Nanovoid Characterization of Nominally Pure Aluminum Using Synchrotron Small Angle X-ray Scattering (SAXS) Methods

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A small angle x-ray scattering (SAXS) study of nanovoids in 99.988 and 99.995 at.% aluminum is presented. Absolute intensity calibration using a glassy carbon standard is used to extract the weak SAXS signature from nanovoids introduced by thermal quenching. SAXS analysis methods, including Guinier, Porod and Indirect Transform, are used to obtain values for the void size, number distribution and volume fraction, as well as measures of the void-metal matrix interface structure in quenched aluminum samples. The SAXS analysis has identified a residual impurity effect on void formation and has been used to characterize trends in nanovoid size, number distribution, and interface structure as a function of aging time at elevated temperatures (artificial aging). The work presented here, 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. This level of information will be useful in developing phenomenological models of void nucleation and growth capable of linking atomic scale phenomena to macroscopic material properties.

Keywords: nanovoids; aluminum; small-angle x-ray scattering; nucleation and growth

1.0 Introduction

Aluminum (Al) and its alloys have many applications, ranging from structural components to electronic devices, which take advantage of its high specific strength, excellent electrical and thermal conducting properties. 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 which create solid solutions and precipitate phases at larger multi-dimensional length scales required to strengthen aluminum for structural applications. The
concentration of vacancies and interstitials in the lattice can be increased by increasing temperature [1], by plastic deformation, or as a by-product of irradiation [2]. Vacancies in Al become mobile at -148 °C [3] and are of special importance due to their role in substitutional diffusion. If supersaturated by quenching from higher temperatures, vacancies can move easily to annihilate with interstitials, dislocations and surfaces, condense into two-dimensional dislocation loops, and coalesce into metastable three-dimensional objects, the latter referred to as voids or nanovoids [4].

Structurally, nanovoids are obstacles to dislocation motion [5], but depending upon their size and population densities, may increase the work hardening rate which enhances resistance to necking. What is more typically observed at the macroscopic scale is that void coalescence during plasticity can lead to failure, thus reducing formability in ductile metals [6-9]. This challenges Al alloy applications in the transportation sectors where formability and crashworthiness of structural components are fundamental engineering design requirements.

Considerable experimental work has been done in studying the growth of voids under deformation [10, 11]. However, this research has generally relied on theoretical assumptions about the sites and mechanisms of void nucleation to focus on void growth and coalescence [11] since void nuclei can theoretically be as small as a cluster of four vacancies, making their dynamic production difficult to probe experimentally. Atomistic modeling methods have been used to simulate the nucleation and growth of voids in pure b.c.c and f.c.c metals in response to very high strain rates induced by shock loading [12-14]. These results clearly identify the role of vacancies in the nanovoid formation process and the importance of the strain rate, lattice stress state, and temperature but are still far from realistically incorporating impurity atoms or larger microstructural elements such as grain boundaries. Recent advances in the application of phase field theory have been used to describe the dynamics of void formation and growth in pure metals with a supersaturated vacancy concentration obtained by irradiation [15]. Simulated void formation and growth is monitored through characterization of void size, the size of the diffuse void-matrix interface, and the overall void volume fraction. Rokkam et al. [15] were successful in reproducing classical model predictions of nucleation and growth [16]. The phase field approach offers the possibility of describing void nucleation and growth in systems with spatially resolved microstructural details, such as grain boundaries and precipitate/matrix interfaces, as well as having vacancy and/or directly formed void sources.
Development of this type of phase field approach is therefore seen as a viable route towards establishing a thorough understanding of the role played by pre-existing microstructure resulting from alloying and process history in the ductile failure of engineering alloys [8]. To advance such modelling further requires quantitative data sets of early stages of void, or more specifically, nanovoid formation.

Direct imaging probes such as transmission electron microscopy (TEM) are the workhorse instrument in characterizing nanostructures, but are limited to small volumes and cannot easily access the statistically averaged static or dynamic quantities that are necessary to obtain a detailed picture of bulk materials. Also, in situ observation of dynamic processes devoid of surface effects is challenging with TEM at standard accelerating voltages. Small angle x-ray scattering (SAXS) is a characterization technique which is sensitive to nanoscale electron density inhomogeneities and provides an in situ, non-destructive probe of structure at these length scales. 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. Over the last 70 years, a comprehensive range of analysis tools has been developed to extract information from SAXS data satisfying these basic criteria [17, 18]. The use of SAXS to study the porosity of materials is not new in general [19]. However, reports of applications of SAXS methods to study nanovoids in metals, particularly Al, have been limited for three main reasons: (1) the weak electron density contrast between voids and the metal matrix (Z=13), (2) the typically dilute density of voids, and (3) the confounding effect of multiple scattering from the crystalline matrix [20]. Synchrotron radiation sources offering high flux are necessary to obtain viable scattering statistics. In addition, it has long been known that careful sample preparation, coupled with thorough scrutiny of the scattering data to identify multiple scattering artefacts [21], is essential. Past applications of the SAXS measurement tool to the study of nanostructures in metals (Antion et al. [22]; Deschamps et al. [23-25]; Dumont et al. [26, 27]; Werenskiold et al. [28]; Westfall et al. [29]) have used Guinier and Porod analysis methods, in combination with detailed modelling of the heterogeneous particle microstructure, to interpret the measured SAXS data in terms of particle size, shape, interface structure, and relative volume fraction. Most of this work has focused on the characterization of particle features in precipitation strengthened aluminum alloy systems.
This paper describes a thermal quench method used to produce a population of nanovoids in two nominally pure Al samples, and details the experimental procedure required to fully quantify the nanovoid structure. For void characterization, absolute intensity calibration methods, in conjunction with varying sample-to-detector distance, are implemented to obtain scattering data in absolute numbers over at least 3 orders of magnitude in scattering angle with good scattering statistics. To allow a straightforward application of our analysis by others, a comprehensive description of the experimental procedure and data processing relationships are given. Analysis of the scattering data reveals the void size, void number fraction, void-matrix interface shape and thickness, and the void volume fraction. Artificial ageing of the nanovoids was done as a preliminary investigation of nanovoid growth kinetics. The general methodology described may be applied to characterization of nanovoids in any aluminum alloy, whether produced by deformation, irradiation, or thermal quenching.

2.0 Experimental procedure

2.1 Material processing
Following the original work of Kiritani [4] as adapted by Westfall et al. [29], a thermal processing method was used to produce a stable population of nanovoids in two nominally pure Al samples: 99.988 and 99.995 at.%, to be designated as 3N and 4N, respectively. The samples were received in the form of cold rolled 120 µm thick foils from Toyo Aluminum. The effective impurity concentrations in ppm of 3N and 4N were 52Si-8Fe-8Cu and 3Mg-16Si-6Fe-18Cu, respectively. Ten coupons of (1.5 × 2.0) × 10⁻⁴ m² were sheared from each Al foil, stacked on a quartz slide, and annealed at 500 °C in air for one hour followed by furnace cooling to room temperature over 36 hours. This heating/cooling process makes the sample relatively strain free. Several coupons from each Al foil were put aside as reference samples. The remaining coupons were further annealed and thermally quenched using a custom apparatus [30] to produce a supersaturated vacancy concentration. Annealing was done using a Research Inc. Model 4141 Infrared Spot Heater. The coupons were individually suspended from a 76 µm diameter K-type thermocouple wire which was spot welded to the coupon and used to provide programmable control of the spot heater. The thermocouple was connected simultaneously (in parallel) to a Keithley 2701 Ethernet Multimeter/Data Acquisition System for temperature logging. For uniform heating and optimal thermal absorption
the coupons were coated in Aerodag® carbon black. Each coupon was first conditioned to the heating and cooling process by heating to just below the quench temperature (the maximum heated temperature before quenching), and then air cooling to room temperature. This heat cycle removes deformations introduced by coupon handling in preparation for the quenching process. The coupons were then heated to the quench temperatures of 500, 550 or 600°C for 15 seconds before quenching in a water bath 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 [31]. Consequently, the level of void scattering is expected to increase with increasing quench temperature and quench rate [29]. Sample naming follows the convention [Al][quench temperature], where [Al] is either 3N or 4N. The quench rates obtained ranged from 10³ °C/sec to 10⁴ °C/sec (Table 1). While reproducible quench rates are highly desirable, the process of physical immersion makes this difficult to achieve in practice. After quenching, the sample surfaces were electropolished in a perchloric-ethanol-water-butyl-cellusolve solution, and promptly stored in dry ice. For our analysis, three samples are used - 3N550, 4N550 and 4N600 - and compared to the 3N and 4N reference samples, which were not thermally quenched. The microstructure for 4N600 around the region where the SAXS beam was positioned is shown in Figure 1, demonstrating the typical observation of large grain size with strong cubic texture [32] which minimizes the probability of multiple scattering from different orientations.

2.2. Artificial aging of quench samples

A preliminary aging experiment was conducted using the 3N550 and 4N550 quench samples heated at different temperatures to test the stability of the nanovoids. Kiritani et al. [33] originally showed that quenched nanovoids in 99.999 Al would grow and stabilize up to 90 °C. Here the 3N550 sample was aged at 90°C and data was obtained for 20 minutes, 60 minutes and 200 minutes. The 4N550 sample was aged at 60°C and data was obtained for 20 minutes and 80 minutes, and then aged at 90°C and data was obtained for 20 minutes and 60 minutes. Also data for 0.5 minutes, 2.5 minutes and 7.5 minutes were obtained with a shorter sample-detector distance for a different 4N550 sample aged at 145°C to test for void dissolution. Experimental limitations (finite beamtime, the need to reject data exhibiting excessive contamination by multiple
scattering artefacts) result in a limited sampling of ageing conditions so that only a preliminary study of artificial aging can be presented here.

2.3. SAXS experiment at CHESS G1 beamline

SAXS data were obtained at room temperature at the G1 station of the Cornell High Energy Synchrotron Source (CHESS) using 8.49 keV x-rays. 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. Three sets of beam shaping slits inside the G1 station provided a beam spot size of 0.6 × 0.6 mm\(^2\) at the sample position. The aluminum samples were attached to a vertical sample holder which was introduced into the beampath by mounting it on a motorized stage capable of moving in the x-z plane with a precision of approximately 3 microns. The sample holder was designed to expose different areas of the aluminum samples with the additional advantage of defining the incident beam and reducing parasitic scattering.

Identical circular apertures of 2.0 ± 0.1 mm diameter, spaced 5.0 ± 0.1 mm vertically and 5.5 ± 0.1 mm horizontally, were milled into the sample holder for this purpose. The consistency of the transmitted beam defined by the apertures was confirmed by comparing background scans from the empty holder to verify the absence of holder artifacts. The detector was protected from the main beam using a pin diode beam stop in the post sample beam-path window\(^2\), also used to measure transmitted intensity. At large sample-detector distances (SDD) additional lead tape (7 mm × 3 mm) was placed near the diode to further decrease intensity from the tail end of the main beam.

Measurements were performed at two different SDDs, 350 mm and 1579 mm (see Fig. 2(a) for a representative sample of the raw 2D images), to investigate high- and low-q ranges, respectively, which could be combined to give a q range (the magnitude of the scattering vector is referred to as \( q = (4\pi/\lambda) \sin \theta \), where \( \lambda \) is the x-ray wavelength and \( 2\theta \) is the scattering angle) extending from 0.025 Å\(^{-1}\) to 0.6 Å\(^{-1}\).

Data for the preliminary artificial aging study were limited to either low-q or high-q regions. As will be discussed later (Section 3.2), the scattering is converted to absolute intensity units. The data from different sample-detector distances (low-q/high-q), in absolute intensity units, can then be directly combined. The resulting combined q range is approximately three times that obtained previously by Westfall et al. [29]. 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 only 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.

SAXS data were obtained using a 1024×1024, slow-scan CCD-based X-ray detector, home-built by Dr. M. W. Tate and Dr. S. M. Gruner of the Cornell University Physics Department, with 69.8 × 69.8 \(\mu\)m\(^2\) pixels. The detector was positioned so that only one quadrant of (ideally isotropic, Fig. 2(a)) scattering data was collected.

Preliminary processing of the 2D SAXS images were performed using FIT2D [34]. Angle calibration (conversion of detector pixel information to units of \(\text{Å}^{-1}\)) is done with a silver behenate calibration standard [35].

### 3.0 Data processing

#### 3.1. Background subtraction

The data obtained from the CHESS G1 beamline are 2D images in tif format giving access to \(x\) and \(z\)-components of the scattering vector, \(\mathbf{q}\). The raw data, obtained using exposure times ranging from 5 s to 100 s, are first corrected for the detector dark count. For every sample image \(I_\text{s}(\mathbf{q})\) a background image \(I_\text{BG}(\mathbf{q})\) is collected with the empty sample holder. The data is normalized for exposure times and incident intensity before background subtraction.

\[
I_{\text{sam}}(\mathbf{q}) = \frac{I_\text{s}(\mathbf{q})}{T_\text{s}} \left( \frac{1}{I_{o,S}} \right) - \frac{I_\text{BG}(\mathbf{q})}{T_{\text{BG}}} \left( \frac{1}{I_{o,BG}} \right),
\]

where \(T_\text{s}\) and \(T_{\text{BG}}\) are the transmission ratios of the sample plus background and background only, respectively. \(I_{o,S}\) and \(I_{o,BG}\) are the incident beam intensities for the same configurations. This calculation is applied to quench and reference samples.

Transmission ratios \((T_\alpha, \alpha = S \text{ or } BG)\) were obtained using the ratios of pin diode readings after the sample \((I_{T,\alpha})\) to helium ion counter readings before the sample \((I_{o,\alpha})\). This simplifies equation (1) to the following,
The sample scattering intensity, \( I_{\text{sam}}(q) \), is therefore normalized for incident intensity and exposure times. Ideally, the background corrected 2-D scattering profiles are completely isotropic and are integrated over one quadrant to obtain 1-D \( I_{\text{sam}}(q) \) versus \( q \) data for further analysis.

### 3.2. Absolute intensity calibration

The normalized, background corrected data, \( I_{\text{sam}}(q) \), can now be calibrated to obtain scattering intensity in absolute units using a glassy carbon secondary standard [36]. The differential cross section for the standard, \( \frac{\sigma}{d\Omega}_{\text{st}}(q) \) (number of photons scattered per unit time per unit incident flux), is known, as is the thickness of the standard, \( d_{\text{st}} \). The corrected scattering intensities for the sample \( (I_{\text{sam}}(q)) \) and the glassy carbon standard \( (I_{\text{st}}(q)) \) are obtained using the same beamline configuration and normalization procedures. Following Dreiss et al. [37], the differential cross section for the sample

\[
\left( \frac{\partial \Sigma}{\partial \Omega} \right)_{\text{sam}}(q) = \left( \frac{\partial \Sigma}{\partial \Omega} \right)_{\text{st}}(q) \frac{I_{\text{sam}}(q)}{d_{\text{sam}} T_{\text{sam}}} \frac{d_{\text{st}} T_{\text{st}}}{I_{\text{st}}(q)}. \tag{3}
\]

Accurate values of the calibrated sample scattering intensities (for both the quench and the reference samples) require accurate measures of the sample thickness \( (d_{\text{sam}}) \), standard thickness \( (d_{\text{st}}) \), sample transmission ratio \( (T_{\text{sam}}) \), and standard transmission ratio \( (T_{\text{st}}) \). 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 section the pre-sample beam intensity was measured by a He ion chamber located upstream of the final beam shaping slits before the sample. Small leaks in this He chamber volume cause the photo-current to drift substantially over time, contributing to a relatively large uncertainty in the measurement of incident intensity and, hence, \( T_{\text{sam}} \). More accurate measurements of this intensity, for example using \( N_2 \), rather than He, in the ion chamber, or using scattered
intensity from a semi-transparent scattering source, could significantly improve the determination of $T_{sam}$.

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, $\frac{d\Sigma}{d\Omega}_{void}(q)$, is obtained by subtracting the normalized, calibrated reference scattering, $\frac{d\Sigma}{d\Omega}_{ref}(q)$, from the normalized, calibrated quench sample scattering, $\frac{d\Sigma}{d\Omega}_{sam}(q)$ (Figure 3) as follows:

$$
\frac{d\Sigma}{d\Omega}_{void}(q) = \frac{d\Sigma}{d\Omega}_{sam}(q) - \frac{d\Sigma}{d\Omega}_{ref}(q). 
$$

Nanoscale structural information on the quench-induced voids is accessible through detailed analysis of the isolated void scattering, $\frac{d\Sigma}{d\Omega}_{void}(q)$. The features seen in Fig. 3 at $0.32 \, \text{Å}^{-1} < q < 0.44 \, \text{Å}^{-1}$ are from the presence of scattering from kapton™ windows in the beampath (seen in Fig. 2(a)) which is still evident after background subtraction. This feature is unavoidable in the reduced data which is very sensitive to any non-negligible interference terms involving the scattering amplitudes associated with all scatterers in the beam [18].

4.0 Results

4.1 Void size and number distributions

It should be noted that the analysis methods applied in this work assume that the quench voids have a compact structure and are not fractal in nature [38] in that they do not exhibit a highly branched or network-type of contiguous, connected vacancies. This assumption is confirmed by previously obtained TEM images [29] of quench voids in Al and approximate slopes of “-4” consistently obtained from the $\ln[I(q)]$ versus $\ln q$ plot (Fig. 2(b)), as predicted by Porod’s law [17,18]. It should also be acknowledged that in addition to the presence of 3-D voids, dislocation loops will also be present in the quenched Al samples. However due to the absence of a prominent electron density contrast between a loop and the metal matrix, these structures do not contribute significantly to the observed SAXS data. If dislocation loops acted as sites of agglomeration of non-compact structures (for example, 2-D Guinier Preston zones in
metal alloys), then these structures would likely contribute to the observed SAXS scattering. This would be identifiable through the observation of non-ideal slopes in the $\ln [I(q)]$ versus $\ln q$ plot.

SAXS is an indirect probe and is therefore highly model dependent, unlike electron microscopy which gives direct, local estimates of particle size and shape. As a minimum requirement, realistic limits on values of structural parameters should be obtained for verification of the indirectly measured scattering data. In addition, multiple independent SAXS analyses methods should be employed to monitor the validity of analysis results whenever feasible. Measurement of the void size is therefore undertaken using both the classical Guinier method and the Indirect Transform Method (Appendix A). Estimates of particle size (Table 2, radius of gyration, $R_g$) obtained from reduced data in absolute intensity units, $(\frac{\partial S}{\partial q})_{\text{void}}(q)$, agree with earlier work on similar samples [29]. The range of $q$ used for Guinier analysis of the 3N550, 4N550 and 4N600 data is given by $0.8 < qR_g < 1.6$, consistent with the fact that the method applies only to the very small angle regime.

Application of the ITM to the reduced SAXS data is carried out using the GNOM program package [39]. The realistic assumption of a polydisperse system of scatterers in applying the ITM yields a best fit result (see Fig. 3) for the volume distribution, $V(R)$, which is related to the number distribution in relative units, $N(R)$, through the relation $N(R) = \frac{3}{4\pi} R^{-3} V(R)$ (Appendix A). The values for $R_g$ from the ITM analysis are taken as the average particle size. These numbers are consistent with the results from the Guinier analysis (Table 2). The $R_g$ values characterizing void size are observed to increase with increasing impurity level and decreasing quench temperature.

The volume distribution is obtained from GNOM in relative units (un-normalized). The number distribution denotes the relative number of voids of different radii in the illuminated sample regions with the maximum occurring at the most probable void radius. The number fraction, $N_f(R)$, can be evaluated from the number distribution by normalizing with a factor that is equal to the total number of voids in relative units$^4$, $N^{rel}_{\text{Total}} = \int_{R_{\text{min}}}^{R_{\text{max}}} \frac{N(R)}{R_{\text{max}}^3-R_{\text{min}}^3} dR$. The quantity $\frac{N(R)}{R_{\text{max}}^3-R_{\text{min}}^3}$ 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
is the relative number of voids with radius \( R_i \). If an estimate of the true or absolute total number of voids (\( n_{\text{abs}} \)) is available, the number distribution of voids in absolute units \( N_{\text{abs}}(R) \) can be estimated using the simple relation, \( N_{\text{abs}}(R) = n_{\text{abs}} \times N_f(R) \). Figure 4 shows calculated number fractions, \( N_f(R) \), obtained for voids in the quenched Al samples using the method described above. Given an effective measure of the total scattered intensity (\( Q_{\text{eff}} \), Appendix B) in absolute intensity units and an estimated value for \( \Delta \rho \), the x-ray contrast between the void phase and the aluminum matrix (4.48 \( \times \) 10\(^{15}\) \( \text{m}^{-2} \)), the overall void volume fraction, \( \phi \), can be determined leading to estimates of \( n_{\text{abs}} \) and \( N_{\text{abs}} \).

Values for \( Q_{\text{eff}} \) obtained from absolute intensity data for the void scattering in the three samples of this study yield values for \( \phi \) of 6.3 \( \times \) 10\(^{-5}\) for 4N550, 5.6 \( \times \) 10\(^{-5}\) for 4N600 and 1.6 \( \times \) 10\(^{-4}\) for 3N550 (Table 2). Values of \( \phi \) for the 4N samples do not differ significantly within the estimated uncertainty of about 35%. This uncertainty results from estimates of \( Q_{\text{eff}} \) which rely on the use of the absolute intensity values and, therefore, the transmission ratios. The estimated uncertainty is dominated by the method used to estimate sample transmission ratios, as discussed in section 3.2.

4.2 Void-Metal matrix interface structure

The specific surface area can be found from a Porod plot of the reduced data (Appendix B). In the presence of a finite Laue background Feigin and Svergun [17] showed that a modified form of Porod’s law is required,

\[
I(q) \sim C_0 + \frac{Q S}{\pi N q^4},
\]

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 [40], the slope obtained at high-\( q \) can be used to obtain a measure of the specific surface area (\( S/V \)), assuming an ideal, sharp interface between the void and the metal matrix. However, when a diffuse interface is encountered the meaning of \( S/V \) is not well-defined and obtaining an estimate of interfacial thickness is then 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 [41]. The observed scattering in the Porod region, corrected for the Laue background, has the form,
Non-ideal interfaces were identified in the Porod region for the void scattering. The above equation was used to evaluate the interfacial thicknesses of the voids in the quenched samples (Table 2). This goes beyond the Debye assumption of finite discontinuities of electron densities at interface boundaries, leading to the existence of non-sharp interfaces.

Figure 5 is a Porod plot of the void scattering seen in the 4N550 sample. The presence of Laue background scattering is clearly visible at high-\( q \). When this constant background is removed, a high-\( q \) region of the data exhibiting a negative slope in the region 0.53 Å\(^{-1} \) < \( q \) < 0.58 Å\(^{-1} \) is revealed (Fig. 5) and this slope is used to extract values for the diffuse void interface thickness (Table 2). Low-\( q \) structure (\( q \) < 0.43 Å\(^{-1} \)) visible in Fig. 5 is a result of residual, but localized, scattering from kapton™ windows, as already noted in reference to Fig. 3. 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 physically reasonable as it corresponds to a minimum interface width.

4.3 Characterization of the effects of artificial aging

Artificial aging experiments were performed at CHESS G1 with the 3N550 and 4N550 quench samples to study the evolution of \( R_g \) and the number fraction distribution with time at 60°C and 90°C. Also, high-\( q \) data of the 4N550 sample aged at 145°C were analysed to obtain the evolution of interface thickness, \( \sigma \), and void size, \( R_g \), as obtained by ITM analysis to study the effect of high temperature aging on void dynamics. A limited number of viable samples were available for this study due to problems of multiple scattering and limited beamtime. As a result, 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 and implementation of future, more detailed aging experiments.
4.3.1 Aging – particle size and number distribution

Low-q data obtained for 3N550 and 4N550 samples aged at 60°C and 90°C for varying times were used to perform Guinier analysis to identify trends in the size ($R_g$) of the quench nanovoids. Figure 6 shows the plots of the evolution of $R_g$ with time. The data, though limited in number, indicate that void growth occurs at these two temperatures. ITM analysis of the 3N550 and 4N550 data was performed to verify the $R_g$ values noted in Figure 6 as well as to obtain measures of the number fraction distributions of the polydisperse system of nanovoids. Figures 7 and 8 show trends in these distributions for the 3N550 and 4N550 samples indicating that as the average nanovoid size increases with aging time, smaller nanovoids appear to feed the development of larger nanovoids. This result is consistent with the expectation that Ostwald ripening [15, 16] occurs during nanovoid aging. While the data is suggestive that this is the case, it is not conclusive since the limit to low-q information makes it impossible to obtain viable estimates of the void volume fraction as a function of aging time to provide a secondary check of this result.

4.3.2 Aging – particle size and interface thickness

Aging data for the 4N550 quench sample held at 145°C for varying time was available only for the high-q region of scattering. While Guinier analysis was therefore not possible, ITM analysis could be applied with the underlying assumption (verified through analyses performed on data reported in §4.1) that valid $R_g$ values could be obtained with this limited q-range. Porod analysis (§4.2) of the high-q data was used to obtain estimates of the void-metal matrix interface size, $\sigma$. The results shown in Figure 9 clearly indicate that at the higher temperature the void size is decreasing as the interface thickness increases. This trend signifies dissolution of voids in the metal matrix.

5.0 Discussion

A quantitative study of nanovoids in two nominally pure aluminum samples has been performed using synchrotron SAXS. Using well-established SAXS analysis techniques, nanovoids in two nominally pure aluminum samples have been characterized with significantly greater detail than presented in previous works on aluminum [29, 42]. Different populations of nanovoids were produced in aluminium
using a thermal quench method. The results conclude that the size range of voids generated in the quenched aluminum samples is a function of residual impurity content and is not significantly affected by the value of the quench temperature, within the range of quench temperatures considered. The similarity in the shape of the void number distributions for the 4N samples, contrasted with that of the 3N sample, can therefore also be attributed to the difference in impurity level (Figure 4). In contrast, the less pure 3N materials showed a larger number distribution than 4N, suggesting that impurity level plays a role in void nucleation and growth on quenching.

Absolute intensity calibration has been used to obtain actual values of the total number of voids and the void volume fraction ($\phi$). The calculated values of void volume fractions obtained for all samples are significantly lower than that of the supersaturated vacancy volume estimated from the Boltzmann distribution of vacancies expected at the quench temperature. Using Simmons and Balluffi’s mono-vacancy formation energy of 0.66 eV [1], and an estimated entropy contribution of 3, the supersaturated volume fractions are $2.7 \times 10^{-4}$ and $4.6 \times 10^{-4}$ for 550 and 600 °C, respectively. The void volume fractions obtained by SAXS for the 4N samples (Table 2) are an order of magnitude less than the theoretical supersaturated volume fractions. This result 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 [31], thereby serving as a consistency check of the indirect estimates of void volume fraction obtained in the SAXS study. Measured values of $\phi$ can be used to determine the inter-void distance which plays a direct role in ductile failure of materials [43]. With more precise measures of sample transmission ratios, the void volume fraction can therefore serve as a useful parameter for optimizing material processing conditions to obtain a desired combination of strength and fracture resistance [44].

The power of the analysis techniques discussed in this work were further demonstrated in a preliminary study of nanovoid artificial aging. From the limited data available, it is evident that the growth rate of nanovoids in 3N550 at 90°C is less than the growth rate in 4N550 at the same temperature. This observation can be understood in terms of the effect of the residual impurity content in nominally pure Al samples since Shimomura et al. [45] have shown that the presence of impurities tends to stabilize nanovoids. With only two Al samples studied in the present study, specific impurity
effects could not be identified. Observations of trends in the void-matrix interface in the 4N550 sample at 145 °C (Fig. 9) can be attributed to the dissolution of nanovoids at elevated temperatures. An apparently lower growth rate of nanovoids is seen in the 4N550 sample for aging at 90°C than at 60°C (Fig. 6). This observation initially appears to be counter-intuitive given that one would expect nanovoids to grow faster at higher temperatures. However, this may, in fact, be attributed to the interplay between the identified processes of nanovoid growth and dissolution. Aging trends in the nanovoid number distribution curves (Figs. 7 and 8) suggest that the smaller voids disappear as they feed larger voids thru Ostwald ripening.

An immediate extension of this work will apply the synchrotron SAXS techniques discussed here 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. Systematic studies of nanovoid aging, ideally performed as a function of aging time, aging temperature, and nominal sample purity, can be used to obtain precise descriptions of the void nucleation and growth processes, thereby obtaining some insight as to how these interconnected processes are controlled by material parameters. In particular, quantitative information obtained from measured void sizes, inter-void distances and void-matrix interface structures may be useful in the development of current phase field models of nucleation, growth and coalescence of voids in pure metals [15]. The ultimate goal of this avenue of research is to establish predictive, phenomenological models for the design of novel aluminum alloys by exploiting a detailed knowledge of the relationship between macroscopic fracture behaviour and pre-existing alloy microstructure.

6.0 Summary and conclusions
Nanovoids were produced in 99.988 and 99.995 at.% Al following a quench and aging procedure developed previously [4, 29]. Synchrotron SAXS probing of the quenched specimens over a \( q \) range from 0.025 to 0.6 Å\(^{-1}\) was obtained using two sample-detector positions, and results reveal a weak diffuse scattering which does not show any obvious structure. It is essential to calibrate the absolute intensity of the beam in such experiments in order to reliably apply quantitative statistical SAXS analysis of voids in metals like aluminum. Specifically, the absolute void number density, \( N_f \), void radius, \( R_g \), and interface thickness, \( \sigma \), are determinable. The number density distribution, \( N_f \), was shown to be affected by the level of impurity elements. Furthermore, quench voids
could be grown by artificial ageing at 60 and 90°C, but dissolved after ageing at 145°C. The instrumentation and analysis methods described in detail here will allow design of further research into early stages of voiding in metals.

Acknowledgements
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1. The temperature versus time data is used to measure the quench rate.

2. Both the pre-sample and post-sample beampaths were evacuated.

3. Note that $T_{sam}$ is given by the ratio, $T_{sam} = T_s/T_{BG}$. Experimentally both $T_s$ and $T_{BG}$ are measured to provide a value for $T_{sam}$.

4. Note that $N_f(R) = N(R)/N_{total}^{rel}$.

Appendix A – Particle size estimate and number distribution
In the low-$q$ region the well-established Guinier approximation [18] for a system of isolated, dilute, identical particles of similar shape is given by,

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

where $R_g$ is the radius of gyration (Guinier radius) defined for the electron distribution of the dilute system of particles. The Guinier approximation is based on a power series expansion of the scattering, cut off after the first two terms. Its validity is therefore inherently limited to the low-$q$ region, typically where $qR_g < 2$ [17]. Guinier analysis is therefore not useful when reliable low-$q$ data is not available.

The Indirect Transform Method (ITM) provides an alternative approach for obtaining estimates of particle sizes. When a polydisperse system is assumed, the volume distribution function describing the various particle size contributions is also generated. This method was originally developed by Glatter [46, 47] and later extended...
by Svergun [48] 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 [47, 49],

$$I(q) = \frac{3}{4\pi} \int_0^\infty V(R) R^{-3} i(qR) \, dR,$$  \hspace{1cm} A.2

where $V(R)$ is the volume distribution and $i(qR)$ 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 $V(R) = \frac{4}{3} R^3 N(R)$. The number distribution function is expanded in terms of basis functions, i.e.

$$N(R) = \sum_{i=0}^n c_i \psi_i(R),$$  \hspace{1cm} A.3

where the basis functions are cubic B-splines and $n$ is the number of basis functions, typically less than 30 [47]. 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 $R_{\text{min}} \leq R \leq R_{\text{max}}$. $R_{\text{min}}$ and $R_{\text{max}}$ are the user-supplied estimates of minimum and maximum particle sizes. An average value of the radius of gyration ($R_g$) is then obtained as,

$$R_g^2 = \frac{\int_{R_{\text{min}}}^{R_{\text{max}}} N(R) R^2 \, dR}{\int_{R_{\text{min}}}^{R_{\text{max}}} N(R) \, dR}$$  \hspace{1cm} A.4

Appendix B – Effective invariant, $Q_{\text{eff}}$, and Porod’s law

In the high-$q$ region the ideal SAXS scattering follows Porod’s law [18],

$$I(q) \propto \frac{Q}{\pi} \frac{S}{V} \frac{1}{q^4},$$  \hspace{1cm} B.1

where $Q$ is the invariant which measures the total scattering intensity, $S$ is the total interfacial surface area, $V$ is the total particle volume. Ideally $Q$ is given by the formula,

$$Q = \int_0^\infty I(q) \, q^2 \, dq.$$  \hspace{1cm} B.2
When dealing with a 2-phase system with electron density contrast $\Delta \rho$ between the two phases (in this case, void and aluminum metal matrix), the invariant (assuming absolute intensity data) can alternatively be expressed as [18],

$$Q = 2\pi^2 \phi(1 - \phi)(\Delta \rho^2),$$  \hspace{1cm} \text{(B.3)}

where the void volume fraction is $\phi = V_{\text{void}}/V_{\text{irr}}$, $V_{\text{void}}$ and is the total void volume in the irradiated sample volume, $V_{\text{irr}}$. Note that when working with absolute intensity data, $\Delta \rho$ refers to the excess scattering length density which is just the electron density contrast multiplied by the classical free electron radius [37]. However, there are experimental limitations to the available $q$ range which usually requires working with the effective $Q_{\text{eff}}$ given by,

$$Q_{\text{eff}} \sim \int_{q_1}^{q_2} I(q) \, q^2 \, dq,$$  \hspace{1cm} \text{(B.4)}

where $q_1$ and $q_2$ are the lowest and the highest values of $q$ accessible in the experimental data, respectively. At high-$q$, Porod’s law states that the asymptotic form of scattering is,

$$\lim_{q \to \infty} I(q) = \frac{k}{q^4}.$$  \hspace{1cm} \text{(B.5)}

The high-$q$ contribution to the calculation of effective $Q$ can therefore be accounted for by including the asymptotic scattering term,

$$Q_{\text{eff}} = \int_{q_1}^{q_2} I(q) \, q^2 \, dq + \int_{q_2}^{\infty} \frac{k}{q^2} \, dq,$$  \hspace{1cm} \text{(B.6)}

where $k$ is estimated from the Porod plot.
References

Table 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>

Table 2. Values of $R_g$, $\sigma$, and $\varphi$ of voids for the Al samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>ITM $R_g$ (Å)</th>
<th>Guinier $R_g$ (Å)</th>
<th>$\sigma$ (Å)</th>
<th>$\varphi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N550</td>
<td>20.64</td>
<td>23.4 ± 2.3</td>
<td>2.7 ± 1.0</td>
<td>$1.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>4N550</td>
<td>17.72</td>
<td>21.4 ± 2.4</td>
<td>2.0 ± 1.0</td>
<td>$6.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>4N600</td>
<td>19.56</td>
<td>19.9 ± 1.9</td>
<td>1.1 ± 1.0</td>
<td>$5.6 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Figure 1. Electron channelling 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 artefacts. 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 2. a) 2-D scattering profile for the 3N550 sample in the up-close position. There is a 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. The figure shows the beamstop located in the bottom right of the quadrant.

Figure 2. b) 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 data is shown on a log-log plot with a slope -4 line included as a guide to the eye.

Figure 3. The 1-D integrated data for the high-$q$ range (on a log-log plot) is shown here for the 4N600 sample. The quenched sample scattering includes scattering from both the matrix and the voids. The void scattering is effectively the difference between the quenched sample scattering and the reference sample scattering. The solid line is the result of the GNOM best fit to the data.

Figure 4. The number fraction distribution of voids versus void radius obtained by normalization of the number distribution by the calculated total relative number of voids is shown for the three Al samples. These results are obtained from the ITM analysis of the SAXS data.

Figure 5. Porod plot of the void scattering seen in the 4N550 sample. The presence of a Laue background gives rise to the positive slope, $C_o$ seen at high-$q$ (top straight red line, fit to the original data for $0.04 \, \text{Å}^{-4} < q^4 < 0.08 \, \text{Å}^{-4}$). Removal of the Laue background ($I - C_o$) reveals the region of negative slope at higher-$q$ ($0.085 \, \text{Å}^{-4} < q^4 < 0.10 \, \text{Å}^{-4}$) used to estimate the interface thickness.

Figure 6. Evolution of nanovoids with artificial aging at low temperatures.

Figure 7. a) Time evolution of number fraction distributions (from the ITM SAXS data analysis) of nanovoids in 3N550 aged at 60°C.

Figure 7. b) Time evolution of number fraction distributions of nanovoids in 3N550 aged at 90°C.
Figure 8. Time evolution of number fraction distributions (from the ITM SAXS data analysis) of nanovoids in 4N550 aged at 60°C.

Figure 9. Evolution of the nanovoid radius and interface thickness in the 4N550 sample at 145 °C.
Figure 1
Figure 2(a)
Figure 2(b)
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7(a)
Figure 7(b)
Figure 8
Figure 9