coherent waves carry the information about the internal structure of the sample. Every secondary wave is of the same intensity, \( I \), and according to Thompson [93]:

\[
I(\theta) = I_p \cdot 7.9 \cdot e^{-26} \frac{1}{\alpha^2} P_f
\]

where \( I_p \) is the primary intensity, \( \alpha \) is the distance from the scatterer to the point of detection, the numerical factor is the square of the so-called classical electron radius \( (e^2/mc^2) \), \( P_f \) is the polarization factor which equals \((1+\cos^22\theta)/2\) and \( 2\theta \) is the scattering angle [93]. As the name implies, the scattering range is limited to small angles only. A typical SAXS pattern is usually limited to less than three degrees of scattering angle. This means that the recorded intensity according to eq. 2.5 depends only slightly on the scattering angle \( 2\theta \) [93].

In a SAXS experiment, waves are coherent and the Compton scattering is usually negligible. Coherent waves mean that the amplitudes are added and the scattering intensity is given by the absolute square of the resulting amplitude. The amplitudes are of equal magnitude and differ only by their phase \( \varphi \), which depends on the position of the electron in space [93], according to:

\[
\varphi = \frac{2\pi}{\lambda}
\]
where \( \lambda \) is the X-ray wavelength. The phase \( \varphi \) is the difference between the optical path and the detection point of photons. In a SAXS experiment, bright and dark spots are produced on the detector by constructive and destructive interference, respectively. The scattering pattern is two dimensional with the intensity varying from position to position on the detector plane and is characteristic of the internal structure of the specimen. Every distance \( r \) in the scattering pattern is measured relative to the wavelength \( \lambda \) [97] and for convenience we introduce the scattering vector (or momentum transfer) \( q \) which is:

\[
q = \frac{4\pi}{\lambda} \sin(\theta)
\]  

(2.7)

where \( \lambda \) is the X-ray wavelength and \( 2\theta \) is the scattering angle. Scattering intensity spectra are presented as a function of \( q \) which has dimensions one over length (usually Å\(^{-1}\)). For this reason, the scattering pattern represents the internal structure of the sample in the reciprocal space.

Figure 2.11a [98] shows a typical experimental SAXS set-up. The set-up primarily consists of the X-ray source, the sample and the detector. The beam diameter and shape varies between different X-ray sources and is usually less than 1 mm\(^2\). The larger the beam diameter is, the larger the sampling volume. The resolution of SAXS depends on the X-ray wavelength, \( \lambda \), and the sample to detector distance employed. A smaller wavelength and a shorter sample to detector distance (i.e. larger scattering angles) can resolve smaller internal structure features.

![Image of SAXS set-up and spectrum](image-url)

Figure 2.11 a) A typical representation of SAXS set-up [98] and b) a SAXS spectrum acquired on an Al-Li-Mg alloy showing the contribution of Laue scattering [99].
SAXS has been applied to a diverse range of materials. This versatile technique can be particularly useful when investigating precipitation phenomena because it provides statistically significant results by measuring large numbers of precipitates; typically \( >10^9 \). In metallic systems the recorded scattering intensity derives from the average electron density difference between the precipitates and the matrix and the interparticle correlations. If we assume that these correlations are isotropic, then the total scattering intensity \( I(q) \) is given by [100]:

\[
I(q) = N_p V_p^2 (\rho_p - \rho_m)^2 F(q) S(q) + B
\]

where \( N_p \) and \( V_p \) are the total number and volume of precipitates, \( \rho_p \) and \( \rho_m \) are the scattering length density of precipitates and matrix, respectively, and \( B \) is the background constant. \( S(q) \) represents a structure factor term describing the arrangement of precipitates of a given form factor \( F(q) \), within the illuminated sample volume. Figure 2.11b shows a scattering profile acquired on an Al-Li-Mg alloy [99]. This figure also shows the \( I_{Laue} \), the background constant which is mainly related to a disordered solid solution and fluorescence of elements in the material [99].

2.7.3 Synchrotron Radiation

Laboratory SAXS has been widely used in the past but sources are limited in energy range which constrains the investigation of metallic systems to thin specimens only (i.e. <100 μm). Another restriction is that the low photon flux of the sources makes the data acquisition slow and so the time-resolved experiments are difficult. Recently, due to the rapid development of synchrotron facilities around the world, a great potential for SAXS has emerged. These state of the art facilities produce X-rays of continuous wavelength by forcing electrons to move along an almost circular path at speeds near to the speed of light. Synchrotrons provide a photon flux that exceeds \( 10^{12} \) photons per second, a wide energy range selection and real time data acquisition. Moreover, synchrotron SAXS is more versatile compared to laboratory SAXS because of the ability to modify and design the experimental set-up according to the system’s special requirements. Synchrotron beamlines provide large sample to detector distances that range from 2 to 11 metres. This gives access to a wider range of scattering vectors than is
attainable in laboratory sources. Moreover, the shape and the size of the X-ray beam can be modified depending on the investigation’s requirements.

However, the greatest advantage of employing synchrotron SAXS on metallic systems is the ability to perform time-resolved experiments and study precipitation phenomena under different conditions. Synchrotron SAXS on metallic systems can be performed either ex situ or in situ, both of which are briefly described below.

**Ex situ**: alloys are heat treated in advance and investigated under the beam at room temperature. During an ex situ experiment, multiple samples can be investigated using automated sample positioning. Typical exposure times are less than 1 s for aluminium alloys, which makes the data acquisition fast and enables systematic studies of multiple ageing conditions that otherwise would be challenging. Furthermore, SAXS spectra can be acquired from multiple sample areas. This can be particularly useful when investigating welds where the precipitate size and volume fraction depend on the welding area and the welding speed [101-103]. Dumont *et al.* [102] studied the microstructural response of a 7449 alloy to friction stir welding and provided detailed precipitate size and volume fraction maps at different welding speeds.

**In situ**: in these experiments the precipitation evolution is studied in real time under the X-ray beam. In order to achieve high temperatures, resistance furnaces are employed and alloys are aged either isothermally or isochronally while acquiring SAXS spectra. Depending on the type of furnace employed, metallic systems can be rapidly heated to temperatures that exceed 1200 °C. At elevated temperatures, in order to avoid oxidation, an argon atmosphere is usually used inside the furnace. These experiments can also be composed of multiple-step heating cycles. In situ SAXS can shed light on the precipitate nucleation, growth and coarsening stages and allow one to obtain a holistic understanding of the precipitation kinetics. Figure 2.12 [104] shows the scattering curves acquired during an in situ investigation of an Al-5.4Cu (wt.%) alloy at different temperatures.
Figure 2.12 The evolution of the scattering spectra when investigating in situ an Al-5.4Cu (wt.%) alloy at different temperatures [104].

Overall, the biggest advantage of SAXS when investigating metallic systems is that information is acquired over a large precipitate population, and for this reason SAXS results have a valuable statistical nature. This can be demonstrated when comparing SAXS with a local investigation technique (e.g. TEM). In precipitation studies, TEM usually measures a small number of precipitates and the sampling volume is limited to less than $10^{-3} \mu m^3$. On the other hand, SAXS enables us to acquire information from a very large number of precipitates within a number of grains. Depending on the beam dimensions and the sample thickness, SAXS can investigate volumes that exceed $10^6 \mu m^3$. In Chapter 4, the combination of a large sampling volume and a high precipitate density enabled us to measure more than $10^{11}$ precipitates in a single scattering spectrum. For this reason, SAXS provides a statistically significant understanding of the precipitate size distribution and volume fraction that would be difficult to obtain with traditional means of characterisation. Furthermore, in situ SAXS can provide information about nucleation, growth and stability of precipitate phases [105] at different temperatures. These are considered to be valuable information from SAXS, since modelling techniques require them not only to verify their results but also to support their assumptions, hypothesis and simplifications.

\[1\] assuming a foil thickness of 100 nm and a field of view of 500 $\times$ 500 nm for TEM and a beam diameter of 300 $\mu$m with a sample thickness of 250 $\mu$m for SAXS.
2.7.4 Prerequisites for Successful Precipitation Studies

In this section, the prerequisites for successfully implementing SAXS on aluminium alloys are summarised. The most important parameters to consider when designing an experiment are: sample absorption, electron density difference between the matrix and the precipitates, precipitate volume fraction and reference sample selection.

**Sample absorption**: as mentioned earlier, a fraction of the incoming photons that hit a specimen will be absorbed and transformed to other forms of energy. The fractional decrease of the incoming intensity, $I$, of the beam is proportional to the distance traversed in the matter, $\chi$. This relationship in a differential form is expressed as:

$$I_x = I_0 e^{-\mu x}$$  \hspace{1cm} (2.9)

where $I_0$ is the intensity of the incoming beam and $I_x$ is the intensity of the transmitted beam after passing a specimen of thickness $\chi$. The $\mu$ value is called the linear absorption coefficient and depends on the alloy considered, its density and the X-rays’ wavelength. The linear absorption coefficient is also proportional to the material’s density $\rho$. The higher the material density is, the thinner the specimen should be. Tsao *et al.* [106] employed SAXS on aluminium specimens that were 500 μm thick and the same thickness has also been found in other investigations [107-109]. The large sample thickness can further enhance the statistical nature of the results and can be particularly useful when the precipitate volume fraction is low (*i.e.* <0.5 vol.%).

**Electron density difference**: as mentioned earlier, SAXS is a contrast technique that detects electron density differences at a scale larger than the interatomic distances. In order for the precipitates to become distinguishable and visible they should have a distinct electron density from the matrix. As eq. 2.8 reveals, the contrast increases with the second power of the electron density difference between the element(s) composing the precipitates and the matrix. If the electron density of the precipitates is close to the electron density of the matrix, the former
cannot be distinguished and the scattering will be characterised by a low signal to noise ratio. This will make SAXS spectrum difficult to interpret. In order to overcome the poor contrast of Mg$_2$Si precipitates with the aluminium matrix, Tsao et al. [106] employed a higher X-ray energy and a thicker specimen than normally used. Although they enhanced the scattering intensity from the precipitates, they did not consider the possibility of secondary scattering arising, which might affect the scattering data collected.

**Precipitate volume fraction:** another important experimental parameter for implementing SAXS on metallic systems is the precipitate volume fraction. The higher the volume fraction is, the more effective the scattering will be. However, there is an upper limit of precipitate volume fraction above which interference phenomena between precipitates occur. This interference produces additional scattering which can lead to misinterpretation of results. However, this upper limit is not frequently an issue in metallic systems. Deschamps et al. [110] overcame the interference of closely spaced precipitates in an Al-Li-Mg alloy with precipitate volume fraction higher than 20 vol.% by extending the analysis method (described in section 3.3) to higher scattering vectors. More information can be found in reference [110].

**Reference sample selection:** a key factor for a successful SAXS investigation is the choice of a valid reference sample. When X-rays hit a metallic sample, every illuminated atom will scatter the incident photons in all directions and during the experiment this will be recorded as a constant background. However, we are only interested in the scattering that results from the precipitates. For this reason it is necessary to employ a reference sample which is free from precipitation but which, in other respects, is identical to the alloy under investigation. In this way the scattering signal that results from secondary phases and impurity elements can be subtracted. Depending on the investigation, reference samples can be either specimens at the onset of precipitation [106], as quenched specimens [111], specimens at the solution temperature [108] or alternatively naturally aged samples [109]. In many investigations, information about reference samples is not provided [72, 107, 112].
2.7.5 Previous SAXS Investigations on Aluminium Alloys

Aluminium alloys, which are commonly regarded as wrought alloys, have been studied in the past by employing either laboratory or synchrotron SAXS. The most well-studied aluminium alloys are: Al-Mg-Si, Al-Cu, Al-Cu-Mg, Al-Zn-Mg and Al-Zn-Mg-Cu (see Table 2.4). Depending on the alloy, the experimental set-up and the complementary techniques, these studies focus either on the precipitate evolution, the precipitation kinetics or the evolution of the precipitate composition during ageing. All these systems fulfil the requirements for successful SAXS characterisation (section 2.7.4). To begin with, the composition of these alloys does not result in the formation of secondary phases or large intermetallic particles. This makes the reference sample selection simple, since the resulting scattering is attributed to precipitates only. Secondly, all the aforementioned alloys, except the Al-Mg-Si system, form precipitates that have a distinct electron density difference to the matrix. Finally, the precipitate volume fraction is high enough to secure a sufficient scattering signal. This is especially true for alloys where the precipitate volume fraction exceeds 5 vol.% [104, 110, 113].

More recently, there have been SAXS investigations on aluminium alloys with precipitates composed of transition metals. Deschamps et al. [72] investigated the Al-Zr-Sc alloy by employing in situ SAXS. As mentioned earlier, this alloy attains a low precipitate volume fraction with a non-uniform core-shell chemical composition. The same system was also studied by Clouet et al. [79]. Both studies were primarily focused on the heterogeneity of the precipitate chemical composition and the precipitation kinetics. Although the precipitate volume fraction in both studies was low, the sufficient contrast between the precipitates and matrix made the SAXS implementation successful.

In Table 2.4, a list of investigations on aluminium alloys that employ either laboratory or synchrotron SAXS is given. The list is representative of the research undertaken in recent years but does not include every SAXS investigation found in the literature. In the same table, the purpose of the study is briefly presented and some important experimental parameters are also included.
Table 2.4 A representative list of SAXS investigations on aluminium alloys. When the symbol (-) appears, the information was not provided by the author.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Purpose of Study</th>
<th>S. Thickness (μm)</th>
<th>Energy (keV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Mg-Si</td>
<td>Evolution of the β” precipitates</td>
<td>500</td>
<td>15.00</td>
<td>[106]</td>
</tr>
<tr>
<td>Al-Mg-Si</td>
<td>Precipitation of metastable phases</td>
<td>500</td>
<td>15.00</td>
<td>[109]</td>
</tr>
<tr>
<td>Al-Cu</td>
<td>Transformation mechanisms of non-isothermal precipitation</td>
<td>200</td>
<td>-</td>
<td>[104]</td>
</tr>
<tr>
<td>Al-Cu</td>
<td>Precipitate evolution during non-isothermal heating</td>
<td>200</td>
<td>-</td>
<td>[111]</td>
</tr>
<tr>
<td>Al-Cu-Mg</td>
<td>Characterisation of precipitate evolution</td>
<td>500</td>
<td>16.10</td>
<td>[107]</td>
</tr>
<tr>
<td>Al-Cu-Mg</td>
<td>Influence of excess vacancies on the Cu-Mg cluster formation during cooling</td>
<td>500</td>
<td>16.00</td>
<td>[108]</td>
</tr>
<tr>
<td>Al-Cu-Mg</td>
<td>Effect of welding on the microstructural evolution</td>
<td>80-90</td>
<td>8.40</td>
<td>[101]</td>
</tr>
<tr>
<td>Al-Zn-Mg</td>
<td>Isothermal precipitation kinetics</td>
<td>-</td>
<td>8.05</td>
<td>[114]</td>
</tr>
<tr>
<td>Al-Zn-Mg</td>
<td>Relationship between precipitate composition and volume fraction</td>
<td>-</td>
<td>7.71</td>
<td>[115]</td>
</tr>
<tr>
<td>Al-Zn-Mg</td>
<td>Precipitate evolution during non-isothermal heat treatment</td>
<td>-</td>
<td>8.31</td>
<td>[103]</td>
</tr>
<tr>
<td>Al-Zn-Mg-Cu</td>
<td>Influence of welding speed on the microstructure</td>
<td>-</td>
<td>8.40</td>
<td>[102]</td>
</tr>
<tr>
<td>Al-Zn-Mg-Cu</td>
<td>Quantitative assessment of the microstructure evolution</td>
<td>70</td>
<td>8.05</td>
<td>[113]</td>
</tr>
<tr>
<td>Al-Zn-Mg-Cu</td>
<td>Precipitation kinetics during severe plastic deformation</td>
<td>70-100</td>
<td>-</td>
<td>[116]</td>
</tr>
<tr>
<td>Al-Zn-Mg-Cu</td>
<td>Influence of alloy composition and heat treatment on precipitate composition</td>
<td>-</td>
<td>8.80-9.70</td>
<td>[117]</td>
</tr>
<tr>
<td>Al-Zn-Mg-Cu</td>
<td>Precipitate evolution</td>
<td>70</td>
<td>8.05</td>
<td>[118]</td>
</tr>
<tr>
<td>Al-Zn-Mg-Cu</td>
<td>Quantitative analysis of the precipitate microstructure</td>
<td>-</td>
<td>9.54</td>
<td>[119]</td>
</tr>
<tr>
<td>Al-Li-Mg</td>
<td>Precipitate characterisation</td>
<td>-</td>
<td>-</td>
<td>[110]</td>
</tr>
<tr>
<td>Al-Cu-Li</td>
<td>Relationship between precipitation and yield strength</td>
<td>70</td>
<td>-</td>
<td>[112]</td>
</tr>
<tr>
<td>Al-Zr-Sc</td>
<td>Investigate the precipitation kinetics</td>
<td>70</td>
<td>7.70</td>
<td>[72]</td>
</tr>
<tr>
<td>Al-Zr-Sc</td>
<td>Quantification of the precipitation kinetics</td>
<td>80</td>
<td>7.70</td>
<td>[79]</td>
</tr>
</tbody>
</table>
Table 2.4 summarises a number of successful SAXS investigations on aluminium alloys. Most of these investigations are on binary/ternary alloys and these studies focus either on the precipitate evolution, the precipitation kinetics or the evolution of precipitate composition during ageing. Another similarity is that these investigations are on wrought aluminium alloys. Moreover, precipitates are the only structures evolving during ageing. This greatly simplifies the interpretation of the scattering evolution and makes the reference sample selection simple.

So far, precipitation phenomena in multi-component cast aluminium alloys have not been systematically investigated using SAXS. Secondary phases and intermetallic structures formed during casting from the melt are commonly encountered in industrial alloys and play an important role. Furthermore, although additions of transition elements in the $\text{Al}_3\text{Zr}$ precipitates have been studied before, SAXS investigations are limited to the $\text{Al}_3\text{Zr}_x\text{Sc}_{1-x}$ precipitates only.

### 2.8 Summary

This review has summarised the potential benefits of the metastable cubic $\text{L}_1_2$ trialuminide precipitates as strengthening phases in high temperature aluminium alloys. Specifically, Zr and V is a promising combination for developing high temperature strength in cast aluminium alloys, such as Al-6.8Si (wt.%), as shown by the preliminary studies undertaken by Ford. However, little previous research has been undertaken on conventionally cast alloys containing the $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ precipitates when high Si levels are also present. Thus there is a need to conduct detailed research in order to obtain measurements of precipitate size and precipitate volume fraction in these multi-component cast alloys. This will lead to a better understanding of how to improve alloy strength at elevated temperatures ($>300 \, ^\circ\text{C}$).

Even though much of the past research on trialuminide precipitates has involved the use of TEM, this experimental approach has limitations with regard to the determination of valid statistical results of the precipitate size and volume fraction evolution due to the heterogeneously distributed precipitates. SAXS has proved to be a valuable technique for obtaining statistically significant results in a range of aluminium alloys, but has not been so far applied to the family of alloys known as
foundry alloys, such as Al-6.8Si (wt.%), which is the material of interest in this study.

The aim of this work is to quantitatively characterise the precipitation evolution in two conventionally cast multi-component aluminium alloys using SAXS. Both alloys are based on the Al-6.8Si (wt.%) system with different Zr and V additions. To the best of the author’s knowledge, this is the first time that these alloys have been investigated using synchrotron SAXS.

In the next chapter, the methodology and the SAXS experimental set-up are analytically described.
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Chapter 3: Methodology

Overview: in this chapter the composition and the heat treatments of the investigated aluminium alloys are provided. The aims and objectives of an ex situ and an in situ SAXS experiment conducted on the I22 beamline of the Diamond Light Source are presented. At the end of this chapter, the TEM and SAXS data analysis is described and the SAXS data calibration method is presented.

- Only the ex situ experimental results are used for this MPhil thesis, but for completeness the in situ methodology is included here in case the data are analysed in the future.
- Some portions of this chapter are repeated briefly in Chapter 4 (the results chapter of the ex situ experiment in a journal paper format) but are described here in greater detail.

3.1 Alloy Compositions and Heat Treatments

In this project, two different alloy compositions were investigated. These are referred to as LA and HA (low and high alloy, respectively) and their compositions as determined by optical emission spectroscopy are listed in Table 3.1 (these alloys were referred to as Alloy 1 and 2 in section 2.6). The elements of Mg, Ti, Ni and Sr were below the detection level. The principal difference is that the HA composition has a slightly higher content of Zr and V than the LA one. Both alloys were cast at the Ford Research and Advanced Engineering laboratories in Dearborn, Michigan, USA. Each alloy was prepared from P1020 (>99.7% purity) grade of aluminium and master alloys were employed for alloy element additions. The melt was well stirred and held at 750 °C (which is above the liquidus temperature of the alloys) and cast into a mould to give a cylinder of dimensions 20 mm diameter × 150 mm long. The cooling rate of the casting between 700 and 600 °C was estimated to be 25 Ks⁻¹.

<table>
<thead>
<tr>
<th>Name</th>
<th>Al</th>
<th>Si</th>
<th>Zr</th>
<th>V</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA</td>
<td>bal.</td>
<td>6.77±0.08</td>
<td>0.30±0.001</td>
<td>0.30±0.002</td>
<td>0.13±0.001</td>
</tr>
<tr>
<td>HA</td>
<td>bal.</td>
<td>6.72±0.09</td>
<td>0.37±0.001</td>
<td>0.34±0.001</td>
<td>0.13±0.002</td>
</tr>
<tr>
<td>Reference</td>
<td>bal.</td>
<td>6.80±0.30</td>
<td>-</td>
<td>-</td>
<td>0.10±0.050</td>
</tr>
</tbody>
</table>

*Table 3.1 Alloy compositions (wt.%) as determined by optical emission spectroscopy.*

*Note:* errors for LA/HA alloys are the standard deviation of the optical emission spectroscopy measurements; the error for the Reference alloy is the composition range specified by the supplier.
Both alloys were directly aged from the as-cast condition with no prior solutionising step. Specimens of 20 mm diameter × 30 mm thickness were heat treated in a Carbolite CWF 1300 air furnace, the temperature of which was calibrated using a Fluke 714 thermocouple calibrator. The selected ageing temperature was 400 °C. The LA alloy was aged for 5, 10, 23 and 50 h whilst HA was aged for 3, 5, 23, and 50 h.

For SAXS experiments it is necessary to have a reference sample which is free from fine-scale precipitation but which, in other respects, is identical to the alloys under investigation. In the present study, a cast binary Al-6.8Si (wt.%) alloy was supplied by NewPro Foundries, Middlesex, UK and employed as a reference sample. Five different specimens of dimensions 20 × 50 × 30 mm were cut from the same bar and aged at 400 °C for 3, 5, 10, 23 and 50 h.

### 3.2 SAXS Experiments

In order to quantitatively characterise the precipitate evolution, SAXS was employed. As mentioned earlier, this technique can be particularly useful in obtaining quantitative and statistically significant results in alloys with heterogeneous precipitate distribution. A SAXS proposal (SM13238-1) was successfully submitted and 48 h of beamtime at Diamond Light Source were granted. During the beamtime, two main experiments were conducted. The first was an *ex situ* experiment at room temperature followed by an *in situ* experiment at elevated temperatures. Here, we clarify the aims and objectives of both experiments.

*Ex situ* SAXS was employed on the LA and HA alloys. The LA alloy was aged at 400 °C for 5, 10, 23 and 50 h whilst HA was aged for 3, 5, 23 and 50 h. The *ex situ* experiment was conducted in order to:

- Demonstrate SAXS applicability in multi-component cast aluminium alloys of industrial importance.
- Characterise and compare the precipitate evolution in two Al-6.8Si (wt.%) based alloys with different Zr and V additions.
• Obtain quantitative and statistically significant results of heterogeneously distributed precipitates including the average precipitate size, size distribution, volume fraction and number density.

The in situ experiment was conducted on the LA alloy. At the beginning of the in situ experiment, the LA alloy was in the as-cast condition and was aged at 400 and 425 °C for 3 h. The in situ experiment was conducted in order to:

• Investigate the precipitation kinetics of the $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ precipitates during the nucleation stage.
• Investigate the effect of temperature on the precipitate nucleation and growth.

3.2.1 Methodology and Experimental Details

SAXS specimens of approximately $10 \times 10 \times 0.8$ mm in size were cut from the heat treated samples using a diamond saw. These specimens were mechanically ground on both sides using progressively finer SiC papers down to P4000 grade. Grinding was performed using the Struers AccuStop 30 with a plane-parallel 04386901 insert and the specimens were mounted on the AccuStop using low melting temperature wax. The in situ specimens were 6 mm in diameter and were punched from the centre of the $10 \times 10 \times 0.8$ mm in size specimens. In order to ensure effective transmission and quick data acquisition during the in situ experiment, the average sample thickness was kept constant at $215\pm10$ μm. Thickness variation on each individual specimen was measured to be approximately 10 μm and thickness measurements were performed using the Mitutoyo Dial Gauge Stand (7001-10) equipped with a Mitutoyo ID-S112MS indicator.

Due to the limited time available, the experimental parameters were carefully designed in order to remain constant for both experiments. The aim was to produce an experimental set-up that satisfied the requirements of the investigated alloys.

A monochromatic beam of wavelength of 0.67 Å (i.e. of energy 18.5 keV) was employed. The beam size incident on the sample was $120 \times 350$ μm. The sample to detector distance was set to 2.907 m and kept constant throughout the
beamtime. The accessible range of scattering vectors was thus 0.01 to 0.6 Å⁻¹. The exposure time was set to 1 s and the data were collected by Pilatus P3-2M detector. On every specimen 30 exposures were acquired and averaged in order to reduce noise.

3.2.2 Apparatus and Experimental Set-up

The apparatuses used for both the *ex situ* and the *in situ* SAXS investigations are described below:

The *ex situ* experiment was conducted on LA and HA alloys. In total, 13 different specimens (including the reference binary Al-6.8Si (wt.%) samples) were investigated. The samples were mounted on an aluminium holder of 1 mm thickness and secured in place using Kapton tape. Figure 3.1 shows the *ex situ* samples mounted on the sample holder on the I22 beamline.

![Figure 3.1 The ex situ specimens mounted on the sample holder.](image)

The *in situ* experiment was conducted on the LA alloy. In order to achieve high temperatures during SAXS acquisition, the Linkam CI94 DSC600 furnace was used. This is a resistance furnace that can achieve temperatures up to 550 °C with a heating rate of 50 °C per minute. The temperature stability is better than 0.5 °C and at temperatures above 350 °C water cooling must be employed. In order to effectively control the temperature during the experiment, the Lauda RE 415 water cooler was used and in order to suppress oxidation on the sample surface, inert argon atmosphere was employed inside the furnace. Figure 3.2 shows the set-up of the Linkam furnace.
3.3 SAXS Data Analysis

If the precipitates are not interacting (i.e. the interparticle distance is large compared to the precipitate size) then the total scattering intensity is the sum of the intensity scattered by individual precipitates [99]. In this case, and assuming a size dispersion function \( f(r) \) that corresponds to the density of precipitate of size \( r \), the total scattering intensity is given by [99]:

\[
I(q) = \int_{0}^{\infty} f(r)I(q,r)dr + B
\]

where \( q \) is the scattering vector and \( B \) is the background constant.

Our analysis was primarily based on three types of plots, namely the Guinier, Kratky and Porod plots, and the evaluations were directly carried out from the scattering data. By analysing these plots the average precipitate size, size distribution, volume fraction and their evolution with ageing time were evaluated.

The average precipitate radius was determined by the Guinier Plot (Figure 3.3, \( \ln(I) \) vs \( q^2 \) [99]). The Guinier approximation was used, since it is a well-established analysis method in metallic systems [102, 106-108, 120, 121]. The precipitate parameter that can be extracted is called radius of gyration (\( R_g \)). \( R_g \) is the average squared distance of the scatterers from the centre of the object. In other words, it provides an estimation of the average precipitate radius. However, \( R_g \) contains no information about the shape or the internal structure of the...
precipitates and depends on the size distribution. It has been shown that $R_g$ gives an accurate description of the mean precipitate radius for lognormal distributions with a dispersion parameter ($\sigma$) close to 0.2 [107, 116, 122].

According to Guinier, for small scattering vectors the intensity $I(q)$ is found to be equivalent to a Gaussian:

$$I(q) = (\rho_p - \rho_m)^2 \nu_p^2 \exp\left(-\frac{q^2 R_g^2}{3}\right)$$  \hspace{1cm} (3.2)

The width of this Gaussian function can be obtained by plotting $\ln(I)$ versus $q^2$. This plot is called Guinier plot and at small scattering vectors:

$$\alpha = -\frac{R_g^2}{3}$$  \hspace{1cm} (3.3)

where $\alpha$ is the slope in the Guinier plot. It should be noted that Guinier approximation is only valid in dilute solutions where the interaction between precipitates is negligible. In our study, the concentration of precipitating elements is sufficiently low to make this method valid.

Figure 3.3 A characteristic Guinier plot acquired on an Al-Li-Mg alloy [99]. This figure also shows the scattering vector range where the Guinier approximation was applied.
In the past, Guinier approximation was only applied in monodisperse systems (i.e. systems with particles of identical size) and the method was only employed at small scattering vectors, where \( qR_g < 1 \). In metallic systems however, the precipitate size distribution is polydisperse. In this case the validity range should be extended. Successful investigations have extended the validity range of Guinier approximation up to \( qR_g = 2.8 \) \([102, 114, 122]\). Here, a self-consistent method proposed by Deschamps and De Geuser \([122]\) was followed in order to determine \( R_g \) and more information can be found in Appendix A.

Another representative SAXS plot is the Kratky plot (Figure 3.4), where we plot \( Iq^2 \) vs \( q \) \([99]\). Kratky plots are characterised by a predominant peak, where the curve reaches a maximum at \( q_{\text{max}} \). In the monodisperse case, the position of this peak is related to \( R_g \) through the following relationship:

\[
R_g = \frac{\sqrt{3}}{q_{\text{max}}} \tag{3.4}
\]

However, in polydisperse cases this value deviates from \( R_g \) and here is referred to as \( R_{\text{pseudo}} \). A comparison between \( R_g \) and \( R_{\text{pseudo}} \) provides an indication of the precipitate size distribution and their deviation increases with an increase in size distribution \([122]\).

Another fundamental parameter that can be extracted from Kratky plots is the precipitate volume fraction. Kratky plots provide an indirect estimation of the precipitate volume fraction since the latter is proportional to the integrated intensity \( Q \) via the following equation:

\[
Q = \int_0^\infty I(q) q^2 dq = 2\pi^2 \left( \rho_p - \rho_m \right)^2 f_v (1 - f_v) \tag{3.5}
\]

where \( Q \) equals the area under the curve in the Kratky plot, \( \rho_p \) and \( \rho_m \) are the electron densities of precipitates and matrix, respectively, and \( f_v \) is the volume fraction of precipitates. In the present study, the area under the curve was obtained by fitting the \( Iq^2 \) vs \( q \) plots with a lognormal distribution and extrapolating the fit to \( q = 0 \) and \( q = \infty \) (analytically described in Chapter 4). For low volume fractions:
\[ f_v = \frac{Q}{2\pi^2 \left( \rho_p - \rho_m \right)^2} \]  

(3.6)

It should be noted that this equation is only valid for the homogeneous two-phase model with phases separated by a sharp interface [107].

The Porod plot (Figure 3.5, \( Iq^4 \) vs \( q \)) provides a visual indication of the chemical structure of the precipitates. For example, a uniform precipitate composition produces a different Porod profile compared to a core-shell chemical composition and can be identified by the overall profile of the Porod plot [72, 79, 123]. In conjunction with the \( Q \) parameter we calculate Porod radius (\( R_p \)) with the following relationship:

\[ R_p = \frac{3Q}{\pi K_p} \]  

(3.7)

where \( Q \) is the area under the curve in Kratky plot and \( K_p \) is the horizontal asymptote in Porod plot. \( R_p \) represents the radius of a sphere of surface-to-volume ratio equal to that of the particle size distribution [122]. In other words, \( R_p \) evolution is analogous to the size distribution evolution.

Figure 3.4 A representative Kratky plot [99]. The area under the curve is proportional to the precipitate volume fraction.
The errors associated with $R_g$, $R_{\text{pseudo}}$, $R_p$ and the precipitate volume fraction calculations are given in Appendix A.

3.3.1 Data Calibration

Strict calibration criteria were used in this study. When SAXS data are uncalibrated, the scattering intensity depends on the sample thickness, scattering geometry and exposure time [124] and the raw data are reported in arbitrary units. Although Guinier analysis can be performed on raw data, the determination of the precipitate volume fraction becomes possible only when the scattering intensity is absolutely calibrated. In this case, the scattering intensity is reported in cm$^{-1}$ [125]. In order to calibrate the scattering intensity, two additional tests should be conducted. In these tests, the scattering of an empty sample holder and the scattering of a secondary standard are measured. In our study, we employed a glassy carbon [124] as a secondary standard for absolute intensity calibration. Based on these measurements the scaling factor was determined according to:
Chapter 3
Methodology

$$I_{abs}(q) = \frac{I(q)}{<I_g(q)>} I_g \frac{V_g}{V_s}$$  \hspace{1cm} (3.8)

where $I_g$ and $V_g$ are the absolute intensity and the illuminated volume of the glassy carbon, respectively, $<I_g(q)>$ is an average intensity value in a predefined $q$ range, $V_s$ is the sample volume, $I(q)$ is the raw intensity and $I_{abs}(q)$ is the absolute intensity from the sample, respectively. The scaling factor was determined to be $9 \times 10^8$ and was applied on the raw data that were subsequently converted to absolute scale.

Moreover, the measured $q$ range in units ($\text{Å}^{-1}$) should be determined with respect to pixel position on the detector by measuring a secondary standard of known structure [126]. In our case, the detector pixels were converted to the scattering vector, $q$, by measuring a reference silver behenate sample as a standard.

The SAXS data processing including data reduction, calibration and normalisation were conducted using DAWN software [127]. The data analysis on the fully calibrated data was conducted using Origin (OriginLab, Northampton, MA).

3.4 TEM Data Analysis

The TEM images presented in Chapter 4 were provided by Ford Motor Company. The major part of the image analysis was conducted by the author of the present thesis using open source software (ImageJ). Precipitate radii were measured and, assuming a perfectly spherical shape, the volume of the precipitates was then calculated. The volume fraction was also calculated as the total volume of precipitates divided by the volume of the TEM foil that contained them. In this calculation the TEM foil thickness was measured to be 120 nm and the foil thickness determination was undertaken by Ford. The number density was calculated as the number of precipitates divided by the volume of the TEM foil. The errors associated with the precipitate size, volume fraction and number density represent the standard deviation of the image analysis measurements.
3.5 Summary

In this chapter, the details about the methodology, the experimental set-up and the data analysis of two SAXS experiments were provided. In the next chapter the results of the ex situ experiment are presented in a journal paper format.
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Chapter 4: Characterising Precipitate Evolution in Multi-component Cast Aluminium Alloys using Small-Angle X-ray Scattering

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**Contribution of each author**

P. Panagos: Holistic analysis of SAXS data, experimental planning and work, partial analysis of TEM data and paper writing

D.G. McCartney: Important suggestions and critical revision of manuscript

M. Li, B. Ghaffari, J.W. Zindel: Alloy supply and important suggestions about the research approach

J.E. Allison: TEM data and partial TEM data analysis

O. Shebanova: Experimental planning and support, data calibration

J.D. Robson: Important suggestions about the research approach

Peter D. Lee: Formulation of the initial research questions and revision of manuscript
4.1 Abstract

Aluminium alloys can be strengthened significantly by nano-scale precipitates that restrict dislocation movement. In this study, the evolution of heterogeneously distributed precipitates in two multi-component alloys was characterised by synchrotron small-angle X-ray scattering (SAXS). The use of SAXS allowed the analysis of statistically significant numbers of precipitates (billions) as compared to electron microscopy (hundreds). Two cast aluminium alloys with different volume fractions of Al₃ZrₓV₁₋ₓ precipitates were studied. Data analysis was conducted using direct evaluation methods on SAXS spectra and the results compare well to transmission electron microscopy (TEM). This study underlines the importance of preliminary data treatment in order to successfully characterise low volume fraction of precipitates in multi-component alloys. Precipitates were found to attain a spherical structure with uniform chemical composition. The evolution of these precipitates was quantified including precipitate size, size distribution, volume fraction and number density. The findings from this investigation provide evidence that these multi-component alloys have a short nucleation stage, and the precipitate size is dominated by coarsening.

Keywords: SAXS, cast aluminium alloys, quantitative analysis

4.2 Introduction

For many decades, aluminium casting alloys have been widely used in the automotive industry in a variety of applications including wheels, brake components and engine parts [1]. Despite their low weight-to-volume ratio, their castability and machinability, aluminium alloys are typically limited in use to temperatures below 250 °C [59]. Above this temperature, a significant drop in strength is observed as a result of rapid coarsening of age hardening precipitates. It has been shown that the addition of transition elements to aluminium alloys improves their high temperature properties [32, 33, 59]. Specifically, the addition of Zr promotes the formation of metastable cubic Al₃Zr precipitates (also referred to as dispersoids) with the L1₂ crystal structure. This phase is known to resist coarsening up to 400 °C [35].
The low diffusivity of Zr and low lattice misfit of the precipitates with the matrix are the two key features promoting the good thermal stability of these precipitates at high temperatures [85]. Many low diffusivity transition elements, including Sc, Ti and V, have been proposed to substitute for Zr in the Al₃Zr precipitates [61] in order to further increase the resistance to coarsening. Amongst them, V is one of the most promising candidates since it possesses the lowest diffusivity in aluminium. Furthermore, when V substitutes for Zr, the lattice misfit between the precipitates and the matrix is drastically reduced [34, 87]. The resulting precipitates are Al₃ZrₓV₁₋ₓ and at temperatures below 450 °C the metastable L1₂ crystal structure is favoured [85]. Owing to the low solubility of both Zr and V in aluminium, the Al₃ZrₓV₁₋ₓ precipitates are typically nucleated in low volume fractions and are heterogeneously distributed due to solidification microsegregation of Zr and V. For these reasons, it is difficult to obtain statistically valid results on precipitate volume fraction and size distribution with traditional characterisation techniques (e.g. electron microscopy).

In the present study, we aim to (i) quantitatively characterise the precipitate evolution of two Al-6.8Si (wt.%) casting alloys containing different additions of Zr and V by employing synchrotron small-angle X-ray scattering (SAXS) and (ii) correlate the results with a limited study by transmission electron microscopy (TEM). SAXS is a non-destructive technique that measures bulk material properties. On average, the sampling volume is more than 10⁹ times larger compared to TEM, with billions of precipitates being averaged, instead of hundreds. For this reason, this technique provides quantitative and statistically reliable results including average precipitate size, volume fraction, number density and precipitate size distribution (PSD).

In the past, SAXS has been employed in metallic systems, including wrought aluminium alloys, to characterise precipitation phenomena [101, 102, 106, 108, 109, 116]. However, it was primarily applied to simplified alloys in order to avoid additional scattering from impurity elements, eutectic phases and undesirable precipitation phenomena [99, 120, 122, 128]. Moreover, a number of alloys under investigation featured precipitate volume fractions higher than 5 vol.% in order to

---

2 assuming a foil thickness of 100 nm and a field of view of 500 × 500 nm for TEM and a beam diameter of 300 μm with a sample thickness of 250 μm for SAXS.
ensure effective scattering [104, 113, 116, 117]. Throughout the literature there is an ongoing debate regarding the best reference sample to select and many studies either do not specify details of the reference sample employed [105, 114, 115] or they do not appear to have used one [99, 116, 122].

In the present paper we employ SAXS to quantitatively characterise the precipitate evolution in two multi-component aluminium casting alloys (often termed foundry alloys) with a low precipitate volume fraction. The experimental methodology applied to complex systems, the primary data treatment and the reference sample selection are all discussed in detail. Quantitative results of heterogeneously distributed precipitates including average size, volume fraction, number density and size distribution are reported and correlated with TEM data.

### 4.3 Experimental Details

#### 4.3.1 Materials, Alloy Preparation and Heat Treatments

In this study two different alloy compositions were investigated. These are referred to as LA and HA (low and high alloy, respectively) and their compositions as determined by optical emission spectroscopy (OES) are listed in Table 4.1. The elements of Mg, Ti, Ni and Sr were below the detection level. The principal difference is that the HA composition has a slightly higher content of Zr and V than the LA one. Both alloys were cast at the Ford Research and Advanced Engineering laboratories in Dearborn, Michigan, USA. Each alloy was prepared from P1020 (>99.7% purity) grade of Al and master alloys were employed for alloy element additions. The melt was well stirred and held at 750 °C and cast into a mould to give a cylinder of dimensions 20 mm diameter × 150 mm long. The cooling rate of the casting was estimated to be 25 Ks⁻¹.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al</th>
<th>Si</th>
<th>Zr</th>
<th>V</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA</td>
<td>bal.</td>
<td>6.77±0.08</td>
<td>0.30±0.001</td>
<td>0.30±0.002</td>
<td>0.13±0.001</td>
</tr>
<tr>
<td>HA</td>
<td>bal.</td>
<td>6.72±0.09</td>
<td>0.37±0.001</td>
<td>0.34±0.001</td>
<td>0.13±0.002</td>
</tr>
<tr>
<td>Reference</td>
<td>bal.</td>
<td>6.80±0.30</td>
<td>-</td>
<td>-</td>
<td>0.10±0.050</td>
</tr>
</tbody>
</table>

*Note: errors for LA/HA alloys are the standard deviation of the optical emission spectroscopy measurements; the error for the Reference alloy is the composition range specified by the supplier.*

Table 4.1 Alloy compositions in wt.% as determined by optical emission spectroscopy.
Both alloys were directly aged from the as-cast condition with no prior solutionising step. Specimens of 20 mm diameter × 30 mm thickness were heat treated in a Carbolite CWF 1300 air furnace, the temperature of which was calibrated prior to use. The selected ageing temperature was 400 °C. The LA alloy was aged for 5, 10, 23 and 50 h whilst HA was aged for 3, 5, 23 and 50 h.

For the SAXS measurements it is necessary to have a reference sample which is free from fine-scale precipitation but which, in other respects, is identical to the alloys under investigation. In the present case, a cast binary Al-6.8Si (wt.%) alloy was employed as a reference (supplied by NewPro Foundries, Middlesex, UK). Five different specimens of dimensions 20 × 50 × 30 mm were cut from the same bar and aged at 400 °C for 3, 5, 10, 23 and 50 h.

4.3.2 Microstructural Characterisation

Metallurgical examination of cast alloys using optical microscopy was undertaken using an Olympus GX51 microscope. Specimens were mounted, ground using SiC papers and polished to a 0.25 μm surface finish using an alumina suspension.

TEM was undertaken in a JEOL 2100 microscope, operated at 200 kV in scanning TEM mode (STEM), equipped with an EDAX-Ametek Octane T Optima 60 detector. Foils for TEM observations were prepared by mechanically polishing sections of specimens to a thickness of 45 μm followed ion beam milling to electron transparency by using a Gatan PIPS operated at 5 keV at 5° to -5° with dual beam mode.

Quantification of TEM images was conducted using open source software (ImageJ) [129]. Precipitate radii were measured and, assuming a perfectly spherical shape, the volume of the precipitates was then calculated. The volume fraction was also calculated as the total volume of precipitates divided by the volume of the TEM foil that contained them. In this calculation the TEM foil thickness was measured to be 120 nm. The number density was calculated as the number of precipitates divided by the volume of the TEM foil.
4.3.3 Small-angle X-ray Scattering Measurements

Specimens for the SAXS measurements of approximately $10 \times 10 \times 0.8$ mm in size were cut from the heat treated samples using a diamond saw. These specimens were mechanically ground on both sides using progressively finer SiC papers down to P4000 grade. In order to ensure effective transmission the average sample thickness was kept constant at approximately $215 \pm 10$ μm. Thickness variation on each individual specimen was measured to be approximately 10 μm.

SAXS experiments were performed on the I22 beamline of the Diamond Light Source (DLS) in the UK. A monochromatic beam of wavelength $\lambda=0.67$ Å (i.e. of energy 18.5 keV) was employed. The beam size was $120 \times 350$ μm and samples had an average grain size of approximately 70 μm. This combination enabled the beam to illuminate a large number of precipitates within a number of grains. The sample to detector distance was set to 2.907 m and kept constant throughout the experiments. The accessible range of scattering vector, $q$, was thus 0.01 to 0.6 Å$^{-1}$. The exposure time was set to 1 s and the data were collected by Pilatus P3-2M detector. On every specimen 30 exposures were acquired and averaged in order to reduce noise. In total 13 different specimens (including the reference binary Al-6.8Si (wt.%) samples) were investigated. The photon counts on the detector were converted to absolute scale by measuring a glassy carbon sample as a secondary standard for absolute intensity calibration and detector pixels were converted to the scattering vector, $q$, by measuring a reference silver behenate sample as a standard [124].

4.4 SAXS Methodology and Data Analysis

If the precipitates are not interacting (i.e. the interparticle distance is large compared to the precipitate size) then the total scattering intensity is the sum of the intensity scattered by individual precipitates [99]. In this case, and assuming a size dispersion function $f(r)$ that corresponds to the density of precipitate of size $r$, the total scattering intensity is given by [99]:
where \( q \) is the scattering vector \((q=(4\pi \sin \theta)/\lambda \) where the scattering angle is \( 2\theta \) and \( \lambda \) is the wavelength\) and \( B \) is the background constant.

Our analysis was primarily based on three types of plots, namely the Guinier, Kratky and Porod plots, and the evaluations were directly carried out from the scattering data.

The precipitate size was determined by the Guinier plot \((\ln(I) vs q^2) [122]\). The Guinier approximation was used, since it is a well-established analysis method in metallic systems \([102, 106-108, 120, 121]\). The precipitate parameter that can be extracted is called the radius of gyration \( (R_g) \). \( R_g \) depends on the size distribution and has been shown to give an accurate description of the mean precipitate radius for lognormal distributions with a dispersion parameter \( (s) \) close to \( 0.2 \) \([107, 116, 122]\). Here, a self-consistent method proposed by Deschamps and De Geuser \([122]\) was followed in order to determine \( R_g \). It should be noted that Guinier approximation is only valid in dilute solutions where the interaction between precipitates is negligible.

Another representative SAXS plot is the Kratky plot, where \( Iq^2 \) is plotted versus \( q \). Kratky plots are characterised by a predominant peak, where the curve reaches a maximum at \( q_{\text{max}} \). In the monodisperse case \((i.e. \) particles of identical size\), the position of this peak is related to \( R_g \) through the following relationship:

\[
R_g = \frac{\sqrt{3}}{q_{\text{max}}} \quad \quad (4.2)
\]

However, in polydisperse cases this value deviates from \( R_g \) and here is referred to as \( R_{\text{pseudo}} \). A comparison between \( R_g \) and \( R_{\text{pseudo}} \) provides an indication of the precipitate size distribution \([122]\).
Kratky plots can also provide an indirect estimation of the precipitate volume fraction since the latter is proportional to the integrated intensity $Q$ via the following equation:

$$Q = \int_{0}^{\infty} I(q)q^2dq = 2\pi^2 (\rho_p - \rho_m)^2 f_v (1 - f_v)$$

(4.3)

where $Q$ equals the area under the curve in the Kratky plot, $\rho_p$ and $\rho_m$ are the electron densities of precipitates and matrix, respectively, and $f_v$ is the volume fraction of precipitates. Eq. 4.3 is only valid for the homogeneous two-phase model with phases separated by a sharp interface [107].

The Porod plot ($Iq^4$ vs $q$) provides a visual indication of the chemical structure of the precipitates. For example, a uniform precipitate composition produces a different Porod profile compared to a core-shell chemical composition and can be identified by the overall profile of the Porod plot [72, 79, 123]. In conjunction with the $Q$ parameter we calculate Porod radius ($R_p$) with the following relationship:

$$R_p = \frac{3Q}{\pi K_p}$$

(4.4)

where $K_p$ is the horizontal asymptote in the Porod plot. $R_p$ represents the radius of a sphere of surface-to-volume ratio which is equal to that of the precipitate size distribution [122].

### 4.5 Results

In order to support the objectives of this study, the yield strength measurements of both the LA and HA alloys (referred to as Alloy 1 and Alloy 2, respectively) were provided in section 2.6. Here the microscopy and SAXS results are presented.

#### 4.5.1 Microstructure of the Alloys

Optical microscopy was employed to characterise the large-scale microstructure of samples whilst TEM provided local qualitative information that can be used to support the interpretation of the SAXS measurements.
4.5.1.1 Optical Microscopy

Both alloys exhibit an equiaxed dendritic microstructure comprising $\alpha$-Al dendrites and eutectic silicon as shown in Figures 4.1a and 4.1b for the LA and HA alloys, respectively. A small fraction of dark grey faceted particles was found to be present in both alloys (e.g. the arrowed features in Figure 4.1a and 4.1b). These were identified by energy dispersive X-ray analysis in the scanning electron microscope to be mainly Zr-rich and are presumably primary pro-peritectic $\text{Al}_3(Zr,V)$ [130]. This would have formed during alloy solidification as the cooling rate was 25 Ks$^{-1}$, which has been shown to be insufficient to suppress the formation of primary pro-peritectic phases in the Al-Si-Zr-V alloy [17].

![Figure 4.1 Optical images of a) LA and b) HA alloy in the as-cast condition. It is evident that secondary phases are present.](image)

4.5.1.2 Transmission Electron Microscopy

STEM was used to examine alloys in the as-cast state and following ageing for different times with images obtained in both bright field (BF) and high angle annular dark field (HAADF) modes. In the as-cast condition, an aluminium sub-grain structure was found with no evidence for precipitation as seen in the BF image of the HA alloy in the insert of Figure 4.2a. Following ageing at 400 °C, fine-scale spherical precipitates, typically 12 to 20 nm in diameter, were observed as revealed in the BF and corresponding HAADF image of Figures 4.2a and 4.2b, respectively, taken from the HA alloy following ageing for 50 h. The precipitate distribution is clearly heterogeneous and their spherical shape (insert of Figure 4.2b) strongly suggests that they are the cubic L1$_2$ form of $\text{Al}_3(Zr,V)$ which are commonly seen in alloys containing appreciable levels of Zr and V [34, 85, 87].
Figure 4.2 TEM a) bright-field and b) dark-field images acquired on HA alloy after ageing at 400 °C for 50 h showing spherical precipitates. Inserts: a) the as-cast microstructure showed no evidence for precipitation and b) high magnification image of the spherical precipitates.

The heterogeneous nature of the precipitate distribution, combined with the small field of view required, makes quantification through TEM difficult and hence it was undertaken only on the HA alloy. The main results are summarised in Table 4.2 which lists the mean precipitate radius ($R_{\text{TEM}}$), volume fraction and number density of precipitates for three different ageing times. The measurements reveal a monotonic increase in precipitate mean size with time. After 50 h at 400 °C, the mean precipitate radius in the HA alloy was 7.8 nm. However, the measured volume fraction, following ageing for different times, was found to fluctuate around 0.25 vol.% which could be due to the difficulties in obtaining representative data from heterogeneous precipitate distributions. In conjunction with the increase of the precipitate size, the precipitate number density continuously decreased with ageing time. Errors in Table 4.2 represent the standard deviation of the image analysis measurements.

<table>
<thead>
<tr>
<th>Ageing Time (h)</th>
<th>$R_{\text{TEM}}$ (nm)</th>
<th>Volume Fraction (vol.%</th>
<th>Number Density ($\text{m}^{-3}$)</th>
<th>Precipitates Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.7 ± 0.4</td>
<td>0.29 ± 0.13</td>
<td>37.0 ± 14.8×10^{21}</td>
<td>500</td>
</tr>
<tr>
<td>23</td>
<td>6.2 ± 0.8</td>
<td>0.19 ± 0.08</td>
<td>2.0 ± 0.9×10^{21}</td>
<td>354</td>
</tr>
<tr>
<td>50</td>
<td>7.8 ± 0.9</td>
<td>0.25 ± 0.07</td>
<td>1.3 ± 0.5×10^{21}</td>
<td>202</td>
</tr>
</tbody>
</table>

Table 4.2 Values of precipitate radius, $R_{\text{TEM}}$, precipitate volume fraction and number density for different ageing times in the HA alloy, as determined from the TEM images. Errors represent the standard deviation of the image analysis measurements.
4.5.2 SAXS Measurements

In every specimen tested, scattering was found to be isotropic with no evidence of perpendicular variations in the detector image. Raw scattering measurements in the range 0.01 to 0.35 Å⁻¹ for the Al-6.8Si (wt.%) reference alloy at five different ageing times are shown in Figure 4.3. It is clear that ageing the reference alloy did not affect the SAXS spectrum.

![Figure 4.3 Raw scattering intensities of the binary Al-Si reference alloy. The scattering spectrum remained unaffected following the heat treatment.](image)

However, when scattering data were collected from the LA and HA alloys, the spectra continually evolved with ageing time as seen in Figures 4.4a and 4.4b. It is apparent that the deviations from the reference alloy spectrum increased with ageing time. Figures 4.4c and 4.4d, in which the reference alloy spectra have been subtracted from the LA and HA alloy spectra respectively, confirm this. It is evident that there is a progressive change in the characteristic shape of the SAXS profiles with ageing time in the range 0.02 to 0.1 Å⁻¹. In this range, every specimen features a slope change that progressively shifts towards the lower q region and is accompanied by an increase in intensity. This increase in intensity presumably reflects an increasing volume fraction of precipitate and the shift to lower q is indicative of an increase in precipitate size. This is observed in both the LA and HA alloys, correlating well with the TEM study. Furthermore, the average slope of the scattering data at the high q region was found to be -4 which is characteristic of precipitates that are separated from the matrix by a sharp interface [99].
It should be noted that the spectra in Figures 4.4c and 4.4d have been also corrected for Laue scattering. Laue scattering is independent of $q$, and is related to a disordered solid solution and fluorescence of elements in the material [99]. In all subsequent plots of the SAXS data the intensity has been corrected for this Laue scattering using the standard methodology described elsewhere [99]. The determination of $I_{\text{Laue}}$ is given in Appendix B.

Figure 4.4 The raw scattering spectra of a) LA and b) HA alloy and the scattering spectra after subtracting the reference sample and correcting for Laue scattering of c) LA and d) HA alloy. The average slope at the high $q$ region is characteristic of precipitates that are separated from the matrix by a sharp interface.

In order to establish that micron-sized secondary phases (i.e. the coarse eutectic Si plates and needles seen in the optical microscope images) did not produce additional scattering in the range quantified, a limited number of scattering spectra were acquired outside the normal observation range. In these experiments, the accessible range of scattering vectors was from 0.0045 to 0.01 Å$^{-1}$, so that length scales of the order of 60 to 140 nm could also be investigated. A representative example is shown in Figure 4.5 for the HA alloy aged for 5 h. In this figure, there is no evidence of deviation from linearity which confirms that additional
scattering from large secondary phase particles was not detected. It also indicates that the presence of such structural features will not influence the measurements of nano-sized precipitates in the normal observation range of 0.01 to 0.6 Å⁻¹.

Azimuthally integrated SAXS data for the HA alloy are presented in Figure 4.6 for different ageing times. Figure 4.6a is the Guinier representation (ln(I) vs q²), Figure 4.6b is the Kratky representation (Iq² vs q) and Figure 4.6c is the Porod representation (Iq⁴ vs q). Their detailed interpretation is provided in the following section. These plots are representative of those that were also obtained from the LA alloy, which are given in Appendix B.

4.5.3 Quantification of precipitate development

Figure 4.6a shows the Guinier representation of SAXS data acquired from HA alloy. It is clear that there is a progressive change in slope with ageing time and the same trend was also found in LA alloy. As the ageing time progresses, the slope below 0.02 Å⁻² becomes more negative as a result of precipitate growth. The Guinier radius was calculated from the slope of a linear part of the scattering curves and was determined using the self-consistent method proposed by Deschamps and De Geuser [122]. The uncertainty in \( R_g \) was determined from the error associated with the slope of the linear fit. Table 4.3 summarises the calculated \( R_g \) values and the associated errors for both LA and HA alloys.
Figure 4.6 The three basic plots of the HA alloy a) Guinier, b) Kratky and c) Porod.

Table 4.3 $R_g$, $R_{\text{pseudo}}$ and $R_p$ values calculated at different ageing times for both alloys. The errors calculation is described in the text and is given in Appendix A.

<table>
<thead>
<tr>
<th>Ageing Time (h)</th>
<th>$R_g$ (nm)</th>
<th>$R_{\text{pseudo}}$ (nm)</th>
<th>$R_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.44±0.01</td>
<td>2.47±0.05</td>
<td>1.23±0.21</td>
</tr>
<tr>
<td>5</td>
<td>3.17±0.02</td>
<td>2.71±0.05</td>
<td>2.83±0.05</td>
</tr>
<tr>
<td>10</td>
<td>5.32±0.06</td>
<td>4.57±0.10</td>
<td>2.05±0.35</td>
</tr>
<tr>
<td>23</td>
<td>6.94±0.12</td>
<td>6.30±0.15</td>
<td>5.04±0.15</td>
</tr>
<tr>
<td>50</td>
<td>8.82±0.12</td>
<td>7.28±0.20</td>
<td>6.79±0.20</td>
</tr>
</tbody>
</table>

Figure 4.6b shows the Kratky representation for HA alloy. In this representation, the maxima in the plots arise from precipitates of approximate size indicated by the upper $x$-axis scale and the area under the curves is related to the precipitate volume fraction. Two trends can be readily seen. The first one is that the main peak shifts towards smaller $q$ values which is representative of precipitate growth.
The dimension $R_{p\text{seudo}}$ was calculated using eq. 4.2 and uncertainties were determined by the error associated with identifying the $q_{\text{max}}$ (Table 4.3). The second trend is the evolution of the area under the curve ($Q$). As ageing time progresses $Q$ becomes larger which is an indication of an increase in the right hand side of eq. 4.3. In order to calculate the volume fraction using eq. 4.3 we need to determine the $Q$ and the contrast parameter $(\rho_p - \rho_m)^2$.

Determination of $Q$ necessitates integration between $q=0$ and $q=\infty$ which is an extremely difficult procedure as described in detail in reference [131]. In the present study the approach used was to fit the $Iq^2$ vs $q$ data with a lognormal distribution and extrapolate the fit to 0 and $\infty$. The lognormal distribution is described by two parameters, namely a mean and a standard deviation; the latter termed the dispersion parameter, $s$. The best lognormal fit was determined by an iterative sequence which stopped when the deviation was less than $10^{-7}$ from the previous fit. This provides a systematic and unbiased estimate of the area under the curve although there is uncertainty associated with the definition of the fitting range. Moreover, by employing a lognormal distribution the dispersion parameter, $s$, of the distribution was also obtained. A lognormal distribution was selected because $s$ is reported to provide a valid approximation of the precipitate size distribution in many metallic systems [113, 116, 122].

In order to convert this integrated intensity into volume fraction, the difference in scattering length densities between the precipitate phase ($\rho_p$) and the matrix ($\rho_m$) must also be calculated. We therefore need to determine their compositions. Based on energy dispersive spectroscopy (EDS) measurements in the TEM, the precipitate composition was found to be close to the stoichiometric Al$_3$Zr; the V content in the precipitates was below the detection level. However, as shown for the Al-Zr-Sc system [77], due to the difference in partition coefficient during solidification, the precipitate composition is expected to vary; i.e. the precipitates towards the dendrite centres are expected to contain more V than those towards the dendrite edges. For this reason, the volume fraction of precipitate phases was calculated for two assumed compositions, namely Al$_3$Zr and Al$_3$Zr$_{0.8}$V$_{0.2}$. The matrix composition was assumed to be pure aluminium and additions of silicon in
Chapter 4: Characterising Precipitate Evolution in Multi-component Cast Aluminium Alloys using Small-Angle X-ray Scattering

The precipitates do not significantly affect the results. The resultant volume fractions for both compositions are listed in Table 4.4.

**Table 4.4** SAXS measurements of precipitate volume fraction for different ageing times in both alloys. Values given for two assumptions of precipitate composition. Error calculation is given in Appendix A.

<table>
<thead>
<tr>
<th>Ageing Time (h)</th>
<th>Volume fraction (%)</th>
<th>LA</th>
<th>HA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al$_3$Zr</td>
<td>Al$<em>3$Zr$</em>{0.8}$V$_{0.2}$</td>
<td>Error</td>
</tr>
<tr>
<td>3</td>
<td>0.11</td>
<td>0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td>10</td>
<td>0.23</td>
<td>0.24</td>
<td>0.04</td>
</tr>
<tr>
<td>23</td>
<td>0.24</td>
<td>0.26</td>
<td>0.04</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.6c is the Porod plot for the HA alloy. For clarity only two Porod profiles are presented; one for 23 h and one for 50 h. Both curves feature a main well-defined peak and with a smaller one at the higher $q$ range. This form of Porod plot is reported to be characteristic of the spherical polydisperse, chemically uniform composition [72, 79, 123] for the precipitate phases. Every LA and HA specimens produced a similar Porod profile and the oscillations in amplitude around the smaller peak were found to decrease with increasing dispersion parameter as calculated from the lognormal distribution fit.

The Porod radius, $R_p$, was calculated from $K_p$ and $Q$ using eq. 4.4. For consistency, $K_p$ which is the horizontal asymptote in the Porod plot, can be also determined by the intercept in the $I_{sub}q^4$ vs $q^4$ plot [122] which is given in Appendix B. The uncertainty on $R_p$ was determined by the error associated with the volume fraction calculation and the definition of $K_p$. In both alloys $R_p$ was found to increase with ageing time and $R_p$ values with the associated errors are shown in Table 4.3.

### 4.6 Discussion

SAXS and TEM provide complementary information about the precipitate evolution. In this study, unlike prior TEM investigations on similar alloys [84, 85, 87, 89], at every ageing stage, billions of precipitates were measured. The main
difficulty is to determine the validity of SAXS size measurements that compare with the TEM data. This is because the $R_g$ measurement is driven by two changes; a change of the actual precipitate size and a change in the size distribution. Furthermore, based on the SAXS measurements, it is valuable to consider the main features of the precipitate evolution in relation to the existing knowledge of aluminium alloys with Zr and V additions.

![Graphs showing predicted Guinier radius ($R_g$), pseudo-Guinier radius ($R_{pseudo}$), Porod radius ($R_p$) and radius calculated from TEM ($R_{TEM}$) vs the heat treatment time for a) LA and b) HA alloy and c) the normalised Kratky profiles of HA alloy.]

Figure 4.7 Predicted Guinier radius ($R_g$), pseudo-Guinier radius ($R_{pseudo}$), Porod radius ($R_p$) and radius calculated from TEM ($R_{TEM}$) vs the heat treatment time for a) LA and b) HA alloy and c) the normalised Kratky profiles of HA alloy.

4.6.1 Analysis of Precipitate Sizes

Figures 4.7a and 4.7b show the values of $R_g$, $R_{pseudo}$, $R_p$ and radius calculated from TEM measurements ($R_{TEM}$) for LA and HA alloy, respectively. It has been previously shown that $R_g$ gives an accurate description of the average precipitate radius for lognormal distributions with a dispersion parameter close to 0.2 [107, 116, 122]. $R_g$ and $R_{TEM}$ are estimations of the precipitate radius, $R_{pseudo}$ is an approximation of $R_g$ and its difference to the latter provides an indication of size distribution. Finally, $R_p$ also provides an indication of precipitate size distribution.
In order to compare the $R_g$ and $R_{\text{TEM}}$ radii estimations, we first have to validate the size distribution evolution. An estimation of the precipitate size distribution evolution can be directly obtained by normalising the Kratky curves. The procedure applied is as follows. Kratky curves were fitted with a lognormal distribution and the fitting parameters were obtained. It was found that in both alloys the dispersion parameter $s$ becomes larger with time. Based on these parameters Kratky profiles were simulated and extrapolated to $q$ range for which no experimental information is available (0 and $\infty$). Simulated profiles were then normalised and the results for HA alloy are shown in Figure 4.7c. The $q$ axis was normalised by the scattering vector at which profiles show the peak maximum and the $Iq^2$ axis was normalised by its maximum value. In this figure, the progressive change in the width of the normalised Kratky profiles can be either attributed to a change in precipitate morphology or size distribution. TEM provided no evidence of precipitate morphology alternation, so the evolution of the normalised width arises from the size distribution change. Figure 4.7c shows that when size distribution increases, the normalised width of the Kratky profile increases. As expected, the same trend was also found in LA alloy where $s$ was observed to be slightly smaller.

The deviation between $R_g$ and $R_{\text{pseudo}}$ can also provide a relative indication of size distribution evolution. In the monodisperse case, these values are identical and remain in fair agreement up to a dispersion parameter of 0.25. With a dispersion parameter of 0.3 or more the values deviate and $R_g$ is reported to be larger than $R_{\text{pseudo}}$ [122]. In our case, their deviation as a function of time verifies the size distribution evolution which was predicted from the normalised Kratky curves. As seen in both alloys at 3 h and 5 h where $s$ is close to 0.2, $R_g$ and $R_{\text{pseudo}}$ values are close. In both alloys, the difference increases with ageing time. As $s$ increases above 0.3 the deviation becomes larger and at the final ageing stages $R_g$ and $R_{\text{pseudo}}$ deviate strongly as the dispersion parameter exceeds 0.4.

The evolution of $R_p$ was found to be in agreement with the results reported above. In both alloys, $R_p$ was found to constantly increase with the increase of the dispersion parameter. In our investigation, $R_p$ values were found to be constantly smaller than $R_g$ and $R_{\text{pseudo}}$, which fits well for dispersion parameters larger than
0.2 [122]. The large uncertainties involved in the $Q$ and $K_p$ calculations make $R_p$ difficult to determine with high precision. This is the reason why in many investigations $R_p$ is not reported although, direct evaluation methods on SAXS data are employed [106-108, 121, 132].

After establishing the size distribution evolution, detailed above, the $R_g$ and $R_{TEM}$ comparison is discussed here. It should be noted that the $R_{TEM}$ values may be subjected to biases related to the wide size distribution which is associated with the heterogeneous distribution of precipitates. The deviation between $R_g$ and $R_{TEM}$ was found to become larger as size distribution increased. In both alloys, at the first ageing stages, where $s$ is close to 0.2, $R_g$ and $R_{TEM}$ values are almost equal. This relationship between $R_g$ and $R_{TEM}$ at dispersion parameters close to 0.2 was used in a number of investigations [107, 115, 122]. While ageing time progresses and the size distribution evolves, the deviation between $R_g$ and $R_{TEM}$ becomes larger. Overall, $R_g$ provides a better estimate for $R_{TEM}$ at the beginning of ageing where the size distribution is small. The precipitate radii of both alloys at 50 h are in reasonable agreement with values previously reported for similar arc-melted alloys [60, 89].

The coarsening rate constant of the classical Lifshitz, Slyozov and Wagner (LSW) theory was calculated from the $R_g$ measurements (Figures 4.7a and 4.7b). The calculated values are $1.41 \times 10^{-26}$ m$^3$h$^{-1}$ and $1.45 \times 10^{-26}$ m$^3$h$^{-1}$ for LA and HA alloy, respectively. Both values are in broad agreement with values reported for the ternary Al-Zr-V alloy system [34, 85, 87, 89] although slightly larger. However, additions of Si were shown to accelerate the precipitation kinetics in Zr containing alloys [65-67, 133] and $R_g$ measurements are partially driven by the evolution of the precipitate size distribution. Hence, although they provide a valid estimation, these values should be considered as an upper limit of the coarsening rate constant.

4.6.2 Main Features of the Precipitate Evolution

In order to gain a better understanding of the precipitate evolution we compared the volume fraction and number density results for both alloys. Based on the lever rule and assuming that the precipitate volume fraction is dictated primarily by the
Zr concentration, the calculated values are approximately 0.4 vol.% and 0.5 vol.% for LA and HA alloy, respectively.

Figure 4.8a shows the precipitates volume fractions in both alloys assuming an \( \text{Al}_3\text{Zr} \) and an \( \text{Al}_3\text{Zr}_0.8\text{V}_{0.2} \) composition. In both cases, it is apparent that the HA alloy has a larger volume fraction compared to the LA. This is not surprising given the higher concentration of precipitating elements in the HA alloy. However, the volume fraction in both alloys is lower compared to the lever rule prediction. This is attributed to the reduction of the available solute, as a result of the precipitation of primary pro-peritectic phases during solidification (Figures 4.1a and 4.1b). Figure 4.8a also shows that in both alloys the volume fraction continuously increases with time and the increase remains fast up to 23 h. The highest value does not exceed 0.36 vol.% in the HA alloy while the lowest is 0.11 vol.% in the LA aged for 5 h. The volume fraction ratio of the alloys was found to be close to 1.35 for 5, 23 and 50 h. Again, the calculation of the precipitate volume fraction using TEM is subjected to biases related to the heterogeneous distribution of precipitates in the dendritic microstructure. However, the volume fraction values calculated from TEM (Table 4.2) are in broad agreement with SAXS results.

![Figure 4.8 a) Volume fraction and b) number density comparison between LA and HA alloys.](image-url)
The number density of precipitates was determined by assuming a perfectly spherical shape and using the following relationship:

\[ N = \frac{f_v}{\frac{4}{3} \pi R_g^3} \]  

(4.5)

where \( f_v \) is the precipitate volume fraction and \( R_g \) the radius of gyration obtained by the Guinier plot.

Figure 4.8b shows the number density values in both alloys. It is evident that number density continuously decreases with ageing time. During the nucleation stage when the driving force for precipitation is high, small precipitates are formed having a high number density which quickly peaks. This stage was not included in our experiment since this study focused on later ageing stages. In our alloys, despite the significant increase in the volume fraction, the number density declines. This behaviour might be the result of an overlap in the growth and coarsening regimes. Nevertheless, high number densities were recorded with the highest value exceeding \( 2 \times 10^{22} \) m\(^{-3} \) in the HA alloy aged for 3 h. At this condition more than \( 10^{11} \) precipitates were measured. TEM number density results (Table 4.2) show good agreement with SAXS measurements.

### 4.7 Summary and Conclusions

In the present study, the combination of transmission electron microscopy and small angle X-ray scattering has been employed to quantitatively characterise the precipitate evolution in two multi-component cast aluminium alloys, featuring a particularly low volume fraction of precipitates. In detail:

- We analytically demonstrated the methodology and data treatment in order to successfully characterise the precipitate evolution in multi-component casting alloys. The background constant was removed by employing a valid reference sample which was established by SAXS measurements. Furthermore, we proved that coarse secondary phases encountered in multi-component cast alloys cannot deteriorate nano-scale SAXS measurements.
- Using model-independent and self-consistent methods we characterised the precipitate evolution. At every ageing stage, billions of precipitates were
measured. The average precipitate size was obtained and a valid coarsening rate constant was also determined. The volume fraction in both alloys constantly increased with time as a result of slow element diffusivity. However, number density followed the reverse pattern. This was attributed to the precipitate coarsening since the investigation was not conducted during the initial nucleation stage. In both alloys the precipitate size distribution was quantified and was observed to continuously increase with time. This was verified by the normalised simulated Kratky profiles, the $R_p$ evolution and the $R_g$ to $R_{pseud}$ deviation as a function of time.

- The TEM study confirmed the morphology of the precipitates throughout the heat treatment and also provided reliable information over the average precipitate size and composition. Precipitate volume fraction and number density values are in good agreement with SAXS measurements.

Overall, the results indicate that after the nucleation stage, both alloys quickly enter a regime where growth and coarsening overlap and the number density continuously decreases with time. This regime starts in both alloys when the precipitate volume fraction is significantly lower than the one reported at 50 h. We believe that at 400 °C the nucleation stage lasts less than an hour and can be fully characterised during an in situ SAXS experiment where higher number densities will be recorded.

**Acknowledgements**

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Chapter 5: Summary and Conclusions

The work presented in this thesis is intended to help accelerate the development of high temperature cast aluminium alloys for automotive applications. In this study, we investigated the addition of both Zr and V for developing high temperature strength by introducing metastable cubic $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ precipitates. TEM and *ex situ* SAXS have been successfully employed in order to characterise the precipitate evolution in two Al-6.8Si (wt.%) alloys with different levels of Zr and V additions. However, further work is needed in order to establish how V partitions between the different phases in the microstructure, as TEM-EDS was unable to detect V in the L1$_2$ precipitates. Nevertheless, the combination of TEM and *ex situ* SAXS allowed the successful characterisation of the heterogeneously distributed L1$_2$ precipitates, despite their overall very low volume fraction (<0.4 vol.%). The quantitative results include the average precipitate size, precipitate size distribution, volume fraction and number density.

The following observations and conclusions were made:

- In both alloys the average precipitate radius was found to increase with ageing time from approximately 2 nm at 3 h to 9 nm at 50 h. The coarsening at 400 °C suggests that the alloys cannot be used at this temperature. Nevertheless, the operating temperature in an engine is 300 °C, where the precipitates are likely to be thermally stable. For the HA alloy, the average precipitate radius from the TEM measurements was found to be consistently smaller than $R_g$, however the trends with ageing time were consistent.

- Analysis of SAXS data implies that in both alloys, the precipitate size distribution continuously increases with ageing time due to precipitate coarsening. A valid upper limit of the coarsening rate constant was also determined from the SAXS measurements.

- SAXS provided strong evidence that the precipitate volume fraction continuously increases with ageing time up to 50 h, which is attributed to the slow element diffusivity. The HA alloy attained slightly higher precipitate volume fraction compared to LA and the highest value recorded was less than 0.36 vol.% at 50 h. The number density followed the reverse pattern, as expected.
• The TEM investigation confirmed the precipitate morphology throughout the heat treatment and also provided valid information on the mean precipitate size and composition. Precipitate volume fraction and number density, although in broad agreement with the SAXS measurements might be subjected to biases related to the heterogeneously distributed precipitates.

Together, the findings from this investigation provide evidence that these multi-component alloys have a short nucleation stage and quickly enter a regime where the precipitate growth and coarsening overlap, and the number density decreases with time. At 400 °C, the precipitate coarsening starts before 3 h when the volume fraction is significantly lower compared to 50 h.

Overall, the present study demonstrates the advantages and limitations of synchrotron SAXS when characterising multi-component cast aluminium alloys with heterogeneously distributed precipitates and large secondary phases. The methodology and data treatment that were applied on the *ex situ* data can now be used as a guide to analyse the data collected during the *in situ* experiment. The *in situ* data of the LA alloy can shed more light on the effect of ageing temperature on the precipitation kinetics by providing new insights of the nucleation regime and the onset of the precipitate coarsening.

### 5.1 Related Work

Chapter 4 of the present thesis is due to be submitted to the “*Journal of Alloys and Compounds*” for publication under the title: Characterising Precipitate Evolution in Multi-component Cast Aluminium Alloys using Small-Angle X-ray Scattering.

Moreover, this project generated the *in situ* data of the LA alloy that will be analysed in the future and further enhance the collaboration between the University of Manchester and Ford Motor Company.
References

[35] K.E. Knipling, R.A. Karnesky, C.P. Lee, D.C. Dunand, D.N. Seidman, Precipitation evolution in Al-0.1Sc, Al-0.1Zr and Al-0.1Sc-0.1Zr (at.%) alloys during isochronal aging, Acta Materialia, 58 (2010) 5184-5195.


[78] K.E. Knipling, D.N. Seidman, D.C. Dunand, Ambient- and high-temperature mechanical properties of isochronally aged Al–0.06Sc, Al–0.06Zr and Al–0.06Sc–0.06Zr (at.%), alloys, Acta Materialia, 59 (2011) 943-954.


Appendix A

Fitting range determination: this self-consistent procedure to determine $R_g$ was first reported by Deschamps and De Geuser [122]. The procedure applied is as follows. In order to calculate the linear slope in the Guinier plot, it is necessary to define the boundaries of the $q$ range that fits are performed in a self-consistent way. For this reason, fits were performed between constant values of $qR_g$, e.g. in the range $\alpha/R_g < q < \beta/R_g$. In our case, $\alpha=1$ and $\beta=2$. Since the fitting range depends on the $R_g$, at the beginning we had to make an estimation of this value to iterate the process. Our first estimation of the $R_g$ was the $R_{\text{pseudo}}$ radius obtained from the Kratky plot. The linear fitting between these boundaries led to a first value of $R_g$. This value was then employed to refine the fitting boundaries and the iteration process stopped when the fit converged. It is worth mentioning that in Figure 4.6a the fitting range does not remain constant for every Guinier curve since it is defined by the $R_g$.

Errors of SAXS measurements

$R_g$ error: the uncertainty in $R_g$ was determined from the error associated with the slope in eq. 3.3 and calculated from the following equation:

$$\sigma_{R_g} = \frac{1}{2} \sqrt{\frac{-3}{\alpha}} \sigma_\alpha$$

where $\alpha$ is the slope value and $\sigma_\alpha$ is the error of the slope as determined by the fitting software.

Precipitate volume fraction error: the precipitate volume fraction error was calculated from the errors associated with the data calibration and the fitting range. The data calibration error was estimated to be 15% (total error for absolute intensity calibration, background subtraction and Laue correction) and was kept constant for every ageing stage that was investigated. The errors associated with the fitting range ($\sigma_{Rg}$) were individually determined (ranged between 6-9%) by changing the boundaries of the lognormal fit in the Kratky plots. Hence, the total volume fraction error ($\sigma_{fv}$) was calculated as follows:
\[
\sigma_{R_p}(\%) = \sqrt{0.15^2 + \sigma_{R_p}^2} \times 100
\]

\( R_p \) error: the uncertainty in \( R_p \) was calculated by the error associated with the volume fraction calculation and the definition of \( K_p \). The \( K_p \) error (\( \sigma_{K_p} \)) was individually determined for every ageing stage (ranged between 2.5-4\%). The total \( R_p \) error (\( \sigma_{R_p} \)) was calculated as follows:

\[
\sigma_{R_p}(\%) = \sqrt{0.15^2 + \sigma_{R_p}^2 + \sigma_{K_p}^2} \times 100
\]

Number density error: the uncertainty in number density was determined from the errors associated with the \( R_g \) and the precipitate volume fraction using the following equation:

\[
\sigma_{nd} = \sqrt{\left( \frac{3\sigma_{f_g}}{4\pi R_g^3} \right)^2 + \left( \frac{-9\sigma_{R_g}}{4\pi R_g^4} \right)^2}
\]

where \( R_g \) is the radius of gyration, \( \sigma_{f_g} \) and \( \sigma_{R_g} \) are the errors associated with volume fraction and radius of gyration, respectively.

Scattering length density

The scattering length densities of the precipitate phases and matrix were calculated as follows:

\[
\rho_x = \frac{b_e \rho_m N_A}{M} \sum_i n_i z_i
\]

where \( \rho_m \) is the mass density, \( M \) is the molecular weight, \( N_A \) is Avogadro’s number, \( n_i \) is the number of atoms of type \( i \), \( z_i \) is the atomic number of atom \( i \) and \( b_e \) is the scattering length of an electron which equals 2.85\times10^{-5} \text{ Å}. The scattering length density has units of \( \text{Å}^{-2} \). For a stoichiometric Al\(_3\)Zr composition, the scattering length density was calculated to be 3.3\times10^{-5} \text{ Å}^{-2}, whilst assuming an Al\(_{1}\)Zr\(_{0.8}\)V\(_{0.2}\) composition the result was 3.2\times10^{-5} \text{ Å}^{-2}. The scattering length density of the aluminium matrix was calculated to be 2.2\times10^{-5} \text{ Å}^{-2}. 

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Appendix B

Appendix B will be submitted for publication as supplementary material.

In the two figures below, the reference alloy spectra have been subtracted from LA and HA alloy spectra, respectively. The intensity is now referred to as $I_{\text{sub}}$. It is seen that in the high $q$ region every curve converges to approximately the same intensity value. This behaviour is attributed to Laue scattering, which is independent of $q$, and is related to a disordered solid solution and fluorescence of elements in the material [99].

Laue scattering was determined by plotting $I_{\text{sub}}q^4$ vs $q^4$. The slope is equal to $I_{\text{laue}}$ and was subtracted from $I_{\text{sub}}$. The result is presented in Figures 4.4c and 4.4d, in which for simplicity the intensity is called $I$.

Also in the $I_{\text{sub}}q^4$ vs $q^4$ plot, the intercept equals $K_p$ and was used in the Porod radius calculation.
The Guinier, Kratky and Porod representation of LA alloy. The plots follow the same trends as those reported for HA alloy.

The three basic plots of the LA alloy a) Guinier, b) Kratky and c) Porod.

SAXS was employed on the HA alloy aged at 400 °C for 10 h and the same specimen was also investigated using TEM (300 precipitates were quantified). This specimen was not included in the main results chapter because it was cut from a different bar (unlike all the other specimens) and was heat treated separately by Ford. However, the comparison between the two techniques shows good agreement with the results presented previously.

<table>
<thead>
<tr>
<th>Radius (nm)</th>
<th>Volume Fraction (vol. %)</th>
<th>Number Density (m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM</td>
<td>SAXS</td>
<td>TEM</td>
</tr>
<tr>
<td>2.90±0.30</td>
<td>4.39±0.05</td>
<td>0.21±0.07</td>
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