Quantitative Characterization of Nanovoids in Quenched Aluminum
Using Small Angle X-ray Scattering Studies

by
Arnab Chaudhuri

A thesis submitted to the Department of Physics, Engineering Physics and Astronomy
in conformity with the requirements for
the degree of Master of Science

Queen’s University, Canada
October, 2011

Copyright © Arnab Chaudhuri, September 2011
To my parents
Abstract

A small angle X-ray scattering (SAXS) study of quenched-in nanovoids in 99.988 and 99.995 at.% aluminum (Al) is presented. Nanovoids are agglomerations of point defects (vacancies) in the metallic host. SAXS is a non-destructive, dynamic probe which is ideally suited to characterize nanoscale electron density inhomogeneities, e.g., electron density difference between void and metal matrix. Previous SAXS studies of nanovoid structures in metals were limited by the presence of multiple scattering from the metal matrix. The first published report of nanovoid characterization in quenched Al using the SAXS method took place in 2008. In the present work, meticulous material processing methods were applied to induce a significant nanovoid concentration in nominally pure Al while minimizing the introduction of multiple scattering artifacts through sample deformation. Absolute intensity calibration with a secondary glassy carbon standard was performed. Data analysis procedures were developed to extract void scattering by subtracting calibrated reference scattering from calibrated quenched sample scattering, independent of their thicknesses. SAXS analyses were used to estimate void size as well as the void-metal interface structure, void number distribution and void volume fraction in quenched aluminum samples, an extension over the previous work where only estimates of void sizes
were obtained. This work, including identification of experimental tools that can be readily improved, demonstrates that SAXS studies are capable of providing precise characterization of nanovoid structure in aluminum. SAXS analysis provides statistically averaged parameters from scattering data collected from a macroscopic sample volume, which is an advantage over electron microscopy studies. Also, preliminary aging studies of nanovoids in Al revealed some interesting trends in the kinetic properties of the nanovoids which can be extended to test and develop the existing phenomenological models of void nucleation and growth. This level of information, i.e., at the nanoscale and, ideally, yielding kinetic information about the early stage formation and growth of nanovoids, has the potential to be used to develop novel aluminum alloy materials.
I am indebted to my supervisor, Dr. Marsha Singh, for all the help and guidance throughout the entire two years. It was a great experience to work under her supervision and without her sincere efforts, the thesis would not have been possible. I also owe sincere gratitude to my co-supervisor, Dr. Brad Diak whose expertise in Materials Science was the key to understand and interpret my studies. I am thankful to Dr. Arthur Woll of Cornell High Energy Synchrotron Source (CHESS) beamline. He provided a very nice and efficacious atmosphere to work in. I also thank the CHESS for providing us with an excellent X-ray source, beamline instrumentation and support. Also I owe a lot to Queen’s University at Kingston, the Department of Physics, Engineering Physics, and Astronomy for the financial support for this project.

Friends and family are the elixir of life; for me it is not otherwise. Among friends Avik, Agnita and Debartha need special place. They made Kingston a bearable and fun place to live in. Finally I would express my respect and love to my parents, you are all my inspiration. Last but not the least, thank you Mampi for all your love and care.
# Contents

Abstract i

List of Tables viii

List of Figures ix

List of Acronyms xii

1. Introduction 1

2. Literature Review 9

   2.1. Study of Voids in Metals 9

   2.2. Development of SAXS as a Tool for Nanostructure Characterization 13

   2.3. Voids: Thermodynamics, Nucleation and Growth, Phase Field Theory 16

      2.3.1. Thermodynamic Properties of Vacancies 16

      2.3.2. Theory of Nucleation and Growth of Voids 18

         2.3.2.1. Classical Theory of Nucleation 19

         2.3.2.2. Classical Theory of Growth 21
2.3.2.3. Late Time Behaviour ........................................... 22
2.3.2.4. Johnson, Mehl, Avrami, Kolmogorov (JMAK) Transformation Laws ........................................... 24
2.3.3. Phase Field Theory ......................................................... 25
2.3.3.1. Temporal Equations of the Field Variables .................. 28
2.4. Summary of the Chapter ....................................................... 32

3. Small Angle X-ray Scattering .................................................. 33
3.1. X-ray Scattering: A General Theory ..................................... 34
3.2. Small Angle Scattering ......................................................... 36
3.2.1. Guinier Formula ................................................................. 38
3.2.2. Porod’s Formula ................................................................. 39
3.2.3. The Invariant $Q$ ................................................................. 42
3.2.4. Indirect Transform Methods (ITM) ........................................ 43
3.3. Summary of the Chapter ......................................................... 45

4. Experiment ................................................................. 46
4.1. Material Processing .............................................................. 47
4.1.1. Pre-Quench Heat Treatments ............................................ 47
4.1.2. Quench Treatment ............................................................ 51
4.2. Synchrotron SAXS Experiment at CHESS G1 ......................... 54
4.2.1. CHESS G1 Set Up ............................................................. 57
4.2.2. Data Collection ............................................................... 58
4.3. Artificial Aging Experiments .................................................. 61
5. Results

5.1. Data Processing ................................................................. 66
  5.1.1. Background Subtraction .................................................. 66
  5.1.2. Absolute Intensity Calibration ......................................... 72

5.2. Nanovoid Characterization ................................................. 73
  5.2.1. Radius of Gyration - Variation with Sample Purity and Thermal
         History .......................................................................... 76
  5.2.2. Porod Analysis and the Interface Thickness ....................... 78
  5.2.3. Application of Indirect Transform Methods - Variation of Num-
          ber Fraction Distribution, $N_f(R)$, with Sample Purity and Thermal
          History .......................................................................... 79
  5.2.4. Effective $Q$ and Void Volume Fraction ............................ 86

5.3. Artificial Aging Analysis .................................................... 88
  5.3.1. Effect of Aging Temperature and Time on Radius of Nanovoids 88
  5.3.2. Evolution of Number Distributions of Nanovoids ............... 93

5.4. Summary of the Chapter .................................................... 97

6. Discussion

6.1. Nanovoid Characterization Results ..................................... 98

6.2. Aging Studies: Interpretation and Limitations ...................... 102
  6.2.1. Power Law Dissolution of Voids: A Consistency Check ........ 106

6.3. Summary of the Chapter .................................................... 109
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7. Conclusions</td>
<td>110</td>
</tr>
<tr>
<td>Bibliography</td>
<td>114</td>
</tr>
<tr>
<td>Appendix A. Derivation of Porod’s Formula</td>
<td>121</td>
</tr>
<tr>
<td>Appendix B. Thickness of Diffuse Interface: Modification of Porod’s Law</td>
<td>122</td>
</tr>
<tr>
<td>Appendix C. Determination of Average Radius of Gyration from Indirect</td>
<td>124</td>
</tr>
<tr>
<td>Transform Methods</td>
<td></td>
</tr>
<tr>
<td>Appendix D. Growth Coefficients for Diffusion Limited Growth of Nanovoids in Metals</td>
<td>125</td>
</tr>
<tr>
<td>Appendix E. 2-D Detector Image Showing Multiple Scattering</td>
<td>127</td>
</tr>
</tbody>
</table>
List of Tables

4.1. Quench rates obtained for the Al samples. .......................... 53

5.1. Values of radius of gyration ($R_g$) for different samples having different thermal history (quench rates) .......................... 78

5.2. Table showing the variation of $\sigma$ with samples differing in impurity content and quench rates .......................... 81

5.3. Table showing the variation of $\phi$ for different samples .................. 88

5.4. Growth rate of nanovoids in different samples with different aging histories 90

5.5. Values of growth exponents and apparent diffusion coefficients assuming diffusion controlled growth of nanovoids during artificial aging ........ 90
List of Figures

1.1. Formation of void from a system of supersaturated vacancies . . . . . . . 3
1.2. Chart laying out the objectives of the present study . . . . . . . . . . . . . 7

3.1. The figure shows the scattering of X-rays by point scatterers O and P . . 35
3.2. The particle with its displaced volume element . . . . . . . . . . . . . . 40

4.1. Schematic diagram showing the thermocouple connections . . . . . . . . 49
4.2. Schematic diagram showing the placement of the thermocouple wires relative the ISH beamspot position . . . . . . . . . . . . . . . . . . . . . . . 50
4.3. Schematic diagram showing the quench apparatus . . . . . . . . . . . . . 52
4.4. Quench curves obtained for the three samples . . . . . . . . . . . . . . . 53
4.5. Electron channeling contrast image of the approximate region of the 4N600 sample probed by the X-ray beam . . . . . . . . . . . . . . . . . . . . . . . . . . 55
4.6. Schematic representation of a general SAXS experimental set up . . . . . 56
4.7. Sample holder and its alignment in the beampath . . . . . . . . . . . . . 60
4.8. Far-back and Up-close configurations . . . . . . . . . . . . . . . . . . . . 62
4.9. Scattering data for the 4N550 sample is shown for the experimentally accessible q range in absolute units. 

5.1. 2-D scattering profile of 4N550 sample in far-back position. The beamstop is at the right bottom corner.

5.2. 2-D scattering profile in 3N550 sample in up-close position.

5.3. 2-D scattering profile of a 4N reference sample in the up-close position.

5.4. Flow chart showing the stages of background subtraction.

5.5. 1-D integrated data (log scale) of 4N550 for SDD=1579 mm showing sample scattering, reference scattering and void scattering.

5.6. Flow chart showing the stages of absolute intensity calibration.

5.7. Guinier Plots of void scattering in the quenched samples.


5.9. ITM fitting of Void scattering from 3N550 (log scale), $T E = 0.64$.

5.10. ITM fitting of Void scattering from 4N550 (log scale), $T E = 0.68$.

5.11. ITM fitting of Void scattering from 4N600 (log scale), $T E = 0.75$.

5.12. Number fraction distributions ($N_f(R)$) of nanovoids in different samples.

5.13. Evolution of nanovoids with artificial aging at low temperatures.


5.15. Time evolution of number fraction distributions ($N_f(R)$) of nanovoids in 3N550 aged at 90°C. For the set of data, $0.58 < T E < 0.66$.

5.16. Time evolution of number fraction distributions ($N_f(R)$) of nanovoids in 3N550 aged at 60°C. For the set of data, $0.61 < T E < 0.64$. 

5.17. Time evolution of number fraction distributions \( (N_f(R)) \) of nanovoids in 4N550 aged at 90°C. For the set of data, \( 0.58 < \text{T} E < 0.7 \). ................................. 95

5.18. Time evolution of number fraction distributions \( (N_f(R)) \) of nanovoids in 4N550 aged at 60°C. For the set of data, \( 0.59 < \text{T} E < 0.68 \). ................................. 96

6.1. Schematic diagram of void kinetics. ......................................................... 103

6.2. Schematic diagram of void dissolution as observed in the data shown in Fig. 5.14. ................................................................. 105

6.3. Void with diffuse interface. ................................................................. 106

6.4. Comparison between experimental and theoretical curves for radius of gyration of voids for 4N550 sample at 145°C. ................................. 108

7.1. Chart laying out the future prospects. ................................................. 112
List of Acronyms

CCD  Charge Coupled Device
CESR  Cornell Electron Storage Ring
CHESS  Cornell High Energy Synchrotron Source
DAS  Data Acquisition System
ISH  Infrared Spot Heater
ITM  Indirect Transform Methods
JMAK  Johnson, Mehl, Avrami, Kolmogorov
PFT  Phase Field Theory
SAS  Small Angle Scattering
SAXS  Small Angle X-ray Scattering
SDD  Sample to Detector Distance
TE  Total Estimate
TEM Transmission Electron Microscopy
1. Introduction

Development of light weight high strength materials, needed to design and build structural components, has been one of the most important research topics in the field of science and engineering for the last few decades. At present, aluminum (Al) and its alloys constitute the basis of structural components in automobile and aircraft due to their high specific strength. In addition, Al possesses excellent electrical and thermal conducting properties and therefore finds plenty of applications in designing electronic components. These macroscopic properties are inherent at the lattice level, and therefore are sensitive to point defects such as vacancies, interstitials and substitutional atoms. The latter defects are introduced by alloying to create solid solutions and precipitate phases at larger length scales required to strengthen aluminum for structural applications. Vacancies (vacant lattice sites) are always present in an atomic lattice because they reduce the free energy of the system. In addition, vacancies can be introduced into the lattice by increasing temperature [Simmons and Balluffi, 1960] and through plastic deformation. Irradiation can produce both vacancies and self-interstitials atoms [Eyre et al., 1978]. Vacancies are highly mobile and when the vacancy concentration is supersaturated they can condense into dipoles, vacancy complexes, two-dimensional dislocation loops and coalesce into metastable three-dimensional...
objects, i.e. nanovoids (Figure 1.1) [Kiritani, 1964]. One process of supersaturating the vacancy concentration above the thermal equilibrium level involves rapid thermal quenching of the Al sample thereby freezing in the high-temperature vacancy concentration at the final, lower quench temperature. Voids, and their vacancy precursors, are of particular interest in deformation processes since at the macroscopic scale nanovoid coalescence decreases formability in ductile metals [Rogers, 1960, Vijayaraju et al., 1986, Saimoto and Diak, Aug, 2011 (submitted)]. This limits Al alloy applications in the transportation sectors where formability and crash resistance are fundamental requirements in engineering designs. Considerable work has been done in studying the growth of voids under deformation [Barnby et al., 1984, Klöckera and Tvergaard, 2003, Roberts et al., 1976]. However this has been done using only theoretical assumptions about the process of void nucleation since void nuclei can be as small as a cluster of four or more vacancies, and their dynamic production is difficult to probe experimentally.

The nucleation and growth of voids in pure metals can be modeled by an implementation of phase field theory [Chen, 2002] which describes the nanostructure evolution with material specific quantities incorporated into the model parameters. This model has demonstrated success [Rokkam et al., 2009] in reproducing the dynamics of homogeneous nucleation and growth of voids with results shown to be consistent with predictions of well established classical models [Christian, 1975]. Development of this type of model for application to complex alloys depends, to a significant degree, on a detailed knowledge of material properties at the nanoscale level. Therefore experimental techniques are needed to quantify nanovoids to clarify their relationships with the complex alloying and process history of engineering alloys.
Figure 1.1.: Formation of void from a system of supersaturated vacancies
Direct imaging probes such as Transmission Electron Microscopy (TEM) are limited to small volumes and do not readily offer access to the statistically averaged quantities that are often necessary to obtain a detailed picture of global static and dynamic properties. Also, non-destructive in situ study of dynamic processes, devoid of surface effects, is not readily accessible by TEM. Small angle X-ray scattering (SAXS) offers a characterization technique which is sensitive to nanoscale electron density inhomogeneities and that can be also used as an in situ, non-destructive probe of structure, organization and dynamical processes at these length scales. Hence SAXS provides an obvious advantage relative to direct probes such as TEM in experiments dealing with in-situ quenching to produce voids, in-situ deformation void studies, in-situ aging studies etc., all of which are of fundamental importance in developing theoretical models of void formation.

SAXS characterization is most effective when dealing with kinematic scattering from nanoscale structures having a high electron density contrast relative to a uniform background in a two-phase system. There exists a comprehensive range of analysis tools that have been developed over the last 60 years to extract information from SAXS data satisfying these basic criteria [Glatter and Kratky, 1982]. SAXS can therefore be regarded as an ideal tool for the study of nanovoids (nanopores) in metals. The use of SAXS to study the porosity of materials is not new in general [Fratzl, 2003]. However, reports of applications of SAXS methods to study nanovoids in aluminum alloys are limited because of the relatively weak electron density contrast between voids and the metal matrix (Z=13)$^1$, and the effect of multiple scattering from the crystalline matrix contaminating the data at

$^1$The electron density contrast in the case of void and Al is much less than Cu, Zn, Zr (or a mixture of them) precipitates in Al (very common in SAXS literature). Even though Z=13 would signify decent electron density contrast, the latter can still be considered much weaker than other SAXS reports in the existing literature.
small angles [Smallman and Westmacott, 1959]. In cases of voids introduced in pure Al by thermal quenching, the typically dilute system of voids gives rise to weak SAXS scattering profiles. Intense coherent synchrotron radiation sources offering high flux are necessary to obtain good scattering statistics. In addition, careful sample preparation coupled with thorough scrutiny of scattering data to identify and eliminate multiple scattering artifacts are essential.

Past applications of the SAXS measurement tool to the study of nanostructures in metals have generally relied on implementations of well-established Guinier analysis (particle radius) and Porod analysis (specific surface area of interface) methods [Antion et al., 2003, Deschamps et al., 1999, Deschamps et al., 2003, Deschamps et al., 2007, Dumont et al., 2005, Dumont et al., 2006, Werenskiold et al., 2000, Westfall et al., 2008]. The present work reports on a series of procedures developed to use synchrotron SAXS to implement detailed characterization of nanovoids in nominally pure Al. It is noteworthy that nanovoids developed during the production of Al alloys is the subject of ultimate interest. In the present study, artificially produced nanovoids in nominally pure Al are studied using SAXS in order to develop the analysis tools necessary to the complex task of isolating void scattering from a mixture of void and precipitate scattering that is expected for alloy systems. SAXS data for nanovoids in nominally pure Al were obtained at the Cornell High Energy Synchrotron Source (CHESS), G1 station. Absolute intensity calibration methods were developed and implemented to provide an exact method of extracting the nanovoid SAXS signature, independent of the thickness of the samples used. Absolute intensity calibration requires the use of a stable calibration standard, which, unfortunately, is uncommon in the SAXS literature.
The combination of SAXS data obtained from short and long sample-detector distances provided SAXS scattering data in absolute numbers over 3 times the scattering angle range than that of the previous work [Westfall, 2008]. Analysis of the scattering data reveals the void size, void number fraction distribution, void-matrix interface shape and thickness and the void volume fraction. Guinier analysis was used to obtain radii of gyration of voids. Porod analysis was performed assuming the existence of a diffuse interface between void and metal matrix whereby interface thicknesses were obtained. Indirect Transform Methods (ITM) were implemented to analyze SAXS data in terms of a number fraction distribution.

Earlier measurements [Westfall et al., 2008], although successful in identifying trends in the SAXS profiles of voids in Al alloys varying in purity from 99.999 to 99.9 at.%, did not provide quantitative values of true void volume fractions. One of the most important outcomes of this study was to obtain true estimates of void volume fraction from the scattered SAXS intensity of voids, converted to absolute units. The characterization technique was then used to examine void thermal stability by artificial aging of the quench void specimens. The main goal of the present study is to develop the analysis tools, test them out on the limited sample data available, verify that the data is consistent with physically meaningful models of voids and their kinetics, and then use these results as the launch point for the next stage of the work.

This thesis consists of seven chapters. Chapter 2 presents a discussion of the background literature and the basic theory of void nucleation and growth. In discussing the background theory, the connections with the experimentally obtainable parameters through SAXS will

\[\text{Based on the interesting observations from 2010 aging experiment, an experiment chiefly devoted to aging studies of voids in 99.9 \% Al was carried out in 2011. The analysis of the data is in progress.}\]
Figure 1.2.: Chart laying out the objectives of the present study
be clearly identified. Chapter 3 provides a discussion of the theory of SAXS. In chapter 4, the experimental techniques, i.e., material processing and CHESS G1 SAXS beamline set up will be discussed in detail. The most important part of any SAXS study comes next, the data processing and the results. Chapter 5, chiefly dedicated to these topics, will discuss the data processing and SAXS analysis tools that have been developed for the SAXS study of nanostructures in metals. With the analyses in place, the results will follow. The results of data analysis will be broadly divided into two sections- characterization and preliminary aging studies. Chapter 6 deals with the discussion of the significance of the results. The thesis will then conclude with the final chapter summarizing the results of this research effort and proposing the future prospects of this work.

This thesis represents an important step in the comprehensive SAXS characterization and aging study of nanovoids in aluminum (Figure 1.2) as part of a larger project aimed to develop phenomenological models of deformation void nucleation and growth for the purpose of increasing the knowledge base necessary for the design of alloys with enhanced ductility.
2. Literature Review

This chapter contains the current status of the study of voids in metals, in terms of both experiment and theory. In particular, applications of SAXS to the study of nanostructures in metals is discussed along with the limitations of SAXS studies of voids in metals. The history of the development of SAXS analysis techniques in characterizing nanostructures is discussed. The chapter comprises of a discussion of the theory of void nucleation and growth: both the classical and the recently proposed approach using Phase Field Theory (PFT). The detailed discussion of the application of PFT to the study of void nucleation and growth is presented here as it is new and has not yet been tested beyond the original publications [Millett et al., 2009, Rokkam et al., 2009]. This theoretical background is presented as a framework for interpreting future SAXS measurements of void nucleation and growth phenomena in aluminum and its alloys.

2.1. Study of Voids in Metals

Voids, as mentioned earlier, are formed in metals due to agglomeration of vacancies. Voids, being precursors of ductile failure in metals [Thomason, 1981], play important roles in defining macroscopic properties of metals. Voids have been a subject of study from the
1950s. During the 1950s and 1960s, owing to rapid industrialization and also development of nanoscale probes such as TEM, SAXS and positron annihilation spectroscopy, the study of voids and other defects in metals attracted the attention of the researchers around the world. There are numerous reports of quite extensive studies of voids in metals formed by irradiation [Cawthorne and Fulton, 1967] and by thermal quenching [Cotterill, 1965] during this period. Characterization of voids during the 1950s and 1960s employed electron microscopy in general. The first reported observation of voids in quenched Al was by Kiritani [Kiritani, 1964] employing electron microscopy. It was the same group (Kiritani et. al.) which also performed the first reported TEM characterization of shape and size of voids in quenched Al [Kiritani et al., 1964]. Other commonly encountered defects such as Frank dislocation loops [Cotterill and Segall, 1962, Hirsch et al., 1958, Kuhlmann-Wilsdorf and Wilsdorf, 1960], helices [Thomas, 1959, Thomas and Whelan, 1959, Westmacott et al., 1959], tetrahedra [Smallman and Westmacott, 1959] etc. were detected more easily than voids by TEM because of their greater sizes.

The first SAXS observation of voids in quenched metals took place in 1959 [Smallman and Westmacott, 1959], when the researchers identified void scattering for Cu, quenched from 1050°C to 18°C. Although there is a report on SAXS study of voids in irradiated Al [Petersen et al., 1976], there is no evidence of identification of quenched voids in Al employing SAXS, chiefly due to a significantly more dilute system of scatterers which make detection via SAXS (which is sensitive to both the electron density contrast and the overall number of irradiated scatterers) much more difficult.

Along with TEM and SAXS techniques, positron annihilation studies on voids and pores in materials emerged as an important characterization tool. This technique is based on the
principle of matter-antimatter annihilation and the released energy in the form of gamma rays which is used to extract information about the annihilation process. Voids in a metal, which are vacancy clusters, contain negative charge. Hence a positron, inside the metal, is attracted by the negatively charged voids rather than the positive metal matrix. One can define a trapping potential at the void site which is responsible for the mutual interaction of a positron-void pair [Seeger, 1974]. This trapping potential arises due to the change in the electrostatic potential at the defect thus resulting in the decrease of positron kinetic energy in the absence of positive ion cores in the defect. The trapped positron then annihilates with an electron, emitting energy in the form of gamma rays. It is observed that the positron annihilation lifetimes are related to the size, shape and material characteristics affecting the voids and thus can be used as an indirect probe [Hautojärvi et al., 1977]. There is a wide range of reported work dealing with positron annihilation studies on different kinds of defect structures in general [Eldrup and Singh, 1997], namely voids [Triftshäuser et al., 1974], dislocation loops [Szeles et al., 1985], aging kinetics of alloy precipitates [Somoza et al., 2000]. Interestingly, the Department of Physics, Queen’s University has records of both theoretical and experimental work regarding positron annihilation in voids from the 1970s [Hodges and Stott, 1973, McKee et al., 1974]. Although positron annihilation is a very widely used characterization technique, it is a less direct probe than SAXS1. Also SAXS offers an obvious advantage of providing information about void-matrix interface, a parameter of fundamental importance.

It must be noted that SAXS was used extensively during the 1950s in characterizing

---

1Positron annihilation studies to characterize voids employs the dependence of the positron lifetime on the void characteristics. SAXS, on the other hand, depends on the analysis of the scattering profile of X-ray interacting with the voids. As the former depends on the characteristics of a secondary particle (i.e., the positron), hence it is a more indirect probe than X-ray diffraction analysis.
nanostructures in metals [Atkinson, 1958, Atkinson et al., 1959, Atkinson, 1959, Franks and Revell, 1958, Smallman and Westmacott, 1959]. From the 1950s till 2008, there has been hardly any reports on SAXS studies on voids in quenched Al. This is due to the weak electron density contrast between voids and the metal matrix (Z=13)$^2$, the dilute nature of the voids and the effect of multiple scattering from the crystalline matrix contaminating the data at small angles [Smallman and Westmacott, 1959]. As well after the 1960s, due to problems with multiple scattering, SAXS became unpopular as a characterization tool for microstructures in metals relative to soft matter where the use of SAXS is quite extensive [Chu and Hsiao, 2001]. Also the application of SAXS to characterize porosity of materials [Bale and Schmidt, 1984, Calo and Hall, 2004, Crawshaw and Cameron, 2000] is a broad area of study. There has also been considerable work on the application of SAXS on microstructure characterization of ceramics and composite materials [Fratzl, 2003].

It was not until the 1990s that SAXS studies gained resurgence in the characterization of nanostructures in metal alloys, due to the easy availability of high-flux synchrotrons all around the world and improvement of SAXS analysis techniques. However, these recent studies are mostly limited to analyzing precipitates in alloys (which contributes to strong scattering due to a higher electron density contrast). There has been a considerable amount of work done of SAXS characterization on alloy precipitates by Deschamps et.al. [Antion et al., 2003, Deschamps et al., 1999, Deschamps et al., 2003, Deschamps et al., 2007, Dumont et al., 2005, Dumont et al., 2006, Werenskiold et al., 2000] and also by other groups [Fratzl, 2003, Sullivan and Robson, 2008].

$^2$The invariant $Q$, which gives a measure of the total scattered energy is proportional to the square of electron density contrast, $\Delta \rho$. Also, for void-Al matrix, $\Delta \rho = Z/\Omega$ where $\Omega$ is the atomic volume of Al. This gives the corresponding $\Delta \rho = 1.06 \times 10^{30}/m^3$. This is much weaker when compared to a system of precipitate scattering in metal alloys, which is very common in SAXS literature.
It is worth mentioning here that Small Angle Neutron Scattering (SANS) is identified as a characterization technique which does not produce multiple scattering [Atkinson, 1959, Buckley, 2006]. In that sense SANS offers an obvious advantage over SAXS. However, neutron sources are much rarer than X-ray synchrotrons. As synchrotrons offer continuous energy spectrum, one can easily access two or more X-ray energies to work with, thereby immediately identifying and removing artifact scattering.

The first reported work on observation of nanovoids in quenched Al employing SAXS techniques was from Queen’s University in 2008 [Westfall et al., 2008]. Void scattering was clearly observed in that work. An estimate of void size was made and confirmed with complementary TEM studies. The present work is an extension of this early effort, wherein an exact method of identifying the void SAXS data is proposed and the size, interface thickness, number distribution and volume fraction of voids were extracted from SAXS data obtained in absolute intensity units. Also, preliminary aging studies were done on voids in quenched Al employing SAXS techniques, thus laying the foundation for a more rigorous SAXS study on the evolution of void nanostructure in artificially aged Al.

2.2. Development of SAXS as a Tool for Nanostructure Characterization

This section deals with the literature survey and provides the historical development of SAXS characterization tools in the study of nanostructures in materials. The derivation of SAXS theory, necessary for the analysis of work presented in the thesis, from the general X-ray scattering theory will be discussed in detail in chapter 3.
In the SAXS literature one of the most widely used characterization tools is Guinier analysis, which provides an estimate of radius of gyration ($R_g$) of the scattering particle from the low $q$ data, $q$ is the reciprocal wave vector ($q = (\frac{4\pi}{\lambda}) sin\theta$, where $2\theta$ is the scattering angle, $\lambda$ is the wavelength). It was Andre Guinier who derived the formula [Guinier, 1939] which provides the estimate of $R_g$ of the nanostructures,

$$I(q) = I(0)exp(-\frac{q^2R_g^2}{3}),$$ (2.1)

where, $I(q)$ is the scattered intensity and $I(0)$ is the intensity of the main beam. A plot of $ln(I(q))$ versus the square of reciprocal lattice vector, $q^2$, is known as the Guinier plot. Estimates of $R_g$ can be made from the value of slope of the Guinier plot. A reformulation of the Guinier formula to extract measures of $R_g$ is known as a Kratky plot [Deschamps and Geuser, 2011]. Here a plot of $I(q)q^2$ versus $q$ is plotted and the value of $q = q_{max}$ at which the function $I(q)q^2$ attains a maxima is noted. $R_g$ is then given by, $R_g = \sqrt{3}/q_{max}$. It is noteworthy that Kratky plots are a trivial reformulation of the more familiar Guinier plot and are only useful when a clear peak structure is observed. The reformulation in no way changes the fundamental limitation of Guinier analysis methods to small angles. There are reports of work in the literature where researchers have tried to estimate $R_g$ from Kratky plots without well defined peaks [Antion et al., 2003, Dumont et al., 2006]. This tends to lead to estimation of $R_g$ which violates the limitation of the Guinier analysis method to small angle regions, as will be discussed in Chapter 3. Throughout the analysis carried out in this work, $R_g$ is estimated using Guinier plots.

At higher values of $q$, the scattered intensity follows Porod’s law [Porod, 1951],
This formula gives an estimate of the specific surface area, \( \frac{S}{V} \) (\( S \) = surface area of the interface and \( V \) = volume of the scatterer), of the ideal void-metal matrix interface given the fact that the total scattered intensity \( Q \) is known. This formula was later modified to deal with the case of a more realistic diffuse interface [Koberstein et al., 1980]. A diffuse interface is one in which the electron density changes continuously from that of the scattering object to the homogeneous background, a concept beyond the Debye approximation of finite discontinuities of electron densities at interface boundaries [Ciccariello et al., 1988]. In this case the interface thickness (\( \sigma \)) can be estimated by the formula developed by Koberstein, Morra and Stein [Koberstein et al., 1980],

\[
I(q) \propto \frac{1}{q^4} \exp(-4\pi^2 \sigma^2 q^2).
\] (2.3)

The existence of a diffuse interface in any two phase system is physically more sound. This model is implemented for calculation of thickness of void-matrix interface in the present study.

Indirect Transform Methods (ITM) were developed by Glatter in late 1970s [Glatter, 1977, Glatter, 1980]. In these papers Glatter proposed a new method for evaluating small angle scattering data, going beyond the existing methods of Guinier and Porod. ITM can be used to evaluate particle size distributions of the nanostructures contributing to scattering. Svergun developed this technique into a user friendly computation interface called GNOM in the early 1990s [Semenyuk and Svergun, 1991, Svergun, 1991].
has been extensively used for analysis of Small Angle Scattering (SAS) data obtained for microstructures in soft matter [Lin and Tsao, 1996, Koch et al., 2003, Russell et al., 2000]. In this work, ITM has been used as a characterization tool for SAXS studies in metals for the first time. Previous work reporting on number densities and size distributions of microstructures (precipitates) relied on image analysis of electron microscopy data which is, typically, limited to small sample volumes [Deschamps et al., 1999, Dumont et al., 2005, Sullivan and Robson, 2008].

2.3. Voids: Thermodynamics, Nucleation and Growth, Phase Field Theory

As previously noted, this work is part of a larger project intended to develop phenomenological models of void nucleation and growth. It is therefore necessary to review the thermodynamics of point defects or vacancies which agglomerate to form voids. Following this review, the classical time evolution kinetics of void microstructures in metals will be discussed within the context of well-established theories of nucleation and growth. The section will conclude with a discussion of phase field modeling studies recently applied to the study of irradiated voids in metals. Wherever appropriate, the potential role played by experimental data accessible via SAXS measurements will be highlighted.

2.3.1. Thermodynamic Properties of Vacancies

Point defects or vacancies reduce the free energy of a metal, hence they are present in thermal equilibrium [Kittel, 2006]. Consider the case where \( n \) vacancies are present in a
metal containing \( N_a \) atoms at equilibrium temperature \( T \). The number of ways one can choose \( n \) vacant sites from a total of \( N_a + n \) sites is given by, \((N_a + n)!/(N_a! n!)\). Hence the entropy \( (S) \) of the system is given by,

\[
S = k_B \ln \left( \frac{(N_a + n)!}{N_a! n!} \right),
\]

where \( k_B \) is Boltzmann’s constant. The configuration providing the minimum entropy, \( S_{\text{min}} \), is given by equating the derivative of \( S \) with respect to \( n \) to zero. Incorporating Stirling’s Formula\(^3\), we can write for \( n \ll N_a \),

\[
\frac{\partial S}{\partial n} = k_B \ln \left( \frac{N_a + n}{n} \right) \approx k_B \ln \left( \frac{N_a}{n} \right).
\]

From fundamental thermodynamic relations at constant pressure, \( P \), we can write

\[
\frac{\partial G}{\partial n} = \frac{\partial F}{\partial n} + P v_0 - T \frac{\partial S}{\partial n}
\]

where, \( G \) and \( F \) are the Gibb’s free energy and Helmoltz’s free energy, respectively, \( v_0 \) is the volume per atom of the system. Denoting \( \partial F / \partial n = E_0 \), the equilibrium free energy of a point defect we have,

\[
E_0 + P v_0 - k_B T \ln \left( \frac{N_a}{n} \right) = 0.
\]

At normal pressure the quantity \( P v_0 \) is negligible with respect to the formation energy of a vacancy, \( E_0 \), hence we have,

\(^3\ln(x!) \approx x \ln x - x, \text{ for large } x.\)
\[ n = N_a \exp\left(-\frac{E_0}{k_B T}\right), \] (2.8)

which is the classical Boltzmann distribution of vacancies at thermal equilibrium at temperature \( T \).

This expression can be used in calculating the equilibrium vacancy concentration at any temperature \( T \). It is evident that the equilibrium concentration of vacancies will increase with increasing temperature.

2.3.2. Theory of Nucleation and Growth of Voids

In discussing this section, the conceptualization of a system of voids in metals as two separate phases; the metal matrix phase and the void phase will be discussed. The kinetics of void formation and growth can then be discussed within the context of the theory of first order phase transformations.

In general, vacancies are present in the system as lattice imperfections or point defects. As discussed in the previous section, at thermal equilibrium the presence of these vacancies reduces the overall free energy of the system. Hence vacancies contribute to a stable configuration and do not spontaneously coalesce to form voids. Thermal quenching can be used to increase the number of voids above thermal equilibrium level by inducing a supersaturated vacancy concentration [Khellaf et al., 2002]. It is clear from equation 2.8 that the equilibrium number density of vacancies increases with temperature. If the system is rapidly quenched from a high annealing temperature, \( T_i \), to a lower final temperature, \( T_f \), which is below some transition temperature, \( T_C \), a supersaturation of vacancies is gen-
erated. This rapid quenching process helps in freezing the vacancy concentration and the vacancies then agglomerate to form voids. Here $T_C$ is the transition temperature below which a void phase is formed from a supersaturated vacancy phase. If the quench time is much faster than the time required for transformation, two distinct phases are formed, namely the voids and the metal matrix phase (vacancy phase). The matrix phase is a crystalline system with uniformly dispersed vacancies and the void phase results from agglomeration of the excess supersaturated vacancies. Depending on size, vacancy clusters can form di-vacancies, tri-vacancies etc. Vacancy agglomerates with more than four vacancies are generally referred to as voids.

It is worth mentioning that the physical process of void formation, discussed in the following sections, uses the language of nucleation and growth models. It is very important to note that void formation from vacancy coalescence is not, strictly speaking, equivalent to the phase separation of a two-phase system.

### 2.3.2.1. Classical Theory of Nucleation

During nucleation, the new phase (void phase) develops from the old phase (matrix phase incorporating dispersed vacancies) which is controlled by an interplay between nucleation rate and growth rate. The homogeneous nucleation rate ($I(t)$) is a dynamic quantity which assumes zero value in the initial stage and increases monotonically to a steady state value $I^{ss}$. This value remains the same for the rest of the process of transformation. If $V_n$ is the volume available for nucleation, then the total nucleation rate ($I^T(t)$) is given by, $I^T(t) = I(t)V_n$. It is obvious that $V_n$ decreases as transformation proceeds. Hence at later times, $I^T(t)$ decreases in magnitude.
The driving force of transformation from a supersaturated system of vacancies equili-
brating to a void phase is the relative free energies of the two phases ($\Delta F$). The difference
in the free energy can thus be equated to the formation energy of the voids. Thus one can
say [Christian, 1975],

$$\varepsilon_0 = \Delta F = \left(\frac{4\pi r^3}{3}\right) \left(\frac{1}{v^e}\right) (f^e - f^m) + 4\pi r^2 \sigma,$$

(2.9)

where $f^e$ and $f^m$ are the bulk free energies of the equilibrium (void) phase and metastable
(vacancy) phase respectively. $v^e$ is the volume per particle of the equilibrium phase, $\sigma$ is
the surface tension of the void-matrix interface and $r$ is the void radius. If a void is assumed
to be formed by the agglomeration of $n_{\text{vac}}$ number of vacancies, then $f^e$ is related to $n_{\text{vac}}$
times the formation energy of a single vacancy. If $T_C$ is the transition temperature, we have,
for $T > T_C$, $f^e > f^m$ and for $T < T_C$, $f^e < f^m$. Hence above the transition temperature,
the vacancy or matrix phase is favoured and below the transition temperature, nucleation
of voids take place. As $\Delta F$ is a function of void radius $r$, one can define a critical radius
($r_c$) at which $\Delta F$ assumes an extremum. The magnitude of the critical radius is given by
[Christian, 1975],

$$r_c = \frac{2\sigma v^e}{f^m - f^e}.$$

(2.10)

When voids have smaller radii than $r_c$ they are in unstable equilibrium, i.e., they collapse.
Once the radius is greater than $r_c$ they start to grow. So it is obvious that the nucleation
rate depends on how close the radii magnitudes are to $r_c$. If the initial time of nucleation
is defined as $t_0$, then $I(t) = 0$ for $t < t_0$ during which $r < r_c$. This is the incubation time.
Consequently, \( I(t) \propto t^n \) for \( t > t_0 \) during which \( r > r_c \); \( n \) is a positive exponent\(^4\). This is a simple theory to describe the process of homogeneous nucleation in terms of energetics.

It is important to mention that homogeneous nucleation (nucleation in the interior of homogeneous old phase) is very rare. Rather heterogeneous nucleation (nucleation at phase boundaries, grain boundaries, second phase particles e.t.c) is more common and requires lower energy.

2.3.2.2. Classical Theory of Growth

The overall vacancy concentration in the matrix phase is assumed to be constant while void nucleation and growth proceeds. Growth of voids is a phenomenon which depends on the mobility of the vacancies. At temperatures much lower than \( T_C \) growth decreases drastically as the mobility of the vacancies at that temperature is very low.

Growth of microstructures are of two fundamental types: interface controlled and diffusion controlled. In the former, the free energy difference is exhausted in driving mass exchanges in the vicinity of and across the interface of the two phases having same concentration. Hence the growth velocity (referring to rate of change of the particle dimension) is independent of particle dimension and time [Christian, 1975].

In diffusion controlled growth, growth takes place due to diffusion of mass due to a concentration gradient separating the two phases. From dimensional analysis, Christian showed that the growth velocity of the new phase particles \((v_d)\) as a function of time is given by,

---

\(^4\)The exponent \( n \) is no way related to the number of vacancies discussed in section 2.2.1.
\[ v_d(t) = \alpha \sqrt{D/t}, \tag{2.11} \]

where, \( D \) is the diffusion coefficient and \( \alpha \) is the growth coefficient which is related to the concentration of vacancies in the void phase \( (c_{\text{void}}) \), the concentration of vacancies in the matrix phase adjacent to the void interface \( (c_{\text{mat}}) \), and the concentration of vacancies in the initial (as-quenched) metastable state \( (c_m) \). Following Christian, one can assume,

\[ \alpha_h = \sqrt{3} \frac{(c_m - c_{\text{mat}})}{(c_{\text{void}} - c_{\text{mat}})^{1/2}(c_{\text{void}} - c_m)^{1/2}}, \tag{2.12} \]

for high degrees of vacancy supersaturation. For low degrees of vacancy supersaturation,

\[ \alpha_l = \sqrt{2} \frac{(c_m - c_{\text{mat}})^{1/2}}{(c_{\text{void}} - c_m)^{1/2}}. \tag{2.13} \]

A brief discussion of these growth coefficients is in Appendix D.

We will limit our discussion to diffusion controlled growth as the void growth is a similar kind of phenomenon, as is predicted by the Phase Field Theory (PFT), discussed in the next section. The growth discussed here takes part in the early stages of phase transformation. The late time behaviour, i.e., when all the nucleation sites are exhausted will be discussed in the following sections.

2.3.2.3. Late Time Behaviour

In discussing this section, the mechanisms of nucleation and growth will be combined to get at later time behaviour. Say, a void is nucleated at a time \( t_0 \). For diffusion controlled growth of a spherical void, the transformed volume of the new void phase is given by
where, the function \( \Theta(t - t_0) \) is the unit step function\(^5\).

If one aims to calculate the transformed volume fraction (\( \phi \)), then taking into account that the total nucleation rate is nucleation rate times the volume available for nucleation (total volume of matrix phase), one can write for early stages of unimpeded growth,

\[
\phi = \frac{V_T}{V_n} = \frac{4\pi D^{3/2} \alpha^3}{3} \int_{t_0}^{t} I_v(t)(t-t_0)^{3/2} dt,
\]

where \( I_v(t) \) is the nucleation rate per unit volume. For late times, \( I(t) = I^s \) (steady state or a constant growth rate is reached), hence for diffusion controlled growth, \( \phi = \frac{8\pi}{15} \alpha^3 D^{3/2} I^s t^{5/2} \).

The previous discussion considers the nucleation and growth of voids in the untransformed region of the metal matrix. However in reality, the situation is more complicated where the growth takes place both in previously untransformed and transformed regions of matrix phase. Herein comes the concept of extended volume (\( V_E \)), which is the transformed volume from both the domains [Christian, 1975]. For a transformed volume of \( V_T \), the fraction of previously untransformed region is \( (1 - V_T / V) \). In a time \( dt \), if the extended volume in the transformed region increases by \( dV_E \), then the true volume increases by \( dV_T \). Of the new elements making up \( dV_E \), a fraction of \( (1 - V_T / V) \) remains in the previously untransformed region. Hence one can write, \( dV_T = (1 - V_T / V) dV_E \). Integrating this expression, one obtains \( \phi = V_T / V = 1 - \exp(-V_E / V) \). For diffusion controlled growth, this

\(^5\Theta(t - t_0) = 1 \text{ for } t > t_0 \text{ and } \Theta(t - t_0) = 0 \text{ for } t < t_0.\)
takes the form of,

\[ \phi = 1 - \exp(-kt^{5/2}), \quad (2.16) \]

where \( k \) is a time independent constant.

#### 2.3.2.4. Johnson, Mehl, Avrami, Kolmogorov (JMAK) Transformation Laws

From equation 2.16, it is clear that the later time transformation law, in general, can be expressed as,

\[ \phi = 1 - \exp(-kt^n), \quad (2.17) \]

where \( n \) is determined by the nature of the transformation process. Taking this general expression into account, more insight can be obtained on the nature of the nucleation and growth process. Johnson, Mehl, Avrami and Kolmogorov proposed that the initial time transformation law will follow \( n = 5/2 \) law for diffusion controlled growth. A plot of \( \ln[1/(1 - \phi)] \) versus \( \ln(t) \), usually known as JMAK curve is used to track deviations of slopes of the straight line curve in the later times to obtain insight into the nature of transformation processes. Christian [Christian [1975]] provides an extensive discussion on this. Values of \( n > 5/2, n = 5/2, 3/2 < n < 5/2 \) suggests microstructures of all shapes growing from small dimensions with increasing, constant and decreasing nucleation rates respectively. \( n = 3/2 \) suggests zero nucleation rate. Also \( 1 < n < 3/2 \) suggests growth of particles with appreciable initial volume. \( n = 1 \) suggests particles of either cylindrical or planar geometries, \( n = 1/2 \) suggests thickening of large 2-D plates and \( n = 2/3 \) suggests...
precipitations of dislocations in metal matrix. The analysis of these curves thus provides insight on the dependence of transformations on particle geometries.

It is noteworthy that the void volume fraction, $\phi$, is a parameter readily obtained from SAXS data. Hence an isothermal aging study of voids as a function of time can be used study void growth dynamics within the context of the JMAK model to provide insight into the mechanisms of void nucleation in Al.

2.3.3. Phase Field Theory

Phase Field Theory (PFT) [Chen, 2002] is a time dependent statistical mechanical approach to model microstructural evolution in the nanoscale level. This assumes a microstructure evolving in a matrix phase with a diffuse interface in between, identical to the structure referred to in discussing the classical formulation of the nucleation and growth of voids in Al. The development of the PFT is therefore seen as relevant to the interpretation of experimental measurements of void nucleation and growth. Also PFT describes the phenomenon of void nucleation and growth starting from the well established principles of statistical physics, which is more sound than the classical theories. In addition, PFT has the prospect of being used as a predictive model for developing novel Al alloys. The basic formulas of the PFT framework are developed here to augment and clarify the discussions presented in the work by Rokkam et al [Millett et al., 2009, Rokkam et al., 2009] for future application to the study of nanovoids in Al.

In general the free energy of the system (microstructure with matrix) is written in terms of a set of conserved ($c_i$) and non-conserved ($\eta_i$) field variables, which may include the contribution from local bulk energies ($f(c_i, \eta_i)$), interfacial energies ($\sum \kappa |\nabla c_{ij}|^2$),
\[ \sum_i \kappa_i |\nabla \eta_i|^2 \) and long range interaction energies \((f(r-r'))^6. \]

\[
F(c_i, \eta_i) = \int \left[ f(c_i, \eta_i) + \sum_i \kappa_{ci} |\nabla c_{vi}|^2 + \sum_i \kappa_{\eta_i} |\nabla \eta_i|^2 \right] d^3r + \int f(r-r')d^3rd^3r'.
\]

(2.18)

For a real system of voids in metal matrix, Rokkam et. al. [Rokkam et al., 2009] derived the explicit expressions for the individual contributions to the total free energy as follows\(^7\),

\[
F = N \int \left[ h(\eta)G_v(c_v) + \omega(c_v, \eta) + \frac{\kappa_v}{2} |\nabla c_v|^2 + \frac{\kappa_\eta}{2} |\nabla \eta|^2 \right] d^3r,
\]

(2.19)

where, \(N\) is the number of lattice sites per unit volume, \(c_v\) is the vacancy concentration field and the non-conserved field parameter is given by \(\eta\). \(G_v(c_v)\) is the vacancy free energy given by,

\[
G_v(c_v) = E_f^v c_v + k_BT \left[ c_v ln(c_v) + (1-c_v)ln(1-c_v) \right]
\]

(2.20)

where, the first term is the energy of formation (enthalpic contribution) and the second term is entropic contribution to the free energy of the vacancy (matrix) phase and the void phase. It is noteworthy that the void phase and the matrix phase are distinguished by the different values of the field parameters, \(c_v\) and \(\eta\). The matrix phase is given by, \(c_v = c_v^0\), the equilibrium concentration of vacancies and \(\eta = 0\). The void phase is consequently

\(^6\)The interaction terms may be elastic strain induced by deformation, electrostatic interaction, dipole-dipole interaction etc.

\(^7\)In these papers a system of voids in metal produced by irradiation is considered. Like voids produced during quenching, voids are produced by irradiation due to agglomeration of the supersaturated vacancies. Hence the theoretical framework of these papers can be incorporated in discussing our problem.
given by, $c_v = 1$ and $\eta = 1^8$. Here, the vacancy concentration is given by, $c_v = n/(n+N_a)$. Hence $c_v = 1$ for void phase implies that inside a void all the lattice points are occupied by vacancies. The non-conserved field $\eta$ has the additional property of defining the diffuse interface by attaining continuous values of $0 < \eta < 1$ within the interface. In these papers [Millett et al., 2009, Rokkam et al., 2009], no physical interpretation of $\eta$ is provided. However one can interpret $\eta$ if the electron distribution ($\rho(r)$) of the system is considered. As discussed earlier, $\rho(r) = 0$, inside voids and $\rho(r) = \rho_m$ for metal matrix. In the diffuse interface, the electron density varies uniformly from 0 to $\rho_m^9$. We define, $\eta(r) = \frac{1}{\rho_m}(\rho_m - \rho(r))$. With this definition, one can consistently define the void, matrix phase and the diffuse interface.

In equation 2.19 the term $\omega(c_v, \eta)$ is a double well Landau type term [Binder, 1987], representing bistability in a two phase system (void-metal matrix). The term is explicitly written down as follows,

$$\omega(c_v, \eta) = -A(c_v - c_v^0)^2 \eta(\eta + 2)(\eta - 1)^2 + B(c_v - 1)^2 \eta^2.$$  

(2.21)

It is clear that this function is identically zero in both void and the matrix phase, signifying the minima. The shape factor $h(\eta)$ in equation 2.19 is defined as, $h(\eta) = (\eta - 1)^2(\eta + 1)^2$. This assumes values of 1 and 0 in matrix and void phases respectively. So the minimum values of the bulk energy contribution to the free energies in the void and the matrix phases are 0 and $k_B T (1 - c_v^0) ln(1 - c_v^0)$, respectively. These are the two stable wells corresponding

---

8With this definition it is clear that the equilibrium is given by minima of the free energy at $c_v = c_v^0$. One can easily check that this minima gives back the Boltzmann distribution, $c_v^0 = exp(-E_v^f/k_B T)$.

9Later during analysis, the interface will be modeled using a Gaussian convolution consistent with this assumption.
to the two phases, void phase and matrix phase. The shape factor \( h(\eta) \) is included to neglect the infinite contribution of the vacancy free energy density, \( G_v(c_v) \), in the void phase \((c_v = 1, \eta = 1)\).

In this formulation, the fact that the excess vacancy concentration will decrease with time (through surface shedding, annihilation at defect structures, etc.) is being neglected. The framework developed by Rokkam et al. would be ideally valid when vacancies are always being produced, as during irradiation or deformation.

### 2.3.3.1. Temporal Equations of the Field Variables

As discussed earlier, \( c_v \) and \( \eta \) are the conserved and non-conserved field variables denoting the local vacancy concentration field and heterogeneity of a system with diffuse interface, respectively. Consistent with the theory of phase field modeling, the evolution of voids will be determined through the temporal equations of the field parameters. Evolution of \( c_v \) is the generalized diffusion equation, also known as the Cahn-Hilliard equation [Cahn and Hilliard, 1958]. Kinetics of \( \eta \) can be identified with the Allen-Cahn equation \(^{10} \) [Allen and Cahn, 1979].

The kinetic equation of the local vacancy concentration field \( c_v \) will be derived first. It is discussed above that this local field assumes different values in the matrix phase \((c_v = c_v^0)\) and the void phase \((c_v = 1)\). Hence there exists a concentration gradient and the voids grow or shrink by the diffusion of vacancies in or out of the voids respectively. In the absence of any external field the diffusion current \((\vec{J})\) of the vacancies is given by an empirical equation called Fick’s law [Ashcroft and Mermin, 1976],

\(^{10}\)This is a phenomenological equation, thus derived from empirical results and is mathematically consistent.
\[ \vec{J} = -D \vec{\nabla} \mu, \]  
(2.22)

where \( D \) is diffusivity of vacancies in metal matrix and \( \mu \) is the chemical potential. Again as \( c_v \) is conserved, the diffusion process is steady state and the equation of continuity can be written down as follows,

\[ \frac{\partial c_v}{\partial t} + \nabla \cdot J = 0. \]  
(2.23)

Inserting Fick’s law in equation 2.23, the kinetic equation of \( c_v \) is obtained as follows,

\[ \frac{\partial c_v}{\partial t} = \nabla \cdot \left[ D \nabla \left( \frac{1}{N} \frac{\partial F}{\partial c_v} \right) \right], \]  
(2.24)

where, the chemical potential is given by \( \mu = \frac{1}{N} \frac{\partial F}{\partial c_v} \) [Rokkam et al., 2009]. As noted above equation 2.24 is the Cahn-Hilliard equation which provides the temporal evolution of \( c_v \) and hence the diffusion equation.

Next we discuss the phenomenological development of Allen-Cahn equation which gives the kinetic equation of non-conserved field variable \( \eta \). As discussed earlier, \( \eta \) has constant values in different phases with a continuously changing value in the interface region, thus denoting the heterogeneity of the void-matrix system. For the non-conserved field variable \( \eta \) it is postulated that if the total free energy \( F \) is not a minimum for a local variation in \( \eta \), there is an immediate change in \( \eta \) and the corresponding evolution is given by [Allen and Cahn, 1979],

\[ \frac{\partial \eta}{\partial t} = -L \left( \frac{\partial F}{\partial \eta} \right), \]  
(2.25)
where $L$ is a positive kinetic coefficient which represents the mobility of the void surface. This equation is known as Allen-Cahn equation. The quantity $\partial \eta / \partial t$ is identified as a generalized velocity term. The quantity $\partial F / \partial \eta$ has the dimension of force and is equivalent to a linear drag force. The normal surface velocity of the void ($v_n$) at any spatial position determined by the value of $\eta = c$ is given by\(^{11}\),

$$v_n = - \left( \frac{\partial \eta}{\partial t} \right) / \left( \frac{\partial \eta}{\partial r} \right)_{\eta=c}. \tag{2.26}$$

If the change in values of radius size with time is given by $\Delta R / t$, then it is straightforward to equate $v_n = \Delta R / t$. Thus one can find the rate equation in the form of $\Delta R = \lambda t^n$, which can be compared to experimental results from SAXS. In the paper by Rokkam et al., 2009, the temporal equations for $c_v$ and $\eta$ are written down explicitly in terms of the individual contributions of the free energy function as follows,

$$\frac{\partial c_v}{\partial t} = \nabla \cdot D \nabla \left[ h(\eta) \frac{\partial G_v}{\partial c_v} + \frac{\partial \omega}{\partial c_v} - 2\kappa_v \nabla^2 c_v \right] + P_v, \tag{2.27}$$

$$\frac{\partial \eta}{\partial t} = -LN \left[ G_v \frac{\partial h(\eta)}{\partial \eta} + \frac{\partial \omega}{\partial \eta} - 2\kappa_\eta \nabla^2 \eta \right] \tag{2.28}$$

where $P_v$ is the vacancy source term added to the right hand side. This set of differential equations is solved numerically by the method of finite differences.

Results from PFT clearly shows the late stages of void growth is being described as an Ostwald ripening process, a process where smaller voids dissolve in metal matrix and the

\(^{11}\)Note that the radial velocity is $v_n = - \frac{\partial r}{\partial t} = - \left( \frac{\partial \eta}{\partial t} \right) / \left( \frac{\partial \eta}{\partial r} \right)$. The negative sign indicates that velocity decreases as $r$ increases, a direct consequence of linear drag force.
resulting vacancies combine to form bigger voids at late stages of growth. The surface to volume ratio is minimized and hence the surface free energy is reduced. This can be realized by a very simple calculation. Say \( n \) number of small spherical voids of radius \( r \) coalesce to form a bigger void of radius \( R \). So, \( R = n^{1/3} r \). If \( S_r \) determines the ratio of the surface areas of the smaller voids to the single bigger void, then it can be derived that \( S_r = n^{1/3} \). For \( n > 1 \) it is clear that the surface area is reduced for the single bigger void, hence the surface free energy is reduced. During coarsening, formation of a bigger void with smaller surface area with the overall void volume fraction, \( \phi \), remaining the same ensures that the surface to volume ratio is reduced. Hence this is an energetically favorable process and thus Ostwald ripening process can very successfully describe the later stages of void growth.

The development of the PFT approach described above provides direct connections to experimental parameters obtained through SAXS. It is immediately obvious that, from the rate equation \( \Delta R = \lambda t^n \), the PFT provides a framework for interpreting the time dependence of the void volume fraction (void growth). Void volume fraction can be straightforwardly measured using SAXS experimental techniques. It is known [Saimoto and Diak, 2011, Lloyd, 2003] that void volume fraction is related to ductile failure of metals. As noted previously, the late time growth curve of the void volume fraction yields information on the nature of heterogeneous nucleation of voids [Christian, 1975]. Finally, the temporal equations (equations 2.27 and 2.28) derived above can be straightforwardly modified [Millet et al., 2009, Rokkam et al., 2009] to incorporate elastic field terms to accommodate elastic deformation studies of void dynamics. In summary, the development of the PFT is seen to have the potential to be of fundamental importance in terms of interpreting the ma-
Material response to thermal and deformation history and may be useful for the development of predictive models for the design of novel Al alloys.

2.4. Summary of the Chapter

This chapter discusses the literature dealing with past studies of voids in metals, development of SAXS methods and the relevant theories of void nucleation and growth. Phase field theory (PFT) has been discussed in detail in this context for the following reasons: the theory is based on well-established theoretical principles and yields models of kinetic behaviour that converge with classical nucleation and growth models, the theory has the potential of generating more complex kinetic models that can be used to describe subtle aspects of transformation phenomena (eg. void interface) that are not accessible through the classical models. Hence, once the descriptive capabilities of the models derived from the theory are verified through comparison with real data, it is anticipated that the theory can then be used to generate prescriptive models of desired kinetic behaviour which can be related to fundamental material properties.

A rigorous presentation of the PFT is presented here because it is relatively new and, apart from the very recent papers [Millett et al., 2009, Rokkam et al., 2009], the development of the formulas has not yet been independently tested by researchers other than the original authors. In fact, some aspects of the theory have been more carefully defined (eg. the non-conserved order parameter, $\eta$) in this work (to relate them to real physical variables) than in the original publications.
3. Small Angle X-ray Scattering

Structural analysis of materials by X-rays has its roots back in the early 1900s when W.H. Bragg and W.L. Bragg formulated the famous Bragg’s law to explain the occurrence of scattering peaks observed from the interaction of X-rays with crystalline materials. Over the years electron and neutron scattering have also been extensively used for the same purpose. The theoretical premises for all three phenomena are basically the same. When the incident probe beam (photons, electrons or neutrons) get scattered from a material, the scattered waves interfere and produce diffraction patterns. This diffraction profile provides an effective way to analyze the structure of the scattering substance.

In this chapter X-ray scattering from substances in general will be discussed and the theory for small angle X-ray scattering (SAXS) will be laid out by limiting our study to small angles (less than 2 degrees) [Glatter and Kratky, 1982]. The basic analysis models, namely the Guinier analysis, Porod analysis and Indirect Transform methods (ITM) will be discussed. There exists a large body of work dealing with SAXS data analysis for diverse materials [Feigin and Svergun, 1987, Glatter and Kratky, 1982]. In this chapter, the discussion is limited to only about those tools that have proved to be useful for the current study.
3.1. X-ray Scattering: A General Theory

When X-rays are incident on a substance, the electrons in the substance act as sources of secondary scattered waves. These scattered waves interfere coherently to produce a diffraction pattern. The electrons are effectively free as the energy of the X-ray photons is much greater than that of the binding energy of the atom. For scattering from two point centres (Figure 3.1) O and P, the path difference \( l \) introduced \( (l = -(BO - AP)) \) between the two scattered waves is given by,

\[
l = - \mathbf{r} \cdot (\mathbf{s} - \mathbf{s}_0)
\]  

(3.1)

If one introduces the incident and scattered wave vectors as \( \mathbf{k}_0 \) and \( \mathbf{k} \), respectively, then one can define, \( \mathbf{k}_0 = \frac{2\pi}{\lambda} \mathbf{s}_0 \) and \( \mathbf{k} = \frac{2\pi}{\lambda} \mathbf{s} \). So the phase difference is given by \( \varphi = \frac{2\pi l}{\lambda} = - \mathbf{r} \cdot \delta \mathbf{k} \), where \( \delta \mathbf{k} = \mathbf{k} - \mathbf{k}_0 \). From the diffraction condition [Ashcroft and Mermin, 1976], the reciprocal wave vector, \( \mathbf{q} \), equals to the scattering wave vector, \( \delta \mathbf{k} \). For elastic scattering (Thompson scattering), the magnitudes of the incident and scattered wave vectors are the same, i.e. \( k = k_0 \). So if the scattering angle is \( 2\theta \), then we have \( q = 2ksin\theta \).

For scattering from an electron distribution, rather than a single electron, one needs to deal with a system with uniform electron density (number of electrons per unit volume of the scatterer), \( \rho(\mathbf{r}) \). So an infinitesimal volume element \( dV \) contains \( \rho(\mathbf{r})dV \) number of electrons. The total amplitude of scattering is thus given by the integral sum of scatterings from the irradiated volume \( V_{irr} \),

\[
F(\mathbf{q}) = \int dV_{irr} \rho(\mathbf{r})e^{-i\varphi}.
\]  

(3.2)
Figure 3.1.: The figure shows the scattering of X-rays by point scatterers O and P, separated by the displacement $\mathbf{r}$ with $\mathbf{s}_0$ and $\mathbf{s}$ being the propagation directions of the incoming and outgoing plane waves.
It is clear from equation 3.2 that the amplitude is the Fourier transform of the electron distribution of the scatterer\(^1\). The intensity \(I(q)\) is proportional to the absolute square of the scattered amplitude. Hence one can say that, \(I(q) \propto F(q)F^*(q)\). In the explicit form,

\[
F(q)F^*(q) = \int dV_1dV_2 \rho(r_1)\rho(r_2)e^{-iq(r_1-r_2)}. \tag{3.3}
\]

If one denotes the relative distance between the scattering points as \(r = r_1 - r_2\), then one can introduce a density autocorrelation function, \(\tilde{\rho}^2(r) = \int d^3r_1\rho(r_1)\rho(r_2)\). This is related to the probability of finding two scattering points separated by \(r\). The equation 3.3 reduces to,

\[
F(q)F^*(q) = \int d^3r \tilde{\rho}^2(r)e^{-iq\cdot r}. \tag{3.4}
\]

Thus the intensity is directly related to the autocorrelation function, \(\tilde{\rho}^2(r)\), and hence depends on the fluctuation of the electron density in space. This is the basic theory underlying the scattering of X-rays from materials. Essentially the task of structural analysis is reduced to an inverse scattering problem, i.e., one knows \(I(q)\) from our experimental data and then the structural characteristics of the scatterer are found out.

### 3.2. Small Angle Scattering

For nanoscale particles or structures, like nanovoids in aluminum, the scattering profile is limited to less than 2 degrees for a typical X-ray probe of wavelength close to 1 Å. In this

\(^1\)Note that if we treat the electron density as a scattering potential then the amplitude given in equation 3.2 is equivalent to the first order Born Approximation formula, i.e., the amplitude is calculated in the far-field approximation and the incident field is larger than the scattered field.
limit, for the majority of the cases, the system is spherically isotropic and there is no long range order (there is no correlation between points separated widely in space). With the first restriction, the scattering is independent of the direction of \( \mathbf{r} \) and the phase factor can be spherically averaged over all orientations\(^2\) to reduce equation 3.4 to,

\[
F(q)F^*(q) = \int 4\pi r^2 dr \tilde{\rho}^2(r) \frac{\sin qr}{qr}.
\]

(3.5)

From the second restriction, we have that at large distances there is no autocorrelation and the respective electron densities become independent. If one considers the mean value of electron density as \( \bar{\rho} \), then there will be an electron density fluctuation in space which can be modeled as two distinct phases: one with electron density \( \rho(r) - \bar{\rho} \) and another phase of total irradiated volume \( V_{\text{irr}} \) with uniform density \( \bar{\rho} \). In the small angle scattering regime, the scattering will be due to fluctuations in the nanoscale electron density and scattering from the uniform density phase occurs at angles \( q < \frac{2\pi}{L} \) that are too small to be accessible, where \( V_{\text{irr}} = L^3 \) (\( L \) is typically of the order of mm). Thus the autocorrelation function can be expressed in the form, \( \tilde{\rho}^2(r) = V_{\text{irr}} \langle (\rho(r_1) - \bar{\rho})(\rho(r_2) - \bar{\rho}) \rangle = V_{\text{irr}} \gamma(r) \).

Hence we can simplify equation 3.5 as,

\[
F(q)F^*(q) = V_{\text{irr}} \int 4\pi r^2 dr \gamma(r) \frac{\sin qr}{qr}.
\]

(3.6)

This is the most general equation for scattered intensity obeying the two restrictions as stated above. This equation will be used for further discussions.

\(^2\) \( \int d^3r e^{-iqr} = \iiint r^2 \sin \theta dr d\theta d\phi e^{-iqr\cos \theta} = \int 4\pi r^2 \frac{\sin qr}{qr} dr \)
3.2.1. Guinier Formula

At small angles, we have $qr \to 0$, so we can simplify equation 3.6 for a case of isolated and identical particles as following,

$$I(q) \propto V_{irr} \int 4\pi r^2 d\gamma(r) \frac{1}{qr} \left\{ qr - \frac{(qr)^3}{3!} + \ldots \right\}$$

$$\propto V_{irr} \int 4\pi r^2 d\gamma(r) \left\{ 1 - \frac{(qr)^2}{3!} + \ldots \right\}$$

$$= I(0) \left\{ 1 - \frac{q^2}{3} \left( \frac{\int 4\pi r^2 d\gamma(r) r^2}{\int 4\pi r^2 d\gamma(r)} \right) + \ldots \right\}$$

$$= I(0) \left\{ 1 - \frac{q^2}{3} R_g^2 + \ldots \right\}$$

$$= I(0) \exp \left( -\frac{q^2 R_g^2}{3} \right), \hspace{1cm} (3.7)$$

where we define $I(0) = V_{irr} \int 4\pi r^2 d\gamma(r)$, which is the intensity at $q = 0$ and we have defined the radius of gyration $R_g$ (also known as Guinier radius) for the electron distribution of the scatterer as $R_g^2 = \frac{\int 4\pi r^2 d\gamma(r) r^2}{\int 4\pi r^2 d\gamma(r)}$. Equation 3.7 gives the measure of particle size from the scattered intensity profile. Generally one restricts the analysis to the lowest $q$ range possible, without encountering the contamination of the scattering from the tail end of the
main beam, and finds $R_g$ from the slope of $\ln(I(q))$ versus $q^2$ plot. This kind of plot serves as a first check if the resultant scattering is from spherical, cylindrical or flat particles. An absence of a straight line in the low $q$ range for the above plot may be a result of scattering from non-spherical particles. A more general plot will be $\ln(I(q)q^x)$ versus $q^2$. Straight lines obtained for $x = 1$ and $x = 2$ will identify scattering from cylindrical and flat particles respectively [Glatter and Kratky, 1982]. Then the resulting slopes for the two cases will be $-\frac{R_C^2}{2}$, where $R_C$ is the radius of gyration of cylinder cross-section, and $-\frac{d^2}{12}$ respectively, $d$ is the thickness of the flat particle.

3.2.2. Porod’s Formula

Porod’s law gives an approximate formula for high-$q$ scattering in the small angle scattering limit in terms of the specific surface ($S/V_p$) of the particle where $S$ is the particle surface area and $V_p$ is the particle volume. Before going into the details of the formula, the form of the correlation function, $\gamma(r)$ will be examined closely. For the ideal case of a particle of density $\rho$ in a uniform background of density $\bar{\rho}$ with negligible interface thickness, the correlation function is given by,

$$\gamma(r) = (\Delta \rho)^2 \gamma_0(r),$$  \hspace{1cm} (3.8)

where, $\gamma_0(0) = 1$ and $\gamma_0(r \geq D) = 0$, $D$ being the maximum particle dimension and $\Delta \rho = \rho - \bar{\rho}$.

If one considers a particle of density $\rho$ and volume $V_p$ being shifted by a position vector $\mathbf{r}$. Then the common volume, $\hat{u}(\mathbf{r})$, contains all the points that contributes to $\gamma_0(r)$. Hence,
Figure 3.2.: The particle with its displaced volume element is shown here. The shaded region is the common volume and every point inside it contributes to the correlation function $\gamma_0(r)$.

one can express, $\gamma_0(r) = \langle \hat{u}(r) \rangle / V_p$. Defining a surface element, $dS$, the thickness of the volume excluded is given by $r.dS = rdScos\phi$. Hence for small $r$, it can be approximated that $\gamma_0(r) = \frac{1}{V_p} \langle V_p - rdScos\phi \rangle$. Performing the average over all directions, the formula reduces to\(^3\),

\[ \gamma_0(r) = 1 - \frac{\langle cos\phi \rangle}{2} \frac{S}{V_p} r = 1 - \frac{S}{4V_p} r. \quad (3.9) \]

Putting this back into equation 3.6, one obtains Porod’s formula (Appendix A) for scattered intensity at high $q$ (small $r$) which is given by,

\(^3\)Note that the $r$ is directed towards inside of the volume element. Hence while taking the average over $r$, the $1/2$ factor comes in. The second $1/2$ factor results from the fact that $\langle cos\phi \rangle = 1/2$. 
\[ I(q) \propto \frac{Q}{\pi V_p} \frac{1}{q^4}, \]  

(3.10)

where \( Q \) is the invariant which measures the total scattering intensity. The specific surface area can be found from a plot of \( I(q) q^4 \) versus \( q^4 \). In the presence of a finite Laue background [Feigin and Svergun, 1987] the above equation for Porod’s law is modified to

\[ I(q) \propto C_0 + \frac{Q}{\pi V_p} \frac{1}{q^4}, \]  

(3.11)

where \( C_0 \) is the slope of the \( I(q) q^4 \) versus \( q^4 \) plot and denotes the Laue background. When the constant background term \( C_0 \) is removed [Yu et al., 1999] the slope obtained at high \( q \) can be used to obtain a measure of the specific surface area, assuming an ideal, sharp interface between the void and the metal matrix.

When a diffuse interface is encountered the meaning of \( S/V_p \) is not well defined and obtaining an estimate of interfacial thickness becomes more meaningful. For a diffuse boundary the effect of the non-ideal interface can be accounted for using a Gaussian smoothing function \( \exp(-2\pi^2 \sigma^2 q^2) \) where the standard deviation \( \sigma \) gives a measure of the interfacial thickness [Koberstein et al., 1980]. The observed scattering in the Porod region, corrected for the Laue background, has the form (Appendix B),

\[ I(q) \propto \frac{1}{q^4} \exp(-4\pi^2 \sigma^2 q^2). \]  

(3.12)

This formula is useful for determining the interface thickness of the nanovoids in aluminum and will be discussed in detail in the following chapters.

\footnote{A more detailed discussion on \( Q \) is given in section 3.2.3.}
3.2.3. The Invariant $Q$

The total scattered intensity $Q$ is a fundamentally important parameter that can be evaluated from SAXS data, which will be discussed in detail in this section. It is clear that the Fourier transform of equation 3.6 can be written as,

$$V_{irr} \gamma (r) = \frac{1}{2 \pi^2} \int_0^\infty q^2 I(q) dq \frac{\sin qr}{qr}. \quad (3.13)$$

Putting $r \to 0$, the equation reduces to,

$$V_{irr} \gamma (0) = \frac{1}{2 \pi^2} \int_0^\infty q^2 I(q) dq = \frac{Q}{2 \pi^2}, \quad (3.14)$$

where, the invariant $Q$ is defined as,

$$Q = \int_0^\infty q^2 I(q) dq. \quad (3.15)$$

In the current consideration of a heterogeneous two-phase model, the average electron density, $\bar{\rho}$, can be evaluated in terms of the individual electron densities, $\rho_1$ and $\rho_2$, and the volume fractions, $\phi_1$ and $\phi_2$, of the two phases respectively. Hence defining $\bar{\rho} = \rho_1 \phi_1 + \rho_2 \phi_2$, equation 3.14 can be modified to,

$$Q = 2 \pi^2 V_{irr} \langle (\rho (r) - \bar{\rho})^2 \rangle$$

$$= 2 \pi^2 V_{irr} (\rho_1 - \rho_2)^2 \phi_1 \phi_2. \quad (3.16)$$
In evaluating $Q$ from real experimental data the integration in the equation 3.15 cannot be performed from $q = 0$ to $q = \infty$. Instead an effective, $Q_{\text{eff}}$, is calculated for an estimate of the total scattered intensity which is given by,

$$Q_{\text{eff}} = \int_{q_{\min}}^{q_{\max}} I(q) q^2 dq + \int_{q_{\max}}^{\infty} (\lim_{q \to \infty} I(q)) q^2 dq,$$

(3.17)

where, $q_{\min}$ and $q_{\max}$ are the minimum and maximum values of $q$ available in the experimental range. For the extrapolated part, the formula for the intensity $I(q)$ goes as (equation 3.10),

$$\lim_{q \to \infty} I(q) = \frac{k}{q^4}.$$  

(3.18)

Hence the final equation for the invariant reduces to,

$$Q_{\text{eff}} = \int_{q_{\min}}^{q_{\max}} I(q) q^2 dq + \frac{k}{q_{\max}^3}.$$  

(3.19)

This expression is used for calculating $Q_{\text{eff}}$ for the void scattering. It must be noted that if one neglects the loss of information at low $q$, i.e., from $q = 0$ to $q = q_{\min}$, then the value of $Q_{\text{eff}}$ is independent of the shape of particles and is related to the scattering volume of the particles. Hence it is an invariant.

### 3.2.4. Indirect Transform Methods (ITM)

The Indirect Transform Method (ITM) provides an alternative approach for evaluating SAXS data from polydisperse systems under the assumption that all particles have same shape and the size distribution depends only on the linear size parameter $R$. This method
was originally developed by Glatter [Glatter, 1977, Glatter, 1980] and later extended [Semenyuk and Svergun, 1991] into a user-friendly interface for computation purposes. In this work the ITM is implemented by representing the total scattered intensity from a system of dilute and identical spherical particles of different sizes as the sum of scattered intensities from individual particles [Glatter, 1977, Vonk, 1976], i.e.,

\[ I(q) = \frac{3}{4\pi} \int_0^\infty V(R)R^{-3}i(qR)dR, \]  

(3.20)

where \( V(R) \) is the volume distribution, \( i(qR) \) is the single particle scattering of a particle of radius \( R \). The volume distribution in this integral can be straightforwardly replaced by the number distribution where \( V(R) = \frac{4\pi}{3}R^3N(R) \). The number distribution function is expanded in terms of basis functions, i.e.,

\[ N(R) = \sum_{i=0}^{n} c_i \psi_i(R), \]  

(3.21)

where the basis functions are cubic B-splines and \( n \) is the number of basis functions which is typically less than 30 [Glatter, 1980]. The distribution is then found by the best fit of the experimental data with the restriction that \( N(R) \neq 0 \) only within the range \( R_{min} \leq R \leq R_{max} \). \( R_{min} \) and \( R_{max} \) are the user supplied estimates of minimum and maximum particle sizes.

In this work, ITM analysis is carried out with the help of the GNOM package [Semenyuk and Svergun, 1991] to obtain estimates of void sizes and volume distribution of voids. It is noteworthy that GNOM provides a number distribution in relative units, irrespective of the fact whether the intensity is provided in arbitrary or absolute units. In
addition, the average value of radii of gyration of voids are obtained (Appendix C), pro-
viding an independent check of the values obtained using Guinier analysis.

3.3. Summary of the Chapter

This chapter discusses the theory behind the SAXS analysis methods that will be used in
the present study. The detailed characterization of nanovoids in which the void size, void-
matrix interface thickness, void volume fraction and void number fraction distribution are
determined from void scattering data rely on the analysis methods that have been discussed
here.
4. Experiment

The SAXS experiments that were performed in the present study can be broadly divided into two stages - material processing and synchrotron SAXS data acquisition. The first stage involves careful sample preparation, i.e., processing of Al samples to produce quenched in voids while minimizing physical damage so that the void scattering is not contaminated by scattering from artifacts. The second stage, SAXS data collection, involves precise set up of the synchrotron beamline to ensure access to good scattering statistics over as wide a scattering angle range as possible.

This chapter describes the following stages of the experiment - the preparation of Al samples containing voids, the synchrotron beamline setup and an overview of the data collection process at the beamline. The material processing was performed at the Department of Mechanical and Materials Engineering, Queen’s University. SAXS data on the resulting Al samples were obtained at the Cornell High Energy Synchrotron Source (CHESS), Cornell University.
4.1. Material Processing

As mentioned earlier, this stage of experiments deals with the preparation of the Al samples. Two nominally pure Toyo Al alloys, 99.988 and 99.995 at.%, to be designated as 3N and 4N, respectively, were used in this experimental study. The alloys were received in the form of 120 μm thick foils. The effective impurity concentrations in ppm of 3N and 4N were 52Si-8Fe-8Cu and 3Mg-16Si-6Fe-18Cu, respectively. In order to produce voids in these Al samples multiple steps of careful heat treatments were performed which will be discussed in detail in this section.

4.1.1. Pre-Quench Heat Treatments

The sample foils were received as 120 μm thick rolled foil. Ten rectangular coupons of 1.5 × 2.0 cm² were cut from each of those previously rolled metal foils. These were then stacked on a quartz slide, inserted inside a furnace and annealed at 500°C for one hour. The annealing was followed by furnace cooling to room temperature over a span of 36 hours. This heating/cooling process relieves strains that may have been previously introduced while cutting and handling. Several coupons from each alloy were put aside as reference samples. Reference samples thus will contain only the room temperature equilibrium concentration of vacancies. Appropriately scaled SAXS data obtained for the reference samples will be subtracted later on from that of the quenched samples in order to obtain SAXS scattering from voids.

With the heat treatment described above the foils become very soft. Henceforth they need to be handled very carefully in order to avoid any physical damage. In order to
monitor temperature during the next stage of annealing and quenching, 0.076 mm diameter K-type thermocouple wires were spot-welded on the Al samples. In order to spot-weld the thermocouple wires, small pieces of Al foils and steel foils are used, which serve as the welding material. It was observed that steel foils served as better welding materials.

The thermocouple welded Al samples were then connected simultaneously (in parallel) to a Research Inc. Model 4141 Infrared Spot Heater (ISH) and a Keithley 2701 Ethernet Multimeter / Data Acquisition System (DAS) for temperature logging (Figure 4.1). The ISH consists of a controller which can be programmed to control the annealing cycles. The program allows one to control for the number of ramps, ramp rates and dwell time at any target temperature. To minimize overshooting of the sample temperature during annealing, the autotune function of the controller is used to optimize the stabilization of the sample temperature. The DAS is a buffer system which registers temperature of the sample as a function of time during the heat cycles for later transfer to a computer.

Due to the handling of the samples during welding, some strain was introduced. The specimens were subjected to deformations near the edges where the welding took place. The coupons were supported by sandwiching between two Al plates during welding which minimized deformation for the other parts of the coupon. In order to condition the coupon to the ISH heating method, the sample is subjected to a heat cycle as follows. The samples are suspended in front of the spot heater and heated up to the desired quench temperatures (550°C or 600°C) in two steps. They are heated to 300°C at a ramp rate of 150 C°/sec, then to the final temperature at a ramp rate of 250 C°/sec, held there for 15 seconds and then air cooled to room temperature at a ramp rate of 100 C°/sec. In addition to the conditioning, this heat cycle also removes the residual strain introduced in the coupons during handling.
Figure 4.1.: Schematic diagram showing the thermocouple connections.
Figure 4.2.: Schematic diagram showing the placement of the thermocouple wires relative to the ISH beamspot position. (b) constitutes the more desired configuration than (a) due to the proximity of the thermocouple wires to the ISH beamspot.

While suspending the sample, it is important to ensure that the ISH beamspot on the sample is close to the thermocouple weldings (Figure 4.2). Otherwise the thermocouples will read a temperature which is lower than the actual temperature of the ISH. This introduces an error in the parameters of the thermal history of the Al samples. For optimal thermal absorption giving uniform heating, the samples were coated in Aerodag carbon black. In addition, to optimize the heating process a concave silver reflector was placed behind the suspended sample in such a way that the sample is roughly at the focus of the reflector. Throughout this process the samples were handled carefully to avoid any kind of bending and twisting of the samples which minimizes the introduction of deformations which can create artifacts in the SAXS data.
4.1.2. Quench Treatment

Following the previously discussed heat treatments comes the important step of thermal quenching the different coupons, the key step to produce voids. This step involves applying identical heat treatments to the different coupons with the ISH: heating to the maximum quench temperatures (550°C and 600°C) with the same ramp rates, holding at those temperatures for 15 seconds and then rapid quenching to a water bath maintained at 5°C. The quench and bath temperatures were chosen to optimize the thermally induced vacancy concentration; faster quench rates to lower bath temperatures have been shown to maximize the number of thermal vacancies while reducing vacancy agglomeration [Khellaf et al., 2002]. Sample naming follows the convention (alloy)(quench temperature), where the alloy is either 3N or 4N. The data registered in the DAS is used to measure the quench rates. Figure 4.4 shows the quench curves for the three samples, namely 3N550, 4N550 and 4N600. The quench rates obtained ranged from $10^3$°C/sec to $10^4$°C/sec (Table 4.1). The quenching was performed by physical immersion of the samples into the water bath (Figure 4.3). While reproducible quench rates are highly desirable, the process of physical immersion makes this difficult to achieve in practice.

It is clear from Figure 4.4 that the quench curve for 3N550 sample consists of lesser number of data points during the quenching process than that of the 4N samples. This is due to the fact that the DAS was operated in a slow mode. As the quench rate is calculated from the steepest part of the quench curve, the lesser number of quench data of 3N550 compared to that of the 4N samples may result in the lower quench rate obtained from our experiment.

After quenching the coupons were aged in a water bath at 5°C for approximately 12
Figure 4.3.: Schematic diagram showing the quench apparatus. Spot heater emits visible and infra-red radiation which heats up the suspended Al sample. A silver reflector is placed behind the sample in order to focus the reflected radiation back on the sample. A quench bath, beaker with water and dry ice maintained at 5°C is kept directly below the suspended sample. The sample can be rapidly immersed in the bath to achieve good quench rate. The temperature of the sample is monitored with the help of the thermocouple wires welded, which is fed to the temperature acquisition system.
Table 4.1.: Quench rates obtained for the Al samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quench Rate (°C/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N550</td>
<td>$2.48 \times 10^3$</td>
</tr>
<tr>
<td>4N550</td>
<td>$1.08 \times 10^4$</td>
</tr>
<tr>
<td>4N600</td>
<td>$2.58 \times 10^4$</td>
</tr>
</tbody>
</table>

Figure 4.4.: Quench curves obtained for the three samples.
hours. Then the sample surfaces were electropolished in a perchloric-ethanol-water-butyl-cellusolve solution, and promptly stored in dry ice. Substantial void scattering is expected for the coupons having higher quench temperature and quench rate [Westfall et al., 2008]. For our analysis, three samples are used - 3N550, 4N550 and 4N600 - and compared to the reference samples, which were not thermally quenched. The microstructure for 4N600 around the region where the SAXS beam was positioned is shown in Figure 4.5 demonstrating the typical observation of large grain size with strong cubic texture, which minimizes the probability of multiple scattering from different orientations.

4.2. Synchrotron SAXS Experiment at CHESS G1

The next stage of the experiment involves SAXS data collection at the CHESS G1 station with the processed samples. CHESS is a national user facility supported by the National Science Foundation and the National Institute of Health/National Institute of General Medical Sciences under Award DMR-0225180.

In general the X-rays emitted from the source are shaped using a set of beam-shaping slits to minimize the spread of the beam thereby giving access to scattering information at low angles near the direct beam. The shaped beam passes through the sample under investigation and the resultant scattering is recorded on a detector, which is protected from the main beam by an opaque beam stop. Figure 4.6 shows the schematic layout of the beam shaping process. In this section, the SAXS data collection procedure will be discussed in detail.
Figure 4.5.: Electron channeling contrast image of the approximate region of the 4N600 sample probed by the X-ray beam. The image shows relatively large grain areas extending through the thickness of the foil. This minimizes the occurrence of grain boundaries and resultant multiple scattering artifacts. The rectangular hole in the middle of the sample was bored using Focused Ion Beam methods to measure the thickness of the sample (108 microns). The horizontal lines indicate the roll processing direction.
Figure 4.6.: Schematic representation of a general SAXS experimental set up, ss1 and ss2 are a set of beam-shaping slits and the sample is placed between the final beam-shaping slit ss2 and the detector.
4.2.1. CHESS G1 Set Up

The Cornell Electron Storage Ring (CESR) contains electrons and positrons rotating in counter-rotating directions with relativistic speed, with an energy of 5.3 GeV. The circular motion is produced by a series of bending magnets. Due to the accelerated motion of the charged particles, radiation is emitted in the form of X-rays in the tangential direction. Like every synchrotron, CHESS G1 offers a continuous spectrum of energy to work with.

For the present study, SAXS data were obtained at room temperature using a beam energy of 8.49 keV (generally the desired energy is obtained by adjusting the monochromator system), with an energy resolution, $\Delta E/E$, of about 1% where $E$ is the energy of the monochromatized beam. This source offers an intense, well-collimated beam with a flux of $5 \times 10^{12}$ photons/second/mm$^2$ and angular divergence of approximately 0.1 mrad in both vertical and horizontal directions.

The X-ray beam is fed into the G1 station through an evacuated beampath (pressure 12 mTorr). Three sets of beam shaping slits inside the G1 station provided a beam spot size of $0.6 \times 0.6$ mm$^2$ at the sample position. The slit size is precisely measured by tracking the motorized positions of the beam shaping slits. The sample is placed in air in a narrow region within the beampath. The post sample beampath is sealed by Kapton windows. A Si diode supported on a piece of lead (3 mm $\times$ 8 mm) acts as the main beam stop as well as an intensity counter. It is placed on the final beampath window, near to the detector.

The CHESS G1 detector consists of a $1024 \times 1024$, slow-scan Charge Coupled Device (CCD), home-built by Dr. M. W. Tate and Dr. S. M. Gruner of the Cornell University Physics Department, with $69.8 \times 69.8$ micron$^2$ pixels.
4.2.2. Data Collection

As a first step, the beamline needs to be set up according to the particular experiment as discussed in the previous section. Firstly, the monochromator system was adjusted to obtain the desired beam energy which is determined by the nature of the sample and the sample thickness [Glatter and Kratky, 1982]. The beam shaping slits were adjusted to minimize the beam size spot size while maintaining high flux. Computers with a Linux based operating system are used to control the motors responsible for the motion of all of the slits, the detector, and the sample stage. A final pair of guard slits located just before the sample position were adjusted to cut off parasitic scattering generated by the beam shaping slits to a final beamspot size of $0.6 \times 0.6 \text{ mm}^2$ at the sample position. The beamstop, supposed to protect the detector from the main beam was precisely positioned using burn paper to provide a physical location of the direct beam and the Si pin diode which provides an electronic reading of the incident beam. Finally, the relative positions of the detector and downstream beampath were adjusted to obtain the desired sample to detector distance (SDD).

Next step is the alignment of the sample holder in the path of the beam. The sample holder was machined to high precision in the machine shop of the Department of Physics, Engineering Physics and Astronomy, Queen’s University. Identical circular apertures of $2.0 \pm 0.1 \text{ mm}$ diameter, spaced $5.0 \pm 0.1 \text{ mm}$ vertically and $5.5 \pm 0.1 \text{ mm}$ horizontally, are milled into the sample holder, a $3.18 \text{ mm}$ thick rectangular Al piece (Figure 4.7). The aluminum samples were attached by adhesive tape to this vertical sample holder which was introduced into the beampath by mounting it on a motorized stage capable of moving in the x-z plane, perpendicular to the X-ray beampath, with an accuracy of approximately 3
microns. The consistency of each aperture was confirmed by comparing background scans obtained by positioning the different apertures in the main beam (without sample) to verify the absence of holder artifacts. Macros were written in order to efficiently automate this motor movement to expose the different apertures. With this arrangement, the best spot of any sample can be easily identified by taking scans of the different parts of the sample by moving the sample holder without physical movement of the sample as required by the use of the single aperture support which was used in previous work [Westfall, 2008], thereby reducing the possibility of damage through handling\(^1\).

The next step involves the set up of the detector. The detector was positioned in such a way that only one corner of the detector was exposed to the direct beam. As noted previously, the detector was protected from the main beam using the Si pin diode beamstop assembly in the post sample beampath window, also used to measure transmitted intensity. A vertical strip of the detector, about 100 pixels wide, was blocked by Pb tape. The detector signal in the covered region was used to directly monitor the residual dark count signal, which is the offset detector signal in the absence of any X-rays which originates from the electronic noise. At large sample-detector distances (SDD), 1579 mm, additional lead tape (7 mm \(\times\) 3 mm) was placed downstream in front of the detector, in air and after the beampath to block the overly bright tail end of the main beam.

Following the beamline setup, two sets of calibration were needed. Angle calibration (detector pixel to wavevector conversion) was obtained using a silver behenate calibration standard [Huang et al., 1993]. Absolute intensity calibration (conversion of intensity into absolute units) was done using a glassy carbon calibration standard [Zhang et al., 2009].

\(^1\)Still, the coupons sometimes had to be physically moved slightly if artifact scattering was observed, particularly after aging treatments.
Figure 4.7.: Sample holder and its alignment in the beampath.
Measurements on each sample were performed at two different SDDs, 350 mm and 1579 mm, to obtain a $q$ range extending from 0.025 Å$^{-1}$ to 0.6 Å$^{-1}$ (Figures 4.8 and 4.9). As will be discussed in the next chapter the scattering data can be converted to absolute intensity units using data collected from the glassy carbon standard. The data from different sample-detector distances (low $q$-high $q$), in absolute intensity units, can be directly combined. The resulting $q$ range is approximately three times that obtained in previous work [Westfall, 2008]. A He ion counter located upstream from the final set of shaping slits is used to obtain a pre-sample measure of the incident beam. The transmitted beam intensity is monitored by the pin diode located before the detector. The ratio of the readings from the ion counter and the pin diode are used to obtain transmission ratios for the samples. In fact, this method gives an approximate measure of the transmission ratio. Ideally, the transmission ratio should be obtained from the ratio of beam intensities measured immediately before and after the sample. Using the available measures of transmission ratios the calibrated data from the two SDDs do not line up exactly. Minor rescaling was required which results in propagated error in parameters derived from the combined (low $q$-high $q$) absolute intensity data.

Preliminary processing of the 2D SAXS images were performed using FIT2D [Hammersley, 2004], after implementing a residual dark count correction using Matlab.

### 4.3. Artificial Aging Experiments

A preliminary aging experiment was conducted using the 3N550 and 4N550 samples aged at different temperatures. A temperature controller connected to a hot plate (used to heat
Figure 4.8.: Far-back and Up-close configurations.
Figure 4.9.: Scattering data for the 4N550 sample is shown for the experimentally accessible q range in absolute units. Apparent mismatch at about $q = 0.1 \text{ Å}^{-1}$ is due to the tail of the main beam in the up-close configuration.
the samples) was used to artificially age the samples to desired temperatures. The 3N550 sample was aged at 90°C and low $q$ data was obtained for times 20 minutes, 60 minutes and 200 minutes. The 4N550 sample was aged at 60°C and low $q$ data was obtained for times 20 minutes and 80 minutes, and then aged at 90°C and low $q$ data was obtained for times 20 minutes and 60 minutes. Also high $q$ data for times 0.5 minutes, 2.5 minutes and 7.5 minutes were obtained for a different 4N550 sample aged at 145°C. The aging temperatures were chosen in such a way so that within the limited beamtime, one can obtain data that will exhibit void dynamics at low and high aging temperatures.

It is to be noted that limited data was obtained for this preliminary aging experiment due to the limited beamtime available and the need to reject numerous data sets due to contamination by multiple scattering artifacts.

4.4. Summary of the Chapter

The essential details of the sample processing and SAXS beamline setup were discussed. The experiments consists of two parts - material processing and data collection at the CHESS G1 beamline. A brief account of the CHESS G1 beamline set up and its parameters was provided. The procedures required for data processing and analysis leading to the results of nanovoid characterization for this study will be discussed in the next chapter.
5. Results

The first and the most important part in obtaining results from SAXS data is the data processing. There are a few steps involved and each one has its own importance. The first one involves background subtraction. The blank scattering obtained by positioning empty holes of the sample holder in the direct beam was used to obtain background SAXS profiles. The background data contains scattering from air and also from the Kapton windows, covering the beampath windows. With background subtraction this unwanted scattering is removed from the SAXS data to be analyzed. Next, in our study absolute intensity calibration was performed using a glassy carbon calibration standard. The absolute intensity calibration is quite uncommon in SAXS literature, however it provides an efficient way of merging the low $q$-high $q$ data and a true measure of the total scattered intensity, $Q_{\text{eff}}$. The absolute intensity calibration is done using standard formulas discussed by Dreiss et al. [Dreiss et al., 2006]. The void scattering data in absolute units was then found by subtracting the calibrated reference sample scattering from the calibrated quenched sample scattering.

The next stage of analysis pertains to SAXS analyses procedures, namely Gunier analysis, Porod analysis and Indirect Transform Methods. The details of the theory behind
these analyses were discussed in Chapter 3. In this chapter the working procedure will be discussed. Also the parameters obtained for nanovoid characterization will be laid out.

5.1. Data Processing

5.1.1. Background Subtraction

The data obtained from the CHESS G1 beamline are 2D images in tif format. Every 2D image dataset is accompanied by a listing of the total counts registered by the upstream ion counter (located before the sample) and the pin diode (located after the sample, just before the detector). The raw data for each set of samples were inspected in FIT2D to identify artifact scattering (Appendix E). The raw data are first corrected for the detector dark count. As mentioned earlier, a measure of residual dark count is obtained using the counts in the lead tape covered region of the detector. Analyzing the 2D images in FIT2D, it has been observed that the dark count is constant along each row of pixels of the detector. A Matlab program is used to read in the $1024 \times 1024$ 2D image data, identify the average residual dark count as a function of row, and subtract this number from the scattering data. The dark count corrected data is then ready for background subtraction. For every sample image ($I_s(q)$) a background image ($I_{BG}(q)$) is obtained with the empty sample holder. The data are both normalized for exposure times and incident intensity before performing background subtraction. The normalization takes care of the changes in the scattering intensities of the sample and background due to different initial flux and the time of exposure, if any. Thus,
\[ I(q) = \frac{I_s(q)}{T_s} \left( \frac{1}{I_{o,s}} \right) - \frac{I_{BG}(q)}{T_{BG}} \left( \frac{1}{I_{o,BG}} \right), \]  

(5.1)

where \( T_s \) and \( T_{BG} \) are the transmission ratios of the sample with background and background only, respectively. \( I_{o,s} \) and \( I_{o,BG} \) are the incident beam intensities for the same configurations.

Transmission ratios \( (T_x, x = s \text{ or } BG) \) were obtained using the ratios of pin diode readings readings after the sample \( (I_{T,x}) \) to helium ion counter readings before the sample \( (I_{o,x}) \), i.e.,

\[ T_x = \frac{I_{T,x}}{I_{o,x}}. \]  

(5.2)

This simplifies equation 5.1 to the following,

\[ I(q) = \frac{I_s(q)}{I_{T,s}} - \frac{I_{BG}(q)}{I_{T,BG}}. \]  

(5.3)

This gives the sample scattering intensity, normalized for incident intensity and exposure times, in terms of the measured scattering data and pin diode readings. The background corrected 2-D scattering profiles are completely isotropic (Figures 5.1-5.3) and are circularly integrated to obtain 1-D \( I(q) \) versus \( q \) data for further analysis using FIT2D [Hammersley, 2004]. The entire process is summarized in Figure 5.4.

Note that the background was obtained for the empty sample holder, hence defining \( T_{BG} \) may seem physically unrealistic. In fact, \( T_{BG} \) is the ratio of the pin diode reading to that of helium ion counter reading for the empty sample holder in the beampath. The term transmission ratio for the background is used in the discussion to keep the terminology consistent with that of the established SAXS literature which refers to scattering from
Figure 5.1.: 2-D scattering profile of 4N550 sample in far-back position. The beamstop is at the right bottom corner.
Figure 5.2.: 2-D scattering profile in 3N550 sample in up-close position. There is clear shadowing effect at higher pixels due to the cylindrical beam path obstructing the parasitic scattering at higher angles. The double ring structure is background scattering from kapton windows which is useful for confirming effective background correction.
Figure 5.3.: 2-D scattering profile of a 4N reference sample in the up-close position.
Figure 5.4.: Flow chart showing the stages of background subtraction. The equations leading to corrections in each step are discussed in the text.

For angle calibration (pixels to $q$ conversion), a silver behenate (Ag-Be) standard [Huang et al., 1993], a white powder, was supported on a piece of Kapton tape and placed in the path of the beam on the sample holder. The powder scattering pattern yields a series of well defined rings occurring at known scattering angles (first ring at $q = 5.59 \ \text{Å}^{-1}$, second ring at $q = 8.14 \ \text{Å}^{-1}$, etc. for the given energy). The location of these rings, together with the known location of the direct beam on the detector, is used to convert the 1D scattering angle data from units of pixels to inverse angstroms.
5.1.2. Absolute Intensity Calibration

The background corrected data is then calibrated to obtain scattering intensity in absolute units using glassy carbon as a secondary standard [Zhang et al., 2009]. The differential cross section \( \left( \frac{\partial \Sigma}{\partial \Omega} \right)_{st} (q) \) (number of photons scattered per unit time per unit incident flux per unit irradiated volume per unit solid angle) and thickness, \( d_{st} \), for the standard is known. The corrected scattering intensities for the sample \( (I_{sam}(q)) \) and the glassy carbon standard \( (I_{st}(q)) \) are obtained using the same beamline configuration. Following Dreiss et al. (2006) [Dreiss et al., 2006] the differential cross section for the sample \( \left( \frac{\partial \Sigma}{\partial \Omega} \right)_{sam} (q) \) in units of cm\(^{-1}\)sr\(^{-1}\) is given by,

\[
\left( \frac{\partial \Sigma}{\partial \Omega} \right)_{sam} (q) = \left( \frac{\partial \Sigma}{\partial \Omega} \right)_{st} (q) \frac{I_{sam}(q)}{I_{st}(q)} \frac{d_{st}T_{st}}{d_{sam}T_{sam}}.
\]

(5.4)

True values of the calibrated intensities require accurate measures of the sample thickness \( (d_{sam}) \), standard thickness \( (d_{st}) \), sample transmission ratio \( (T_{sam}) \) and standard transmission ratio \( (T_{st}) \). Note that \( T_{sam} = T_{S}/T_{BG} \). Experimentally both \( T_{S} \) and \( T_{BG} \) are measured to provide an estimate of \( T_{sam} \). While it is straightforward to obtain thickness values, accurate measures of the transmission ratios require measures of the beam intensity immediately before and after the sample. As noted in the previous chapter the pre-sample beam intensity was measured by a He ion counter located upstream from the final set of beam shaping slits, not immediately before the sample. This introduces a significant uncertainty in the measure of the incident beam.

Absolute intensity data were obtained for samples with thermally quenched voids (3N550, 4N550 and 4N600) and for the 3N and 4N reference samples subjected to the same pre-
quench heat treatment. Scattering from voids \( I_{\text{void}} (q) \) is obtained by subtracting the reference scattering \( I_{\text{ref}} (q) \) from the quench sample scattering \( I_{\text{sam}} (q) \) (Figure 5.5),

\[
\left( \frac{\partial \sum}{\partial \Omega} \right)_{\text{void}} (q) = \left( \frac{\partial \sum}{\partial \Omega} \right)_{\text{sam}} (q) - \left( \frac{\partial \sum}{\partial \Omega} \right)_{\text{ref}} (q). \tag{5.5}
\]

Information on the voids is obtained from the void scattering, \( \left( \frac{\partial \sum}{\partial \Omega} \right)_{\text{void}} (q) \). The entire process is summarized in Figure 5.6.

In the previous work [Westfall, 2008], absolute intensity calibration was not employed. Equation 5.3 was used to find out the void scattering in arbitrary units. This equation can only provide void scattering intensities that are proportional to the true void scattering if the reference and quench samples are of the same thickness. In the present study, with the use of equation 5.4, the scattered intensities of both the sample and the reference were scaled for the thickness and transmission values. Hence, this approach offers a more general result that can be applied to a set of samples and references of any thicknesses. In addition, the resulting void scattering data is in absolute units which allows for the extraction of quantitative information that is not available when working with arbitrary units (e.g. true estimates of void volume fraction).

### 5.2. Nanovoid Characterization

Once the void scattering data is obtained, the following SAXS analysis procedures were implemented in order to obtain physical parameters, namely void radii, interface thickness, number distributions and the void volume fraction. The following sections provide the details of these analyses. As discussed earlier, SAXS characterization of nanovoids in pure
Figure 5.5.: 1-D integrated data (log scale) of 4N550 for SDD=1579 mm showing sample scattering, reference scattering and void scattering.
Figure 5.6.: Flow chart showing the stages of absolute intensity calibration. The equations needed are discussed in the text.
Al is the most important motivation of this study. Due to the low electron density contrast and the dilute nature of the voids, this is a challenging problem since the void scattering signature is generally very weak relative to the matrix scattering. This requires complete removal of background artifacts, as well as possible multiple scattering artifacts, before the true void scattering can be isolated. A significant amount of data must be discarded as a result of the observation of scattering artifacts that can not be satisfactorily removed [Westfall, 2008]. The Al nanovoid characterization described here goes significantly further than that previously reported through the use of an exact method of removing the reference scattering (section 5.1.2). In addition, an extended scattering angle range was employed allowing for analysis of the high-q Porod region to identify the presence of a finite void-matrix interface. Finally, the use of ITM analysis procedures, in conjunction with absolute intensity values has, for the first time, yielded a measure of the void number distribution.

5.2.1. Radius of Gyration - Variation with Sample Purity and Thermal History

The radius of gyration ($R_g$) determines the size of voids and is the most fundamental characterization parameter. As discussed in chapter 3, $R_g$ is obtained using both Guinier analysis ($I(q) = I(0) \exp \left( -\frac{q^2 R_g^2}{2} \right)$) and ITM analysis methods (Appendix C), thereby providing some validation of the numbers obtained. The order of magnitude of $R_g$ values yielded by the two independent characterization methods are equal within uncertainty. Also TEM studies of voids on similar samples in earlier work [Westfall et al., 2008] show similar void sizes.
Estimates of $R_g$ are made from the $\left( \frac{\partial \Sigma}{\partial \Omega} \right)_{\text{void}}(q)$ data. During Guinier analysis, a plot of $\ln(I(q))$ versus $q^2$ is obtained and the slope of the straight line at low $q$ provides the estimates of $R_g$. Figure 5.7 shows representative Guinier plots of void scattering in the different samples. The range of $q$ for Guinier analysis for all three samples is given by $0.8 < qR_g < 1.6$. This range falls well within what is discussed by Feigin and Svergun [Feigin and Svergun, 1987].

The 3N550 sample has a higher impurity content and exhibits similar void sizes, in general, with that of the purer 4N samples within the estimated uncertainties. Also 3N550 had an order of magnitude lower quench rate than that of 4N samples (Table 4.1). These results are consistent with the $R_g$ values obtained either using Guinier analysis or ITM
Table 5.1.: Values of radius of gyration ($R_g$) for different samples having different thermal history (quench rates)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quench Rate ($^\circ$C/sec)</th>
<th>ITM $R_g$ (nm)</th>
<th>Guinier $R_g$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N550</td>
<td>$2.48 \times 10^3$</td>
<td>2.06±0.18</td>
<td>2.34±0.23</td>
</tr>
<tr>
<td>4N550</td>
<td>$1.08 \times 10^4$</td>
<td>1.78±0.30</td>
<td>2.14±0.24</td>
</tr>
<tr>
<td>4N600</td>
<td>$2.58 \times 10^4$</td>
<td>1.96±0.23</td>
<td>1.99±0.19</td>
</tr>
</tbody>
</table>

The uncertainties quoted here are estimated using a combination of linear regression and calculation of $R_g$ from extended $q$ ranges.

### 5.2.2. Porod Analysis and the Interface Thickness

In the high $q$ region the ideal SAXS scattering follows Porod’s law [Glatter and Kratky, 1982],

$$I(q) \propto \frac{Q S}{\pi V q^4},$$

(5.6)

where $Q$ is the invariant which measures the total scattering intensity, $S$ is the total interfacial surface area, $V$ is the total particle volume. The specific surface area can be found from a plot of $I(q) q^4$ versus $q^4$. In presence of a finite Laue background [Feigin and Svergun, 1987] the above equation for Porod’s law is modified to
\[ I(q) \propto C_0 + \frac{Q S}{\pi V} \frac{1}{q^4}, \]  
(5.7)

where \( C_0 \) is the slope of the \( I(q) q^4 \) versus \( q^4 \) plot and denotes the Laue background.

When the constant background term \( C_0 \) is removed [Yu et al., 1999] the slope obtained at high \( q \) can be used to obtain a measure of the specific surface area, assuming an ideal, sharp interface between the void and the metal matrix. It is evident from equations 5.6 and 5.7 that a plot of \( Iq^4 \) versus \( q^4 \) will yield a positive slope (the slope of the linear region observed at the high-\( q \) limit of the data) in the presence of the constant background, which is reduced to zero when the background is removed. This is an iterative process, Figure 5.8 shows the representative plots.

As discussed in chapter 3, for a diffuse interface, the expression, \( I(q) \propto \frac{1}{q^4} \exp(-4\pi^2 \sigma^2 q^2) \), will be used to obtain interface thicknesses, \( \sigma \). Table 5.2 shows the \( \sigma \) values obtained for different samples with estimated uncertainties of 0.1 nm. Within the estimated uncertainty, no physically significant variation of \( \sigma \) with impurity content and thermal history can be identified. The uncertainty may be decreased experimentally by obtaining higher quality, less noisy high-\( q \) data.

5.2.3. Application of Indirect Transform Methods - Variation of Number Fraction Distribution, \( N_f(R) \), with Sample Purity and Thermal History

The application of the ITM to the void SAXS data is carried out by the GNOM program package [Semenyuk and Svergun, 1991]. In the package the input is provided in the form
Figure 5.8.: a) Porod plots of void scattering in 4N550 sample at high $q$ in presence of a Laue background having a positive slope. b) When the constant background is subtracted, one obtains an overall zero slope (denoted by red) with a slight negative deviation at high $q$ (denoted by green).
Table 5.2.: Table showing the variation of $\sigma$ with samples differing in impurity content and quench rates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quench Rates (°C/sec)</th>
<th>$\sigma$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N550</td>
<td>$2.48 \times 10^3$</td>
<td>0.27±0.10</td>
</tr>
<tr>
<td>4N550</td>
<td>$1.08 \times 10^4$</td>
<td>0.20±0.10</td>
</tr>
<tr>
<td>4N600</td>
<td>$2.58 \times 10^4$</td>
<td>0.11±0.10</td>
</tr>
</tbody>
</table>

$I(q)$ versus $q$ and the program fits the data according to user supplied extrema values of particle radii, $R_{\text{max}}$ and $R_{\text{min}}$. As discussed in chapter 3, the optimized fitting provides number distributions, $N(R)$, of the voids, assuming a polydisperse sphere model. This method of optimized fitting of the scattering data was developed by Svergun [Svergun, 1992], where perceptual criteria were defined to obtain the best fit of the scattering data.

By perceptual criteria, it is meant that a quantitative estimate of the quality of ITM fitting of SAXS data ($I(q)$ versus $q$) will be determined, providing a physically meaningful distribution function, $N(R)$. The quality of the data fitting depends individually on a number of mathematical parameters [Svergun, 1992]. The effect of all the individual parameters is replaced by the value of a single estimate, the total estimate ($TE$), which basically is a weighted average of all the parameters. It is observed that $0 < TE < 0.5$ corresponds to a suspicious solution, $0.5 < TE < 0.7$ corresponds to a reasonable solution and $0.7 < TE < 1$ corresponds to a good solution. In the present study, iterative employment of ITM analyses provided $N(R)$ of voids for all the three samples within the range,
0.58 < \( TE \) < 0.75. The optimized data fitting are shown in Figures 5.9 - 5.11.

It should be acknowledged that the scattering from the 3N sample (Figure 5.9) at high \( q \) is apparently inconsistent with the assumption of compact 3D scatterers, as expected for voids. The ITM fit that is shown is representative of the low \( q \) scattering data which is attributed to the presence of voids, as noted in previous work [Westfall, 2008]. The high \( q \) data that is available to this study for the 3N sample indicates the presence of complex small-scale structures which have not yet been identified.

In the analysis methods discussed above it is assumed that the voids have a compact structure. This assumption is confirmed by previously obtained TEM images [Westfall et al., 2008] of similar samples and slopes of -4 consistently obtained from the \( \ln I(q) \) versus \( \ln q \) plot, as predicted by Porod’s law.
Figure 5.10.: ITM fitting of Void scattering from 4N550 (log scale), $TE = 0.68$. 
Figure 5.11.: ITM fitting of Void scattering from 4N600 (log scale), $TE = 0.75$. 
In this connection it is worth mentioning that apart from the 3-D voids, dislocation loops are also present in the quenched Al samples. However due to the absence of a prominent electron density contrast between a loop and the metal matrix, the loops do not contribute to the SAXS data. However if the loops act as sites of agglomeration of non 3-D structures (for example, 2-D Guinier Preston zones in metal alloys), then they would contribute to SAXS scattering which can be identified from the \( \ln I(q) \) versus \( \ln q \) plot.

The number distribution (in relative units), \( N(R) \), of voids is obtained from the volume distribution \( V(R) \), provided by GNOM, using the relation \( N(R) = \frac{3}{4\pi} R^{-3} V(R) \). The volume distribution is itself obtained from GNOM in relative units (un-normalized). The number distribution denotes the relative number of voids of different radii in the illuminated samples with the maximum occurring at the most probable void radius. The number fraction, \( N_f(R) \), can be evaluated from the the number distribution by normalizing with a factor that is equal to the total number of voids in relative units, \( N_{total}^{rel} = \int_{\text{R}_{\text{min}}}^{\text{R}_{\text{max}}} \frac{N(R)}{\text{R}_{\text{max}} - \text{R}_{\text{min}}} dR \). The quantity \( \frac{N(R)}{\text{R}_{\text{max}} - \text{R}_{\text{min}}} \) is equivalent to a one dimensional number density. Since the distribution can be formulated in both discrete and continuous terms, the integral can be replaced by the sum \( \sum_{i} N(R_i) \), where \( N(R_i) \) is the relative number of voids with radius \( R_i \).

If an estimate of the true or absolute total number of voids (\( n_{abs} \)) is available, the number distribution of voids in absolute units \( N_{abs}(R) \) can be estimated using the simple relation, \( N_{abs}(R) = n_{abs} \times N_f(R) \). Given an effective measure of the total scattered intensity (\( Q \)) in absolute intensity units, the overall void volume fraction can be determined leading to estimates of \( n_{abs} \) and \( N_{abs} \).

Number fraction distributions of voids, \( N_f(R) \), are observed to be directly related to impurity level and not so much to the quench rates. The number fraction distribution curves
Figure 5.12.: Number fraction distributions ($N_f(R)$) of nanovoids in different samples.

show similar shapes for the 4N samples with different thermal histories, but a distinctly different shape is seen for the 3N sample. Thus it can be concluded that the number distribution of quench voids is a strong function of impurity content (Figure 5.12).

5.2.4. Effective $Q$ and Void Volume Fraction

As discussed in chapter 3, the effective value of the total scattered intensity is estimated using the following formula,

$$Q_{eff} = \int_{q_1}^{q_2} I(q)q^2 dq + \int_{q_2}^{\infty} \frac{k}{q^2} dq. \quad (5.8)$$
This is the best approximation that can be used to obtain a true measure of $Q_{eff}$. The values of $Q_{eff}$, for all the three samples were estimated using $q_1 = 0.0238 \text{ Å}^{-1}$ and $q_2 = 0.581 \text{ Å}^{-1}$.

One important parameter, the volume fraction of voids $\phi$, can be calculated from the invariant, $Q$, using absolute intensity data [Brumberger, 1995],

$$Q = 2\pi^2 \phi (1 - \phi) (\Delta \rho^2), \quad (5.9)$$

where $\Delta \rho$ is the electron density difference between void and aluminum metal matrix ($18.1 \times 10^{16} / \text{m}^3$). Physically, void volume fraction is defined as, $\phi = V_{\text{void}} / V_{\text{irr}}$, where $V_{\text{void}}$ is the total void volume in the irradiated sample volume of $V_{\text{irr}}$. This parameter is of fundamental importance owing to two reasons. Firstly void volume fraction is necessary to study JMAK curve of later stages of growth, as discussed in chapter 2. Also void volume fraction is related to ductile failure of metals [Thomason, 1981], a phenomenon of fundamental importance in industrial applications.

Void volume fraction, $\phi$, is defined as the ratio of total void volume to total irradiated volume. As discussed in chapter 3, this parameter is obtained from the Porod Invariant, the effective $Q$, assuming voids with zero electron density and Al matrix with constant electron density. The variation of $\phi$ with the physical conditions is shown in Table 5.3.

It is noteworthy that equation 3.16, defining $Q$, has a term $V_{\text{irr}}$ unlike equation 5.9. This is due to the fact equation 5.9 uses absolute intensity which is normalized for the irradiated volume as discussed in section 5.1.2.
Table 5.3.: Table showing the variation of $\phi$ for different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quench Rates ($^\circ$C/sec)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N550</td>
<td>$2.48 \times 10^3$</td>
<td>0.0090</td>
</tr>
<tr>
<td>4N550</td>
<td>$1.08 \times 10^4$</td>
<td>0.0028</td>
</tr>
<tr>
<td>4N600</td>
<td>$2.58 \times 10^4$</td>
<td>0.0032</td>
</tr>
</tbody>
</table>

5.3. Artificial Aging Analysis

Artificial aging experiments were performed at CHESS G1 with different samples aged under different conditions as discussed in chapter 3. Aging experiments were performed with 3N550 and 4N550 samples to study the evolution of $R_g$ with time at 60$^\circ$C and 90$^\circ$C. Also the high $q$ data of the 4N550 sample aged at 145$^\circ$C were analyzed to obtain the evolution of interface thickness, $\sigma$, and $R_g$, as obtained by ITM analysis, to study the effect of high temperature aging on void dynamics.

Due to the insufficiency of the number of viable samples for this study (due to problems of multiple scattering and limited beamtime), the analysis results can only be used to identify approximate trends as a result of artificial aging. Nevertheless, these trends are sufficiently promising to promote the design of further, more detailed aging experiments.

5.3.1. Effect of Aging Temperature and Time on Radius of Nanovoids

Low $q$ data were obtained for 3N550 and 4N550 samples aged at 60$^\circ$C and 90$^\circ$C. This enables application of Guinier analysis to obtain values of radius of gyration ($R_g$) of the
Figure 5.13.: Evolution of nanovoids with artificial aging at low temperatures.
Table 5.4.: Growth rate of nanovoids in different samples with different aging histories

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aging Temperature (°C)</th>
<th>Growth rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N550</td>
<td>90</td>
<td>0.0032±0.0010</td>
</tr>
<tr>
<td>3N550</td>
<td>60</td>
<td>0.0038±0.0035</td>
</tr>
<tr>
<td>4N550</td>
<td>90</td>
<td>0.0054±0.0025</td>
</tr>
<tr>
<td>4N550</td>
<td>60</td>
<td>0.0114±0.0022</td>
</tr>
</tbody>
</table>

Table 5.5.: Values of growth exponents and apparent diffusion coefficients assuming diffusion controlled growth of nanovoids during artificial aging

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aging Temperature (°C)</th>
<th>Exponent $n$</th>
<th>$D_h$ (m$^2$/s)</th>
<th>$D_l$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N550</td>
<td>90</td>
<td>-0.49</td>
<td>$5.1 \times 10^{-17}$</td>
<td>$5.8 \times 10^{-19}$</td>
</tr>
<tr>
<td>4N550</td>
<td>90</td>
<td>-0.64</td>
<td>$2.9 \times 10^{-17}$</td>
<td>$3.3 \times 10^{-19}$</td>
</tr>
<tr>
<td>4N550</td>
<td>60</td>
<td>-0.84</td>
<td>$3 \times 10^{-17}$</td>
<td>$3.4 \times 10^{-19}$</td>
</tr>
</tbody>
</table>

nanovoids. Figure 5.13 shows the plots of the evolution of $R_g$ of voids with time. The data, though limited in number, were fitted linearly with time showing growth of nanovoids in the quenched Al samples aged at different temperatures. The growth rate is calculated from the slopes of the growth curves (Table 5.4).

Though only a limited number of data points are used to obtain the growth rate (Table 5.4) of voids in different samples aged at different temperatures, the growth rates differ significantly within uncertainty$^1$.

$^1$Only two data points were available to study the growth law of voids in 3N550 sample aged at 60°C. Hence it is less reliable than the others. This is also manifested in the relatively higher value of uncertainty of
The uncertainties of the growth rate are the maximum uncertainties, i.e., they are not calculated from linear regression. This is done in order to demonstrate the fact that the trends obtained from the growth rates are true within the maximum uncertainty limits.

From the aging data of 3N550 aged at 90°C and 4N550 aged at 60°C and 90°C, one can evaluate the growth exponent $n$ and apparent diffusivity of nanovoids, $D$, assuming $\nu_d(t) = \alpha D^{1/2} t^n$, where $\nu_d(t)$ is the diffusion controlled growth velocity. For the ideal case $n = -0.5$ (equation 2.11). The results are shown in Table 5.5. The growth velocity $\nu_d(t)$ is obtained by calculating $\Delta R / \Delta t$ (derived from equation 2.26), where $\Delta R$ is the change in void radius in time interval $\Delta t$ at a fixed aging temperature. Overlooking the significant deviations of the experimentally determined values of $n$ (for the 4N samples) from the ideal value of $-0.5$, values of $D$ are calculated using the velocity equation mentioned above. One can use equations 2.12 and 2.13 to determine the growth coefficients, $\alpha$.

Using $c_{\text{void}} = 1$, $c_{\text{mat}} = 9.8 \times 10^{-11}$ and $6.6 \times 10^{-10}$ (vacancy concentration at the aging temperatures 60°C and 90°C, respectively), and $c_m = 9.1 \times 10^{-5}$ (vacancy concentration at the quench temperature of 550°C), one obtains $\alpha_h = 1.6 \times 10^{-4}$ (for high degree of supersaturation) and $\alpha_l = 1.4 \times 10^{-2}$ (for low degree of supersaturation). These values of $\alpha$ were used to calculate values for $D_h$ and $D_l$ (Table 5.6) for high and low degrees of supersaturation, respectively, providing upper and lower limits of void diffusivity.

The aging data for 4N550 at 145°C, as mentioned earlier, shows signs of dissolution of nanovoids. It should be noted that in this data set, only the high-$q$ data were available so that Guinier analysis was not possible. Nevertheless, it was demonstrated earlier that Guinier and ITM give consistent results. Thus it is sufficient for one to rely on the ITM
Figure 5.14.: Evolution of void radius and interface thicknesses in 4N550 sample at 145°C.
numbers only.

Here evolution of both $R_g$ and interface thickness, $\sigma$, of voids are evaluated which is shown in Figure 5.14. From the figure, it is clear that at higher temperature, the void size is decreasing and the interface thickness is increasing which is a clear sign of dissolution of voids in the metal matrix.

### 5.3.2. Evolution of Number Distributions of Nanovoids

As discussed in section 5.2.3, number fraction distributions can be obtained by employing ITM analysis on the SAXS data obtained for nanovoids in the different samples. Similar
Figure 5.16.: Time evolution of number fraction distributions ($N_f(R)$) of nanovoids in 3N550 aged at 60°C. For the set of data, $0.61 < TE < 0.64$. 
Figure 5.17.: Time evolution of number fraction distributions \( (N_f(R)) \) of nanovoids in 4N550 aged at 90°C. For the set of data, \( 0.58 < TE < 0.7 \).
Figure 5.18.: Time evolution of number fraction distributions \(N_f(R)\) of nanovoids in 4N550 aged at 60°C. For the set of data, \(0.59 < TE < 0.68\).
analyses were carried out for the SAXS data obtained for the aging experiments-3N550 and 4N550 aged at 60°C and 90°C (Figures 5.15-5.18). All of the curves indicate that with aging at 60°C and 90°C, the smaller nanovoids disappear with increasing aging time, i.e., the smaller voids feed to bigger voids as time progresses. As discussed in chapter 2, this phenomenon is known as Ostwald Ripening\(^2\). The significance of this result will be discussed in the following chapter.

### 5.4. Summary of the Chapter

The chapter lays out the critical steps involved in obtaining results for nanovoid characterization. The first step of data processing involves very rigorous routines, namely the background subtraction and absolute intensity calibration. The current data processing is capable of extracting void scattering data from samples, independent of their thicknesses. SAXS analysis techniques have been used to find out physical parameters such as void radius, interface thickness, number distribution and the void volume fraction. All these parameters are important in terms of characterizing the nanovoid structure and also analyzing the effect of artificial aging. The data obtained, though limited, shows interesting and physically meaningful trends which establish the characterization routine developed as a reliable tool. SAXS analysis at this level can be used to study void dynamics as a function of material properties and processing history. The significance of these results will be discussed in the next chapter.

---

\(^2\)It should be noted that one needs the temporal evolution of \(\phi\) for a full proof description of Ostwald Ripening. For the current study meaningful estimates of the same were not obtained for the want of high-\(q\) data.
6. Discussion

With the experimental details and results laid out, this penultimate chapter will deal with the detailed discussion of the outcomes of this study.

6.1. Nanovoid Characterization Results

In this study a rigorous method of data processing was established for extracting parameters characterizing the structure of nanovoids in nominally pure aluminum. An exact method relying on the use of absolute intensity characterization to extract the true void scattering was developed. Using this method of data processing, the radius of gyration, interface thickness, void volume fraction and number fraction distribution of voids in quenched nominally pure Al were obtained.

The void volume fraction ($\phi$) values characterizing nanovoids are observed to increase with increasing impurity level and decreasing quench rate, the size ($R_g$) and interface thickness ($\sigma$) values being same within uncertainty. Higher quench rates are believed to reduce the rate of vacancy agglomeration [Khellaf et al., 2002] during quenching. This effect is clearly observed in this study wherein the overall void volume fraction of the quenched nanovoids are reduced for samples with higher quench rates. The quenched 3N
sample was seen to have greater volume fraction of voids than that of 4N samples. Higher levels of impurity content are apparently reflected in an increased tendency to stabilize void formation. The plots of number fraction distribution also shows a residual impurity effect. The void number distribution curves for the 4N samples with different quench rates are similar, the quenched 3N shows a wider range of void sizes. Hence it may be concluded from the results presented here that the size range of voids generated in the quenched aluminum samples is a function of impurity and is not significantly affected by the value of the quench temperature. The similarity in the shape of the void number distributions for the 4N samples, contrasted with that of the 3N sample, can therefore be attributed to the difference in impurity level (Figure 5.12).

As discussed before, the volume fraction of voids, $\phi$, can be calculated from the invariant, $Q$, using absolute intensity data [Glatter and Kratky, 1982]. Values of $\phi$ for the 4N samples do not differ significantly within the estimated uncertainty of about 35%. This uncertainty results from estimates of $Q$, which rely on the use of the absolute intensity values and, therefore, the transmission ratios. It was mentioned earlier that the transmission of the samples were measured using the ratio of pin diode and helium ion counter with the sample in place and dividing by the corresponding ratio of counter readings for the empty aperture (scattering background). This is an approximate measure of the transmission ratio. Ideally, the transmission ratio should be obtained from the ratio of beam intensities measured immediately before and after the sample. The limitations of the existing beamline configuration results in significant uncertainty in the measured data which is propagated through the calculation of the Porod invariant and leads to the quoted uncertainties in the values of void volume fraction. Within the estimated uncertainty, the data
can be used to obtain an order of magnitude estimate of the total number of voids in the aluminum samples that have been studied.

An order of magnitude estimate for the determination of total number of quenched voids was made using the formulas developed in section 5.2.4. In spite of the difference in the values of void volume fraction for the 3N and 4N samples, the order of magnitude of total number of voids is roughly the same ($\approx 10^{14}$ mole$^{-1}$). With the differences in the quench rates obtained and with all other factors being constant, it was anticipated that the total number of voids produced in the different samples would vary. This was not observed in the current analyzed data and hence it therefore can be concluded that the impurity content has a more pronounced effect on the number of quenched voids than quench rates.

Continuing with the discussion of applications of the measured void volume fraction, an estimate of the vacancy volume fraction at 550°C and 600°C can be obtained from the Boltzmann distribution of vacancies with a formation energy of 0.66 eV [Simmons and Balluffi, 1960] and an estimated vacancy radius of 0.125 nm for aluminum. The values of void volume fractions obtained for both of the 4N samples are an order of magnitude lower than that of the supersaturated vacancy volume fraction (0.0200 for 550°C and 0.0340 for 600°C), as obtained from classical thermodynamics of point defects (equation 2.8). This observation is consistent with the fact that a significant number of vacancies are lost by migration to sinks such as self-interstitials, dislocations, grain boundaries and the surface during the quenching process, or collapse into loops. However, for the 3N550 sample the void volume fraction (0.0090) is about half that of the ideal vacancy volume fraction (0.0200). This result implies an enhanced loss of thermally generated vacancies during the quenching process for the sample with lower impurity level. The observation that the
measured void volume fraction is always significantly less than the ideal vacancy volume fraction serves as a consistency check of the indirect estimates of void volume fraction obtained in the SAXS study.

The value of $\phi$ can be used to determine the inter-void distance ($d_0$) which plays a direct role in ductile failure of materials [Thomason, 1981], $d_0 = r_0(\pi/\phi)^{1/2}$, where $r_0$ is void radius. Since void formation and void coalescence are believed to be the preliminary stages of crack formation (leading to ductile failure), an understanding of the role played by void density/spacing at the nanoscale level is essential to the development of material processing conditions that may be used to control this variable. With more precise measures of sample transmission ratios, the void volume fraction can be a useful parameter for optimizing material processing conditions to obtain a desired combination of strength and fracture resistance [Lloyd, 2003].

It is noteworthy that Porod analysis is mainly used for measuring specific surface area of the interface between void and metal matrix. In this case, estimating interface thickness goes beyond the Debye assumption of finite discontinuities of electron densities at interface boundaries without contradicting the observation of an asymptotic trend towards the -4 slope in the log-log plot. At the length scales accessible by SAXS measurements individual atoms are not resolved. The electron densities associated with the metal matrix and voids are represented as constants separated by an interface. It is physically unreasonable to assume a discontinuous change in electron density when going from void to metal matrix. It is more realistic to assume the existence of non-sharp interfaces. A detailed physical interpretation of the measured interface thicknesses is premature at this point, given the large estimated uncertainties that result from the experimental conditions. Nev-
nevertheless, it should be noted that the atomic radius of Al, and therefore vacancies in Al, is about 1.4 Å. A 1 Å interface thickness may be interpreted as phase mixing on the length scale of a single vacancy. This result is not physically unreasonable, a void formed by 20 vacancies is expected to possess an interface between itself and the metal matrix which is of the dimension of a single vacancy.

6.2. Aging Studies: Interpretation and Limitations

A series of techniques for extraction of nanovoid scattering and characterization of the SAXS data were developed in this study. These techniques were applied to a preliminary study of nanovoid aging in nominally pure aluminum. Given the limited amount of data available\(^1\), only very general trends can be identified.

From Figure 5.13, it is evident that the growth rate of nanovoids in 3N550 at 90°C is less than the growth rate of the same in 4N550 at the same temperature (Table 5.4). The growth rates, though obtained from a limited number of data points, are significantly different within the estimated uncertainties. This can be understood in terms of the effect of the residual impurity content in the nominally pure Al samples. As discussed before, the presence of impurities stabilizes the nanovoids. The observed lower void growth rate in the 3N550 sample when compared to that of the 4N550 sample may be attributed to this effect.

Another interesting result is the lower growth rate of nanovoids in 4N550 sample for

---

\(^1\)Generating samples with reliable thermal histories is a challenging experimental task given the nature of the immersion quench technique. Furthermore, even when the thermal history is well-defined, the usual problems associated with SAXS studies of metals means that much data must be discarded due to the occurrence of multiple scattering artifacts. For the present case, a significant part of the work went into the development of the tools necessary for this kind of study.
Figure 6.1.: Schematic diagram of void kinetics. The dashed lines show the different temperature ranges. At low temperatures, voids grow in size with greater rate than that of higher temperature where growth rate decreases. At much higher temperatures, voids dissolve in the metal matrix. (a) shows the growth rates of the voids and (b) is a pictorial representation of growth and dissolution processes.
aging at 90°C than that at 60°C (Figure 6.1). This observation initially appears to be counter-intuitive given that one would expect the voids to grow faster at higher temperatures. However, this apparent anomaly in the result can be explained if one assumes that at higher temperature dissolution of nanovoids occur, as suggested by the trend observed in the data obtained for the 4N550 sample aged at 145°C. There the voids are seen to decrease in size with increasing time (Figure 5.14). So the decrease of growth rate of voids at 90°C compared to 60°C may be due to interplay between growth and dissolution processes. In fact, growth of voids is driven by Ostwald ripening until a critical solvus temperature at which the large voids start to dissolve (Figures 5.15-5.18). From the number distribution curves it is clear that the smaller voids feeds to bigger voids, which is energetically favorable, as discussed in chapter 2. In addition, the smaller voids may dissolve, but the resulting vacancies may not feed the larger voids, and instead disappear at sinks during heating, resulting in an apparent reduced growth rate.

Another important study performed was to calculate the values of the growth exponent $n$ and the apparent diffusion coefficient, $D$, of the nanovoids in 3N550 aged at 90°C and 4N550 aged at 60°C and 90°C (Table 5.5). Interestingly for 3N550 aged at 90°C, the exponent obtained is the ideal value. For the 4N550 samples the value of the exponent differs significantly from the ideal value of -0.5. The resulting values of $D$ calculated for the voids range from $10^{-17}$ to $10^{-19}$ m$^2$/s and are several orders of magnitude lower than that of vacancies in pure Al at the aging temperatures$^2$ ($10^{-14}$ m$^2$/s). This result is consistent with the fact that voids are significantly less mobile than vacancies.

Figure 5.14 showed the evolution of $R_g$ and the interface thickness, $\sigma$, of nanovoids

$^2$The monovacancy diffusivity is calculated using the data provided by Khellaf et. al., 2002
Figure 6.2.: Schematic diagram of void dissolution as observed in the data shown in Fig. 5.14.

in 4N550 sample aged at 145°C. The decrease of $R_g$ and increase in the values of $\sigma$ are attributed to the dissolution of voids in the metal matrix (Figure 6.2). For this data, $\sigma$ was found using Porod analysis and $R_g$ using ITM analysis. The interesting observation is that the rate of void dissolution appears to follow a power law rather than a linear decay, as one would expect following the linear growths of voids at lower aging temperatures. However, this power law trend is consistent if one assumes the change of the radius of gyration of a sphere, with a constant electron density up to a radius $R_1$ and a diffuse interface with the model Gaussian convolution of spread $\sigma$ and extending up to radius $R_2$. This model calculation is discussed in the following section.
6.2.1. Power Law Dissolution of Voids: A Consistency Check

We consider the realistic case of a void with a diffuse interface. As discussed before, the change in electron density from void to interface can be modeled by convolution of an ideally sharp interface with a Gaussian function having a width that is characteristic of the diffuse interface. Consider a void of radius $R_1$ with an electron density $\rho_0$. The diffuse interface extends up to a radial distance of $R_2$ (Figure 6.3). So the electron density in the interface is given by, $\rho_i = \rho_0 \exp\left(-\frac{r^2}{2\sigma^2}\right)$, where $r$ is the radial distance and $\sigma$ is the variance and is the measure of the interface thickness.

By deriving the moment of inertia ($I$) of this electron distribution, a measure of the radius of gyration of electron distribution can be obtained. If the volume element is $dV$, then one can write,

\[ I = \int \rho_i r^2 dV. \]
\[ I = \int_{0}^{R_1} \rho_0 dV (r \sin \theta)^2 + \int_{R_1}^{R_2} \rho_0 dV (r \sin \theta)^2. \] (6.1)

Writing out the volume element explicitly, the above expression transforms to,

\[ I = \frac{8\pi \rho_0}{3} \left[ \int_{0}^{R_1} r^4 dr + \int_{R_1}^{R_2} r^4 \exp\left(-\frac{r^2}{2\sigma^2}\right) dr \right]. \] (6.2)

The resulting expression takes the following form,

\[ I = \frac{8\pi \rho_0}{3} \left\{ \frac{R_1^5}{5} + \left( \sigma^2 R_1^3 + 3\sigma^4 R_1 \right) e^{-R_1^2/2\sigma^2} - \left( \sigma^2 R_2^3 + 3\sigma^4 R_2 \right) e^{-R_2^2/2\sigma^2} \right\}, \] (6.3)

where, \( \text{erf}(x) \) is the error function given by, \( \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} dt \). Now if one considers the situation when the void size decreases and the interface thickness increases but the overall charge content (\( Q_{tot} \)) remains the same, then \( Q_{tot} \) is given by,

\[ Q_{tot} = \frac{4\pi R_1^3}{3} \rho_0 + 4\pi \rho_0 \left[ \sigma^2 \left( R_1 e^{-R_1^2/2\sigma^2} - R_2 e^{-R_2^2/2\sigma^2} \right) - \sqrt{\frac{\pi}{2}} \sigma^3 \left[ \text{erf} \left( \frac{R_1}{\sqrt{2}\sigma} \right) - \text{erf} \left( \frac{R_2}{\sqrt{2}\sigma} \right) \right] \right]. \] (6.4)

For an electron distribution, the moment of inertia can be defined as, \( Q_{tot} R_g^2 = I \). Using this expression, three values of \( R_g \) are calculated for the three obtained \( \sigma \) values from SAXS data. In each case, \( R_1 \) is taken as the void radius and \( R_2 \) is taken as \( R_2 = R_1 + 3\sigma \), as 99.7\% of Gaussian mass is limited within this range [Lifshits, 1995]. Though the \( R_g \) values have come out to be different, one can easily see that the non-linear power law behavior, as
Figure 6.4.: Comparison between experimental and theoretical curves for radius of gyration of voids for 4N550 sample at 145°C.

seen in SAXS data is observed to be consistent with the present model calculation (Figure 6.4).

In spite of the limited data available for characterization of voids during artificial aging, the interesting trends (linear growth of voids and Ostwald ripening at relatively lower temperature and non-linear dissolution at higher temperature) show the need for more detailed aging experiments, ideally performed as a function of aging time, aging temperature, and nominal sample purity. Also better estimates of the transmission ratio leading to the calculation of void volume fraction $\phi$, obtained from the detailed aging experiment can be used to describe the void nucleation and growth processes, thereby obtaining some insight as to how these interconnected processes are controlled by material parameters.
6.3. Summary of the Chapter

This chapter summarizes the importance of the results obtained in the present research effort. The physical significance of the detailed nanovoid characterization for the as-quenched samples and that obtained for the artificial aging experiments clearly demonstrates the prospect of SAXS characterization for more extensive aging experiments to study void dynamics.
7. Conclusions

A quantitative study of quench voids in nominally pure aluminum samples which differ in impurity concentration and heat treatment has been performed using synchrotron SAXS (Figure 7.1). The process of extracting void scattering data developed in this work is applicable for the sample and reference having different thicknesses. Using well established SAXS analysis techniques, quenched voids in aluminum have been characterized with significantly greater detail than presented in previous work [Westfall et al., 2008]. In addition to estimations of void size, the diffuse void metal interface thickness has been measured. For the first time, absolute intensity calibration has also been employed to obtain actual values of the total number of voids and the void volume fraction. A straightforward improvement on the method of measuring sample transmission ratio, namely through the use of beam intensities measured immediately before and after the sample, has been suggested. In this study, imperfect estimates of sample transmission ratios limits the utility of calibrated data in combining data from different sample-detector distances (low q-high q absolute intensity data). This in turn limits the precision of effective measures of $Q$, the scattering intensity, from the void scattering data obtained. Given access to more precise measures of sample transmission ratios, it will be possible to establish total void number
and void volume fraction as a function of sample impurity level and heat treatment.

The aging studies of nanovoids in the Al samples differing in impurity content and thermal histories yielded interesting results. The observation of void growth by Ostwald ripening at lower aging temperatures and the dissolution of the same at higher temperatures clearly demonstrate that the series of SAXS analysis tools developed for the current study is capable of providing precise information of the mechanisms of void growth and dissolution at the nanometer length scale. With more data, SAXS techniques can be used to undertake a thorough study of void dynamics phenomena due to artificial aging.

**Future Work**

An immediate extension of this work will apply these techniques to an extensive range of samples to establish the dependence of void size, interface thickness and void number distribution on impurity content and quench conditions in aluminum (Figure 7.1). As noted earlier, the characterization technique can be applied to an extensive study of void dynamics during artificial aging. A quench temperature of 600°C is preferred in order to obtain good statistics of void scattering at high $q$ [Westfall, 2008]. This aging study may involve artificial aging of 3N600 samples at 60°C, 80°C, 100°C, 120°C and 140°C. These aging temperatures will enable observation of both the temperature-dependent growth processes as well as the onset and nature of dissolution of voids. At all aging temperatures, low-$q$ and high-$q$ data can be obtained for discrete time intervals of 30 minutes steps in order to study temporal evolution of size and interface of the voids. These are just some suggested starting points for temperatures and time intervals for the aging experiments, balancing
the need to design experiments that can be accomplished within a reasonable timescale (a synchrotron beamtime) with the need to obtain a viable range of data. This study will establish a clear framework for the interpretation of void dynamics during artificial aging.

The next step of experimental study may involve in-situ quenching studies, in-situ deformation studies and in-situ aging studies. In-situ quenching studies will be useful in characterizing voids directly as a function of thermal history of metals whereas in-situ aging studies will be an ideal conclusive study of void dynamics during aging.

In-situ deformation studies will be a significant step towards the study of deformation...
voids and the nanoscale mechanisms that lead to crack formation and fracture failure, a long-desired goal of material science in general. This work can be extended to deal with Al alloys, materials of great commercial interest. However, void characterization in alloys will be more challenging; extracting void scattering from a combination of void scattering and precipitate scattering is a non-trivial problem.

Development of SAXS analysis techniques to study ductile failure (obtained from deformation void studies) in conjunction with modeling using PFT is viewed as having great potential to design new high performance Al alloys. That will be a key step in the development of light weight, high strength materials for use in the transportation industry, part of the larger, ongoing effort to reduce current, unsustainable levels of fossil fuel consumption. Material details expressed through free energy contributions are incorporated into the framework of the PFT. In the ideal situation, the PFT can therefore be used to predict values of a desired performance characteristic, (eg. ductility via the resulting void volume fraction) as a function of the chemical composition and thermal history of the alloy. The predicted Al alloy can be manufactured and then SAXS experiments may be performed to determine the actual value of the material parameters of interest. This would be an iterative process used to develop a viable Phase Field Model capable of successfully identifying the composition of new Al alloys specifically tailored to yield desired performance characteristics. Thus further development of the tools for SAXS characterization of nanovoids in aluminum offers an ideal experimental probe which can be applied to the development of predictive models for the design of novel high-performance alloy systems.
Bibliography


A. Derivation of Porod’s Formula

Using the expression for $Q$ from equation 3.16 and putting equation 3.9 into equation 3.6, we have the scattered intensity given by,

$$I(q) \approx \frac{Q}{2\pi^2} \int_0^D 4\pi r^2 dr (1 - \frac{S}{4V} r) \frac{\sin qr}{qr}$$

$$= \frac{2Q}{\pi q^3} \int_0^q dx (x - \frac{S}{4V q} x^2) \sin x,$$  \hspace{1cm} (A.1)

where, $x = qr$. Equation A.1 can be integrated by parts to evaluate the expression for $I(q)$. The expression is a series of negative powers in $q$ [Glatter and Kratky, 1982] and due to upper limit and in the limit of high $q$, an approximation to the final slope is given by the leading term given by,

$$I(q) \propto \frac{Q S}{\pi V} \frac{1}{q^4} + ...$$  \hspace{1cm} (A.2)
B. Thickness of Diffuse Interface: Modification of Porod’s Law

It is discussed in section 3.2 that the amplitude of the X-ray scattered is the Fourier transform of the autocorrelation function for a sharp electron density contrast between particle and matrix phases (equation 3.6), i.e.,

\[ I(q) = \mathcal{F}\{(\Delta \rho)^2\}, \quad (B.1) \]

where \( \mathcal{F} \) represents the 3 dimensional Fourier transform operator. For a diffuse interface, it is suggested that the electron density profile across the boundaries, \( \Delta \rho_{\text{mod}}(r) \), can be represented by a convolution of sharp electron density profile \( \Delta \rho(r) \) and a smoothing function \( h(r) \) [Koberstein et al., 1980, Ruland, 1971], given by,

\[ \Delta \rho_{\text{mod}}(r) = \Delta \rho(r) * h(r), \quad (B.2) \]

where \( r \) is the distance along an arbitrary vector inside the scattering volume. Hence incorporating equation B.2 into equation B.1, we have,
\[ I_{\text{mod}}(q) = \mathcal{F}\{(\Delta \rho)^2\}.\mathcal{F}\{(h^2(r))\}, \quad (B.3) \]

and thus,

\[ \lim_{q \to \infty} I_{\text{mod}}(q) = I(q).\mathcal{H}^2(q), \quad (B.4) \]

where, \( I(q) \) is the intensity determined by Porod’s formula and \( \mathcal{H}^2(q) \) is the Fourier transform of the autocorrelation of the smoothing function. The term \( \mathcal{H}^2(q) \) represents negative deviations from Porod’s law due to diffuse interface.

The form of the smoothing function is chosen according to the geometrical shape of the diffuse interface. For a sigmoidal gradient model [Hashimoto et al., 1977, Ruland, 1971], the smoothing function is Gaussian, i.e.,

\[ \mathcal{H}^2(q) = \exp(-4\pi^2\sigma^2q^2), \quad (B.5) \]

where the standard deviation, \( \sigma \), gives a measure of the interface thickness. Therefore equation B.4 transforms to the form given in equation 3.12, i.e.,

\[ I(q) \propto \frac{1}{q^4}\exp(-4\pi^2\sigma^2q^2). \quad (B.6) \]
C. Determination of Average Radius of Gyration from Indirect Transform Methods

It is discussed earlier that the number distribution of particles, \( N(R) \), can be expanded in terms of basis functions, \( N(R) = \sum_{i=0}^{n} c_i \psi_i(R) \). Also \( N(R) \) assumes non-zero value for the user defined maximum and minimum limits of particle dimension, \( R_{\text{min}} \leq R \leq R_{\text{max}} \). The average value of the radius of gyration (\( R_g \)) is obtained as follows,

\[
R_g^2 = \frac{\int_{R_{\text{min}}}^{R_{\text{max}}} N(R) R^2 dR}{\int_{R_{\text{min}}}^{R_{\text{max}}} N(R) dR}.
\] (C.1)

As this method uses the smeared data points from the entire scattering curve within the range of \( R_{\text{min}} \) to \( R_{\text{max}} \), more precise measures of the radius of gyration are usually obtained compared to Guinier analysis [Glatter and Kratky, 1982].
D. Growth Coefficients for Diffusion Limited Growth of Nanovoids in Metals

In discussing the diffusion limited growth of nanovoids, it is stated that the growth law is given by, \( \nu_d(t) = \alpha D^{1/2} t^{-1/2} \). Following the arguments by Christian [Christian, 1975], one can consider the following conditions that the present discussion on diffusion limited growth will be subjected to:

1. For growth, the radius of the voids are much greater than the critical radius \( r_c \). Then one can consider a planar interface between the voids and the metal matrix, i.e., the effect of curvature of the interface can be neglected.

2. The void growth will be considered similar to the growth of an isolated particle in an infinite matrix, so there is no impingement of voids due to void-void interaction.

Under these conditions, the growth velocity of 3 dimensional voids for higher degrees of supersaturation \( (c_{void} - c_m \ll c_{void} - c_{mat}) \) is,
\[ v_d(t) = \sqrt{3} \frac{(c_m - c_{mat})}{(c_{void} - c_{mat})^{1/2}(c_{void} - c_m)^{1/2}} D^{1/2} t^{-1/2}, \]  

(D.1)

with the growth coefficient given by, \( \alpha_h = \sqrt{3} \frac{(c_m - c_{mat})}{(c_{void} - c_{mat})^{1/2}(c_{void} - c_m)^{1/2}}. \)

For lower degrees of supersaturation \( c_{void} - c_m \gg c_m - c_{mat} \), the growth coefficient takes the form, \( \alpha_l = \sqrt{2} \frac{(c_m - c_{mat})^{1/2}}{(c_{void} - c_m)^{1/2}}. \)
E. 2-D Detector Image Showing Multiple Scattering

This is a figure showing the unused 2-D data of sample scattering from a 3N550 sample in far back position. The sharp streaks confirm the presence of scattering artifacts which cannot be removed by background subtraction and hence is not used for analysis.