Abstract

The crystallization of melt spun Al\textsubscript{85}Ni\textsubscript{11}Y\textsubscript{4} ribbon has been studied through systematic heat treatment in the 200-550°C temperature range using the techniques of nuclear magnetic resonance (NMR) spectroscopy, electrical resistivity, differential scanning calorimetry (DSC) and X-ray diffraction (XRD). \textsuperscript{27}Al NMR spectroscopy provides a direct and sensitive method for determining the atomic fraction of \(\alpha\)-Al and analysis of the \(\alpha\)-Al crystallization kinetics. NMR results revealed low concentrations (3.9 at.\%) of Al configurations in the as-quenched material and confirm that they have \(\alpha\)-Al short range order. The ability of NMR to directly detect \(\alpha\)-Al configurations in the as-quenched state is compared and contrasted with XRD. Volume fractions of \(\alpha\)-Al phase calculated from NMR are also compared and contrasted with that calculated from XRD for samples subjected to isothermal annealing. Qualitative and quantitative agreement between the two techniques is found after the XRD fractions are
corrected according to literature methods. Heat treatment at moderate temperatures (200°C) is shown to result in transformation kinetics dominated by the growth of α-Al consistent with heterogeneous nucleation while higher temperatures (300°C) lead to kinetics consistent with growth from homogenous nucleation sites.

**Keywords:** metallic glass; crystallization; nucleation and growth; nuclear magnetic resonance (NMR); electrical resistivity

1. Introduction

Modern alloy design relies on the ability to quantitatively monitor the competition in phase formation as well as the ability to predict phase transformation pathways. The stages of phase formation from the solid solution have therefore been the subject of intense research both in age hardenable and glassy aluminium alloys. In past work Bastow has pioneered the use of solid state NMR as a sensitive quantitative method to follow phase evolution in age hardenable light alloys [1-5] allowing the partitioning of solute to the various phases to be quantitatively followed as functions of thermal treatment and mechanical treatment. Here we report the first application of NMR to quantify the atomic fraction of α-Al and to follow the α-Al crystallization kinetics in metallic glasses.

Ductile aluminium based metallic glasses comprised of > 80 at.% Al, a late transition metal (e.g. Ni), and a lanthanide metal (e.g. Y) were first reported in 1988 [6, 7]. This family of metallic glasses is of interest because they are lightweight and show significant strength and ductility upon primary crystallization of the Al yielding a microstructure consisting of α-Al nanocrystals with diameters ranging from 5-20 nm which may contribute up to a 50% volume fraction [7]. This α-Al/amorphous matrix nano-composite microstructure can show extremely high strengths > 1.2 GPa, more than three times that of conventional age-hardened
polycrystalline Al alloys [8]. The α-Al crystal size, number density, and composition are important parameters contributing to the peak enhancement in mechanical properties [8]. Intermetallic phase formation consumes potentially useful Al atoms, depletes the solute content in the amorphous phase, and reduces hardness [9] and fracture toughness [10, 11]. Knowledge of phase composition, crystallization kinetics, and phase transformation pathways – particularly in the early stages of decomposition of the glass – is therefore important for property optimization.

Solid state NMR has some unique and advantageous features when compared to conventional alloy characterization tools. NMR can detect low concentrations of small crystals or pre-crystalline configurations because the nucleus is only sensitive to the atomic configurations within a short range, hence entities need not possess long range order to be detected. In metals, the phases can be resolved because of enhanced chemical shift (Knight shift) due to s-electron contact interaction. Relatively large amounts of material are measured using NMR ($10^{20}$ atoms) as compared with techniques such as transmission electron microscopy ($10^{10}$ atoms) or atom-probe tomography ($10^{8}$ atoms), and NMR results are therefore representative of the bulk. Furthermore, NMR is element specific, and long signal averaging times can be employed to enhance weak signals [4].

$^{27}$Al NMR has been previously used to study the structure of metallic glasses including Zr$_{60}$Ni$_{25}$Al$_{15}$ [12], Zr$_{59}$Cu$_{20}$Al$_{10}$Ni$_8$Ti$_3$ [13], Cu$_{46}$Zr$_{47-x}$Al$_7$Gd$_x$ [14] and La$_{100-x}$Al$_x$ ($18 \leq x \leq 45$) [15]. These papers examine the glass forming ability of the alloys by detecting the atomic configurations of the constituents around the Al atoms. $^{63}$Cu NMR [13] has been used to follow crystallization in Zr$_{59}$Cu$_{30}$Al$_{10}$Ni$_8$Ti$_3$ suggesting icosahedral ordering. $^{27}$Al Knight shift and linewidth have been used to detect crystallization of the intermetallic phase La$_3$Al in glassy La$_{75}$Al$_{25}$ [15]. Previous studies of metallic glasses predominantly rely on analysis of nuclear spin lattice relaxation rates to compare local environments of the nuclei.
None of the previous works address the issues of detecting $\alpha$-Al precursors and quantifying the crystalline fraction of $\alpha$-Al but instead aim to shed light on what is structurally responsible for frustrating crystallization in these alloys. Here we report results from the quantification of $\alpha$-Al formed during devitrification of melt spun amorphous $\text{Al}_{85}\text{Ni}_{11}\text{Y}_{4}$ using NMR. This quantification is achieved by line shape simulation of spectra followed by integration of the component line shapes enabling us to analyze the kinetics of $\alpha$-Al crystallization and the fraction of Al atoms in the various phases present.

2. Materials and Methods

Melt spinning was used to prepare foil specimens of $\text{Al}_{85}\text{Ni}_{11}\text{Y}_{4}$ (at.%) using a substrate velocity of $\sim 50$ m/s and cooling rate of $\sim 2 \times 10^6 \degree\text{C/s}$. This process resulted in ribbons with a nominal thickness of $50 \mu\text{m}$ and a width of 1 cm. For NMR and XRD measurements ribbons were cut into pieces with dimensions of $\sim 1$ mm x 1 mm prior to heat treatment. A silicon oil bath was used for heat treatments at 200°C, higher temperature heat treatments were performed in a muffle furnace under air or a quartz tube furnace under 50 l/hr Ar flow. Specimens for electrical resistivity measurements were cut into 5 cm long ribbons.

NMR spectroscopy was performed using the $^{27}\text{Al}$ nucleus, which is a 100% naturally abundant isotope, as the probe of atomic environment. The spectra were recorded on a Bruker Avance 400 spectrometer at a frequency near 104.2 MHz, using a static specimen in a 9.39 T magnetic field and a standard two pulse echo sequence ($2 \mu\text{s}$ pulse length, $12.5 \mu\text{s}$ delay between pulses, and $50$ ms repetition time). A half echo was collected with at least $10^5$ scans for each spectrum before exponential filtering for noise reduction. Collecting the half echoes using short echo times enables a true quantification of phases with very different $T_2$ relaxation times. Ribbon samples are ideally suited to NMR as the RF penetration depth is of the same order of magnitude as the sample thickness. To calculate the atomic fraction of $\alpha$-
Al, the Fourier transformed NMR spectra were peak fit and integrated with the DMFIT program (ver. 2009) [16]. The $\alpha$-Al peak was fit with a pure Gaussian curve while the peak associated with residual Al in the matrix was fit using a pseudo-Voigt curve. The intermetallic Al$_3$Ni contains two non-axial Al sites [17] fit using Gaussian-Lorentzian curves. Subsequent modeling of the crystallization kinetics using the Johnson-Mehl-Avrami (JMA) equation [18, 19] and correlation of NMR and resistivity results were performed using Matlab (ver. R2009a, The Mathworks) and the Optimization toolbox.

Electrical resistivity measurements were performed manually using a laboratory built four point probe system incorporating a micro-voltmeter and constant current supply. All resistivity measurements were performed in-situ during heat treatment in a furnace. The sample with contacts was inserted into the furnace at temperature and data collection was started immediately. Electrical contacts to the sample were made with mechanically clamped Ag wires.

A Stanton Redcroft instrument was used for DSC at a heating rate of 40 K/min over a temperature range from 50°C to 510°C. The temperature was calibrated with pure In and Zn samples; heat flow was calibrated with pure In.

A Bruker D8 Avance X-ray diffractometer was used for XRD analysis. CuK$_\alpha$ radiation (40 kV, 40 mA) with a graphite monochromator was employed. Samples were scanned from 10° to 130° with a 0.02° step size and 6 s count time per step. The sample heat treated at 300°C was mounted on a polymer zero background plate and spectra were collected using a LynxEye silicon strip detector with a count time of 1.6 s. The 185 sensor strips gave an equivalent count time of 296 s per step. Peak identification was performed using the Bruker XRD program EVA, and crystalline phases were identified using the ICDD-PDF+4 2010 powder diffraction database. Crystal sizes were calculated using the Scherrer equation from full width at half maximum (FWHM) values obtained with the Bruker TOPAS program.
A minimum of three Al diffraction peaks were curve fit with a pseudo-Voigt function taking an instrument FHWM broadening of 0.068° into account.

High energy synchrotron X-ray diffraction measurements were made on the powder diffraction beamline at the Australian synchrotron with an X-ray wavelength of 1.001 Å on some of the samples in an effort to discern smaller features such as nanocrystals [20].

3. Results

3.1 Differential Scanning Calorimetry

DSC reveals three prominent exothermic peaks (Fig. 1), the primary crystallization peak at 230°C (α-Al), and a further two large peaks at 332°C and 357°C. No indication of a glass transition temperature (T_g) was observed prior to primary crystallization. Observation of T_g has been shown to depend on alloy composition [21-23], and the lack of an observable T_g has been attributed to the presence of quenched-in nuclei [24]. A fourth small exothermic peak is also noticeable at 446°C as previously observed in Al_{87}Ni_{16}Y_{7} [22]. NMR and XRD spectra of samples heat treated at 200°C (shown subsequently), just below the first DSC peak, confirm that the peak at 230°C is due to crystallization of α-Al. XRD spectra from a sample heat treated at 300°C, just below the second peak, also show peaks for α-Al, but after 40 min peaks from Al_3Ni and Al_{19}Ni_{5}Y_{3} are also observed. This result suggests that the DSC peaks at 332°C and 357°C are due to Al_3Ni and Al_{19}Ni_{5}Y_{3} crystallization. The fourth (446°C) peak is related to the crystallization of Al_{9}Ni_{3}Y as shown by XRD results in section 3.3. Small high temperature DSC peaks in Al-Ni-Y alloys have been previously attributed to dissociation of a metastable phase [25] or morphological changes [26].

3.2 Nuclear Magnetic Resonance
Progressive crystallization of $\alpha$-Al at 200°C and 300°C is shown in the $^{27}$Al NMR spectra of samples progressively heat treated for various times at constant temperature (Fig. 2). The spectrum for the as-quenched sample (Fig. 2a, 0 min) shows a broad peak centered at a Knight shift of 1100 ppm with a small peak at 1635 ppm. As the broad peak centered at 1100 ppm is dominant in the as-quenched sample it is attributed to Al atoms contained in the amorphous phase. The Knight shift of 1635 ppm corresponds with the measured shift from samples of $\alpha$-Al of 99.95% and 99.999% purity. During heat treatment of our metallic glass samples this peak can be clearly seen to increase in intensity with respect to the broad peak. This sharp peak at 1635 ppm is attributed to Al atoms with $\alpha$-Al short range order.

Manna et al. [27] have used $^{27}$Al NMR to follow the amorphization of Al-Ti-Si elemental powder blends by ball milling showing a sharp peak attributed to alloyed $\alpha$-Al after 5 hr of milling, at a Knight shift of 1590 ppm. This sharp peak gradually disappears as a function of milling time and a broad peak emerges, at a lower Knight shift of 309 ppm, after 10 hr of milling that is attributed to amorphous Al-Ti-Si.

The $\alpha$-Al peak position in Al$_{85}$Ni$_{11}$Y$_4$ does not change during heat treatment. This result indicates that there is no significant change in the ordering of the Al atoms in the $\alpha$-Al crystallites during heat treatment. The broad peak attributed to Al in the amorphous matrix undergoes a gradual but substantial change in position during heat treatment (11% decrease in Knight shift to 976 ppm after 4h at 200°C, or 26% decrease after 5 min at 300°C). This result indicates that there is a significant change in the atomic environment of the Al atoms remaining in the amorphous matrix as it is progressively depleted of Al. In samples heat treated at 300°C the broad peak is substantially reduced in intensity after only 5 min. From 15 min to 75 min the mean value of the broad peak’s Knight shift has undergone a change to 667 ppm. This Knight shift of 667 ppm corresponds with that of the highest intensity peak measured for the intermetallic Al$_3$Ni [17].
Fig. 3 compares the $^{27}$Al NMR spectra for Al$_{85}$Ni$_{11}$Y$_4$ heat treated 75 min at 300°C with spectra for high purity polycrystalline α-Al, melt-cast Al$_3$Ni, and high purity α-Al alloyed with 0.86 at.% Cu. The α-Al linewidth of Al$_{85}$Ni$_{11}$Y$_4$ is substantially broader than that for high purity polycrystalline Al samples (99.95%), melt-cast Al$_3$Ni with excess Al and solution treated and quenched α-Al (0.86 at.% Cu) as shown in Fig. 3. The position of the Knight shift allows phase identification whilst the NMR linewidth indicates compositional heterogeneity or the presence of impurity atoms.

Results for the calculated atomic fraction of α-Al obtained from integrating the NMR peaks are shown in Fig. 4. We calculate that 3.9 % (at.) of the Al in the starting material is in the fcc α-Al phase. For heat treatment at 200°C, the fraction of crystallized α-Al steadily increases with heat treatment time but saturates at 57 ± 5% after 2 hours. The crystallization is expectedly faster at 300°C with 18% of the Al in the fcc α-Al phase after just 2 min and 67% after 5 min of heat treatment. Further heat treatment beyond 5 min, at 300°C, results in a moderate increase in α-Al leading to a plateau at 75 ± 5%. From these results, it is clear that the heat treatment temperature plays a dominant role in controlling the fraction of α-Al formed. Note that these atomic crystalline fractions are not directly comparable to volume fractions obtained from other techniques; quantitative comparison is further discussed in Section 4.1.

The data in Fig. 4 were curve fit with the JMA equation. Best fits were obtained with Avrami exponents of 1.6 ± 0.6 and 2.4 ± 0.7 for crystallization at 200°C and 300°C respectively. An Avrami exponent of 1.5 suggests site saturation of nuclei and diffusional growth from precursors, whilst an Avrami exponent of 2.5 suggests a constant nucleation rate followed by diffusional growth [28]. Both mechanisms have been previously reported [22, 29] in Al-Ni-Y glasses. These results suggest that the growth of quenched-in α-Al (which dominates at 200°C) may be swamped by the generation of new crystals via continuous
nucleation at the higher annealing temperature (300°C) leading to a higher fraction of Al atoms in the α-Al phase. Although direct support for heterogeneous nucleation [30, 31] and homogeneous nucleation [32] exists, further detailed experimental studies -including TEM- would be required to confirm these nucleation mechanisms in our alloy.

3.3 X-Ray diffraction

The XRD spectrum of the as-quenched material contains broad peaks consistent with an amorphous structure (Fig. 5a). High energy synchrotron X-ray measurements of the as-quenched material (Supplementary Data, Fig. S1) also revealed two broad bands consistent with amorphous structure. Samples heat treated at 200°C for 4 hours show α-Al peaks superimposed on the broad amorphous bands (Fig. 5b). This is also the case for 300°C 30 min heat treated samples (Fig. 5c). Heat treatment for 40 min at 300°C, however, leads to peaks corresponding to intermetallic Al₃Ni and Al₁₉Ni₅Y₃ (Fig. 5d) as well as those for α-Al. The XRD spectrum for a sample fully crystallized by heating to 550°C for 40 hours shows the disappearance of Al₃Ni and Al₁₉Ni₅Y₃ peaks and the appearance of peaks indexed as intermetallic Al₉Ni₃Y (Fig. 5e). As many of the peaks have a low intensity relative to those from α-Al, higher resolution spectra are provided in supplementary data (Fig. S2). It should be noted that although the Al-Ni-Y ternary phase diagram at 500°C indicates that Al₂₃Ni₆Y₄ is the equilibrium ternary intermetallic [33], Al₂₃Ni₆Y₄ cannot be fitted to the peaks in our spectra. This result indicates that devitrification from the amorphous state does not reach true equilibrium in our material with a 40 hour heat treatment at 550°C.

Volume fractions of crystalline phases ($V_f$, Fig. 6a) were calculated for samples heat treated at 300°C, using integrated areas under peaks [34, 35], $V_f = A_c/(A_c + KA_a)$, where $A_c$ and $A_a$ are the total integrated areas for the crystalline Al peaks and the amorphous band respectively. A value of 0.37 for the correction factor $K$ is used, as determined by Gloriant et
al. [34] for Al-Ni-Sm. The values of $V_f$ from XRD correlate well with NMR data showing that crystal fractions plateau after just 5 minutes of heat treatment. Further quantitative comparison with atomic fractions determined from NMR data will be discussed in Section 4.1.

Scherrer analysis of the $\alpha$-Al peaks gave nanocrystal dimensions of 19 ± 3 nm after heat treatments at 200°C for 4 hr while results for heat treatment at 300°C are shown in Fig. 6b. Growth of fcc Al is not apparent until 40 minutes of heat treatment which also coincides with the commencement of crystallization of $\text{Al}_3\text{Ni}$ and $\text{Al}_{19}\text{Ni}_5\text{Y}_3$. Since these crystallite sizes are an average for the $\alpha$-Al nanocrystals present, the observation that there is little growth in crystal size during the early stages is consistent with JMA analysis of NMR data indicating constant nucleation at 300°C. Further heat treatment results in growth of nanocrystals in all three phases.

3.4 Electrical resistivity

Isothermal resistivity measurements appear to show an initial incubation stage characterized by little change in resistivity (Fig. 7). The duration of this incubation stage correlates well with the measured time required for the sample to reach 195°C after insertion into the furnace, i.e. approximately the temperature required for primary crystallization. At temperatures up to 275°C, measurements show resistivity decreasing in a single stage with the observed resistivity reducing to 67% of the initial value at most. A second stage of rapid reduction was observed after 30 min, 15 min, and 3.5 min at 300°C, 315°C and 350°C respectively (arrows, Fig. 7). This second stage represents a reduction in resistivity to ~32% of the initial value.

The fraction of $\alpha$-Al and the magnitude of the reduction in resistivity show a strong linear correlation for all data at 200°C and for 300°C heat treatments up to 30 min
(correlation coefficient $|r| > 0.98$). Along with XRD evidence, these results indicate that the initial reduction in resistivity is due to $\alpha$-Al crystallization. After 30 min at 300°C the drop in resistivity exceeds any increase in the fraction of Al atoms in $\alpha$-Al crystals, indicating that a separate mechanism is responsible for this second stage reduction in resistivity. The timing of this second stage reduction in resistivity coincides with the emergence of intermetallic peaks ($\text{Al}_3\text{Ni}$ and $\text{Al}_{19}\text{Ni}_3\text{Y}_3$) in the XRD spectra as well as the growth of $\alpha$-Al nanocrystals as determined using Scherrer analysis.

The effect of temperature on the kinetics of phase transformation can be further investigated by Arrhenius analysis of the resistivity data. We have adapted the method of Sahoo et al. [36] where the heat treatment time required to reach a threshold volume fraction of crystallized $\alpha$-Al was analyzed. We instead analyze the time taken for the relative resistivity to reduce to a characteristic fraction ($t_c$). This method is adapted in order to avoid any assumptions involved in calculating the volume fraction from resistivity [37]. A threshold of 0.85 was taken for the first stage and 0.5 for the second stage, approximately the time when the resistivity drop in each stage has reduced by half. The temperature dependence of this time is taken to have an analogous behavior to the time taken to reach a threshold crystallized fraction ($t_{c}^{*}$) [38], $\ln(t_c-t_0) = \ln(a) - E_a/k_BT$, where $t_0$ is the incubation time, $T$ is the heat treatment temperature, and $a$ is a constant. The Arrhenius plots are shown in Fig. 8 and the activation energies ($E_a$) are calculated from the linear regression of the data. This method gives activation energies of $102 \pm 6$ kJ/mol for primary crystallization and $158 \pm 1$ kJ/mol for the second stage reduction in resistivity. Typically activation energies for crystallization processes in melt spun glasses are determined from Kissinger analysis of DSC peak positions. For studies that report activation energies for primary crystallization of $\alpha$-Al and subsequent crystallization of $\text{Al}_3\text{Ni}$ for Al-Ni-Y based alloys, the latter is typically greater than the former, consistent with our data (see Table 1). The values of activation
energy reported in the literature (Table 1) vary widely but, in general, are much higher than those calculated from our resistivity data. The widely ranging values for activation energy of primary crystallization of α-Al in amorphous alloys have been shown to be highly dependent on alloy composition [38], and differences of >100 kJ/mol in activation energies have been attributed to the presence or absence of pre-existing α-Al nuclei [39]. The activation energy for the second stage reduction of resistivity is close to a published value of 145 kJ/mol for Al$_3$Ni formation in thin film Al/Ni diffusion couples [40].

4. Discussion

Analysis of NMR spectra for the two heat treatment temperatures gives a clear quantitative picture of the crystallization kinetics. The sensitivity of NMR is also exhibited by the fact that α-Al configurations can be readily detected in the as-quenched material (Fig. 2a) but not in the XRD spectra collected using either laboratory XRD (Fig. 5a) or synchrotron X-rays (Fig. S1). This is the first report of detection and quantification of quenched-in fcc Al configurations by $^{27}$Al NMR.

These Al configurations may be the sub-nanometer precursor particles proposed by Nitsche et al. [41] which may be too small to be observed by transmission electron microscopy (TEM) [23, 30, 42] and not always in high enough concentrations to be discerned from XRD [43, 44]. The concentration and size of nanocrystals affect their observability by XRD since α-Al XRD peaks are superimposed on the broad scattering peak from the amorphous matrix, complicating quantification of XRD spectra [43]. This insensitivity is particularly prevalent in the early stages of devitrification when crystals are small and corresponding diffraction peaks are broad. As a result, other techniques such as fluctuation electron microscopy (FEM) [45] and atom probe tomography (APT) [42] have been used to study quenched-in nuclei. Sample preparation and analysis with these techniques, however, is
time consuming and only small regions of sample are examined. Furthermore, accurate quantification of crystal fractions with TEM relies on accurate calculation of foil thickness [43].

As discussed subsequently, these pre-existing fcc Al configurations may act as heterogeneities for nucleation during heat treatment and their role is critical to the stability of quenched Al-based glasses [31]. The pre-existing fcc Al configurations detected by NMR are present at comparable concentration to the nanoscale Al-rich zones or nanoregions detected by other atomic resolution techniques such as APT [42]. These APT results for AlYFe glass show nanoscale regions of pure Al with a concentration of $10^{24}-10^{25} \text{ m}^{-3}$. Each region had up to 50 Al atoms but no evidence of crystallographic planes in these nanoregions. This concentration of Al in the pure Al nano-regions indicates that approximately 1 atomic percent of the Al atoms are located in these regions. Our NMR results indicate that in our glass 3.9 atomic percent of the Al atoms are located in a configuration that has identical short range order to fcc $\alpha$-Al (Knight shift fingerprint at 1635 ppm). Al-rich clusters with medium range order (MRO) have been detected in AlSm, AlYFe and AlYFeCu glasses using FEM [45-47]. These MRO clusters are referred to as Al-like nanocrystals too small to have a signature in diffraction and are proposed to act as nanocrystal nucleation sites.

As discussed in our recent paper [48], NMR detects the nearest and next-nearest neighbor configurations and may not be able to distinguish between the different degrees of ordering present in clusters with short range order and nanocrystals with medium to long range atomic order. A recent review of metallic glasses by Cheng and Ma [49] has highlighted the need for more information on how atoms pack on the short-to-medium range. The NMR results clearly show for the first time that the short range order atomic configuration of the quenched-in Al clusters detected by NMR in Al$_{85}$Ni$_{11}$Y$_4$ glass is
indistinguishable from the atomic configuration of atoms in fcc α-Al, which is fingerprinted by the resonance line at 1635 ppm (Fig. 3).

The NMR results for the as-quenched glass can be compared to the XRD results. The presence of the shoulder at $2\theta \approx 44^\circ$, for Cu K$_\alpha$ X-ray wavelength, has been previously attributed to quench-in nuclei of α-Al or Al-rich configurations that precede nucleation [50-53]. The original work on Al$_{87}$Ni$_{8.7}$Y$_{4.3}$ attributed the broad shoulder at $2\theta \approx 44^\circ$ to the presence of short range order within the glass [6]. Subsequent researchers attribute this shoulder to small crystallite Al particles [43, 52] and use the breadth and area of the shoulder to quantify crystal size and fraction, respectively, inside the amorphous matrix of melt spun Al-Ni-Y alloys [50, 51, 53]. It has also been reported that some samples exhibiting the shoulder at $2\theta \approx 44^\circ$ show featureless amorphous structure in bright field TEM [50]. Alternatively it has been shown that samples containing small amounts of tiny α-Al crystallites by TEM display amorphous scattering in the XRD pattern because the volume fraction of the crystallites is lower than the resolution of the XRD [54].

Because $^{27}$Al NMR is sensitive to the local Al atomic environment, the presence of α-Al configurations can be readily detected. In Fig. 9 the comparison of NMR and XRD is further illustrated for Al-Ni-Y alloys where it is clearly shown that the shoulder at $2\theta \approx 44^\circ$ cannot be attributed to α-Al and should not be integrated to estimate the volume fraction of α-Al. In contrast the NMR peak at 1635 ppm does clearly indicate the presence of α-Al configurations and can be integrated to quantify the atomic fraction of Al in that environment.

4.1 Quantitative comparison between XRD and NMR

While the quantification of crystal fractions of samples crystallized at 300°C with XRD and NMR both show that crystal fraction plateaus after 5 minutes, it is important to
note that NMR provides the atomic fraction of aluminium in the crystalline phase \( (\phi_c) \) and amorphous phase \( (\phi_a) \), while XRD provides the volume fraction of the crystalline phase \( (f_{V,c}) \). It is possible to convert atomic fraction \( (\phi_c) \) to crystalline volume fraction \( (f_{V,c}) \) if the density of the amorphous phase \( (\rho_a) \) and the composition of the amorphous phase are known in order to be able to determine the molar mass of the amorphous phase \( (M_a) \). The converted volume fraction for Al\(_{85}\)Ni\(_{11}\)Y\(_4\) is shown in Appendix A to be given by:

\[
f_{V,c} = \frac{\phi_c}{\rho_a M_a + \frac{\phi_c}{85 \rho_a M_{Al}}} \tag{1}
\]

where \( M_{Al} \) is the molar mass of aluminium. The density of the amorphous phase \( (\rho_a) \) can be calculated from the measured overall density of a partially crystallized material \( (\rho) \). This can be expressed in terms of the density of the constituent phases:

\[
\rho = \frac{\rho_c + \rho_a (f_{V,a} / f_{V,c})}{1 + (f_{V,a} / f_{V,c})}, \tag{2}
\]

where \( f_{V,i} \) is volume fraction of phase \( i \) and subscript \( a \) refers to the amorphous phase, and \( c \) the crystalline phase.

The density of a sample heat treated at 300ºC for 2.5 min was measured to be 2.99 ± 0.03 g/cm\(^3\). From Eq. 2, using the corrected crystalline volume fraction determined from XRD for this sample (39%) and equating the density of the crystalline phase, \( \rho_c \), to 2.71 g/cm\(^3\) for fcc Al leads to a calculated density for the amorphous phase of 3.18 g/cm\(^3\). This is a reasonable value compared to the as-quenched material which was measured to have a density of 3.05±0.03 g/cm\(^3\). The corresponding crystallized atomic fraction determined from NMR for this sample is 48%, implying a residual amorphous composition of Al\(_{44}\)Ni\(_{11}\)Y\(_4\) with a molar mass of 2194 g/mol. From Eq. 1, the corresponding crystallized volume fraction is calculated to be 37%, in good agreement with the corrected crystalline volume fraction obtained from XRD.
Similarly, the plateau of 75 at.% $\alpha$-Al observed from NMR data is calculated to be equivalent to a volume fraction of 50%, in good agreement with corrected XRD results and the expected equilibrium volume fraction [33]. This consistency indicates that the XRD correction factor determined by Gloriant et al. [34] for their Al-Ni-Sm system is suitable for our Al-Ni-Y material.

By comparison of XRD and NMR measurements it can be noted that an average $\alpha$-Al crystal size of ~20 nm is reached after 4 hr at 200°C or 2.5 min at 300°C when (at both temperatures) ~50% of the Al atoms are present in the $\alpha$-Al phase. It can also be noted that the increase in the crystal size between 30 min and 75 min at 300°C, from 26 nm to 75 nm, is not associated with an increase in $\alpha$-Al fraction. This result could be attributed to a change in nanocrystal morphology from spherical to branched/dendritic, consistent with TEM results for other Al-Ni-Y based glasses during isothermal annealing [41]. The increase in $\alpha$-Al nanocrystal size at constant $\alpha$-Al fraction could be indicative of coalescence or classical coarsening [55].

4.2 Second stage reduction of resistivity

There is strong experimental evidence that the second stage rapid decrease in resistivity is associated with intermetallic crystallization. XRD spectra of samples heat treated at 300°C (Fig. 5c, 5d) show that the timing of the second stage in resistivity coincides with crystallization of Al$_3$Ni and Al$_{19}$Ni$_5$Y$_3$. This interpretation is consistent with that proposed previously by comparing DSC data with resistivity results for isochronally heated samples [56]. The lack of a second rapid decrease in resistivity at temperatures below 300°C is consistent with DSC and XRD results which indicate that intermetallic crystallization requires the higher temperatures. Furthermore, the calculated activation energy associated with the second stage reduction in resistivity is consistent with Al$_3$Ni crystallization [40]. It is
possible that $\text{Al}_3\text{Ni}$ crystals provide conducting links between Al nanocrystals as $\text{Al}_3\text{Ni}$ has a relatively low resistivity [57] compared to melt spun $\text{Al}_{85}\text{Ni}_{11}\text{Y}_4$. These results indicate that isothermal resistivity measurements may provide a useful method to test for intermetallic formation in metallic glasses. Crystallization kinetics with two stages of growth has previously been observed in isothermal DSC by Nitsche et al. [41]. The second stage was attributed to morphological changes in the Al nanocrystals of isochronally heated $\text{Al}_{85}\text{Ni}_{8}\text{Y}_5\text{Co}_2$ observed with HRTEM. Their results showed that spherical nanocrystals became irregular dendritic structures. A morphological change cannot alone account for the second rapid decrease in resistivity observed in our data unless the dendrites overlap to form conducting pathways. This possibility cannot be ruled out without further experiments.

4.3 Activation energy

The lower activation energies obtained from resistivity measurements compared to published values obtained from DSC (Table 1) may indicate a discrepancy between the techniques. The effect of crystallization on the resistivity may be somewhat different to the effect on heat transfer in DSC, since resistivity is also sensitive to effects due to crystal size and spacing. The validity of the Kissinger analysis of DSC peak positions rests on several assumptions. Two key assumptions are that the amount of material transformed does not change during the experiment and that the process is governed by a single activation energy [38]. The latter is not always the case if there is simultaneous nucleation and growth of crystals. This last point is equally applicable to our analysis of resistivity results although a good fit to results is obtained with a single activation energy.

5. Conclusion
The technique of solid state NMR, using $^{27}$Al as a probe, provides an appealing and transparent method for detecting fcc $\alpha$-Al configurations in the as-quenched state. NMR is shown to be sensitive to the presence of $\alpha$-Al configurations at concentrations or sizes below the detection limit of XRD. The atomic fraction of Al detected by NMR to have fcc $\alpha$-Al short range order in the as-quenched Al$_{83}$Ni$_{11}$Y$_{4}$ glass (3.9 atomic %) is comparable to that reported using APT in as-quenched Al$_{88}$Y$_{7}$Fe$_{5}$ to detect 1 atomic % of Al in Al-rich nanoregions [42]. NMR is shown to detect the atomic fractions of the Al atoms in all of the phases and to provide a straightforward means to follow the partitioning of Al to each phase during heat treatment. Volume fractions can be calculated from the atomic fractions if the density and composition of the phases are known. Here we show that for progressive heat treatment at 300°C, the volume fraction of $\alpha$-Al grows and plateaus at 50 volume % after just 5 minutes. During this time the $\alpha$-Al crystal size (once peaks can be detected by XRD), remained at 25 nm and only increased after 30 min at 300°C, attributed to coalescence or classical coarsening. The volume fractions calculated from XRD required a correction factor [35] as previously derived by other workers attempting to correlate XRD with APT, DSC and TEM volume fractions [34]. In our work, we show that NMR can accurately fingerprint and quantify quenched-in fcc $\alpha$-Al and quantify crystal fraction and crystallization kinetics.

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Appendix A

Conversion of crystallized atomic fraction to volume fraction

For a partially crystallized material, the molar concentration of material in phase $i$ can be expressed as, $C_i = N_i / V_i$, where $N_i$ is the number of moles of phase $i$ and $V_i$ the total volume of the phase. Using this expression, the volume fraction of the crystallized phase, $f_{V,c} = V_c / (V_a + V_c)$, can be expressed as:

$$f_{V,c} = \frac{1}{1 + \frac{N_a C_c}{N_c C_a}}, \quad (A1)$$

where subscript $a$, refers to the amorphous phase and $c$ to the crystalline phase.

$^{27}$Al NMR however, provides the atomic fraction of Al in the amorphous phase and the crystalline phase. In order to relate this to Eq. A1, the atomic fractions can be related to the ratio between the mole of atomic base units (ABU) of the amorphous phase ($N_a$) and the mole of Al in the crystalline phase ($N_c$). After partial crystallization the composition of ABU of the amorphous phase of our material is $\text{Al}_{85}\phi_a\text{Ni}_{11}\text{Y}_4$, for an atomic fraction of Al in the amorphous phase of $\phi_a$. The mole of Al atoms in the amorphous phase ($n_{\text{Al},a}$) can be expressed in terms of moles of ABU of amorphous phase, $n_{\text{Al},a} = 85\phi_a N_a$. Assuming that the crystalline phase is pure Al, $N_c = n_{\text{Al},c}$. The atomic fraction of Al in phase $i$ ($\phi_i$) is equal to the mole of Al in that phase ($n_{\text{Al},i}$) divided by the total number in the material ($n_{\text{Al},T}$), $\phi_i = n_{\text{Al},i} / n_{\text{Al},T}$. After substitution of these expressions and simplification, the molar ratio of material in the amorphous phase and crystalline phase can now be expressed as:

$$\frac{N_a}{N_c} = \frac{1}{85\phi_c}, \quad (A2)$$

where the atomic fraction of Al in the crystalline phase ($\phi_c$) can be determined directly from NMR analysis.
The molar concentration of the material in each phase $i$, $C_i$, can also be calculated from the mass density of materials, $\rho_i$, $C_i = \rho_i/M_i$, where $M_i$ is the molar mass of the phase. In our material, the mass of the amorphous phase is given by, $M_a = 85\phi_\text{Al}M_{\text{Al}}+11M_{\text{Ni}}+4M_{\text{Y}}$, for corresponding molar masses, $M$, of the constituent elements. With a pure Al crystalline component, $M_c = M_{\text{Al}}$, Eq. A1 can now be expressed as in Eq. 1 by substitution of Eq. A2 and the expressions for $C_i$ given above.

Nomenclature of parameters used

- $C_i$ molar concentration of base units of phase $i$
- $f_{V,c}$ volume fraction of the crystallized phase
- $\phi_i$ atomic fraction of Al in phase $i$
- $n_{\text{Al},i}$ moles of Al atoms in phase $i$
- $N_i$ moles of base units of phase $i$
- $M_i$ molar mass of base unit of phase $i$
- $\rho_i$ mass density of phase $i$
- $V_i$ total volume of the phase $i$

References


Figure Captions
Fig. 1. DSC plot showing crystallization stages of melt spun $\text{Al}_{85}\text{Ni}_{11}\text{Y}_4$ at a heating rate of 40 K/min. Primary crystallization of $\alpha$-Al occurs at 230°C, and peaks at 332°C and 357°C are identified by XRD as due to $\text{Al}_3\text{Ni}$ and $\text{Al}_{19}\text{Ni}_5\text{Y}_3$. The fourth small exothermic peak at 446°C is attributed to $\text{Al}_9\text{Ni}_3\text{Y}$ formation.

Fig. 2. $^{27}$Al NMR spectra obtained from melt spun $\text{Al}_{85}\text{Ni}_{11}\text{Y}_4$ heat treated at (a) 200°C and (b) 300°C for the times indicated. The sharp peak at 1635 ppm is attributed to $\alpha$-Al while the broader peak around 1100 ppm is associated with the remaining Al in the material. Analysis of the spectra obtained from the as-quenched material shows that 3.9 at.% of Al is present as $\alpha$-Al configurations. The intensity of the $\alpha$-Al peak increases with heat treatment time as the Al crystallizes out of the amorphous matrix.

Fig. 3. $^{27}$Al NMR spectra obtained from pure Al (99.95 at.%), solution treated and quenched Al-0.86Cu (at.%), $\text{Al}_{85}\text{Ni}_{11}\text{Y}_4$ heat treated at 300°C for 75 min, and melt-cast $\text{Al}_3\text{Ni}$ containing excess $\alpha$-Al.

Fig. 4. Atomic percent of Al in $\alpha$-Al phase obtained by numerical integration of the NMR spectra after heat treatment at 200°C (●) and 300°C (○) as a function of heat treatment duration. Lines show the curve fit with the JMA equation. The initial (time zero) value of 3.9% is fit but not shown in this plot as time is on a logarithmic scale. Best fit values of 1.6 ± 0.6 and 2.4 ± 0.7 were obtained for the Avrami exponent for crystallization at 200°C and 300°C respectively. The atomic fraction of Al present as $\alpha$-Al reaches a plateau after 2 hours at 200°C but after only 5 min at 300°C.
Fig. 5. XRD spectra of melt spun Al_{85}Ni_{11}Y_4 (a) starting material, (b) heat treated at 200°C 4 hours, (c) 300°C 30 min, (d) 300°C 40 min, and (e) fully crystallized at 550°C for 40 hours.

Fig. 6. a) Calculated volume fractions after correction and b) crystallite sizes determined from XRD of melt spun Al_{85}Ni_{11}Y_4 as a function of heat treatment time at 300°C for fcc \(\alpha\)-Al (●), Al_3Ni (▼) and Al_{19}Ni_5Y_3 (□). Lines are drawn to guide the eye.

Fig. 7. Isothermal resistivity (relative to initial resistivity) as a function of heat treatment time at temperatures between 200°C and 350°C. Arrows indicate approximate time of second stage change for \(T \geq 300°C\). Plots with error bars indicate standard deviation from 2-3 independent measurements.

Fig. 8. Arrhenius plot of times to reach a characteristic relative resistivity (\(t_c\)) at various temperatures (T). The first stage refers to \(\alpha\)-Al crystallization while the second stage is due to crystallization of intermetallics. The calculated activation energies (\(E_a\)) for the two stages are also indicated. The error in the y scale reflects the error in calculating \(t_c\), measurement error in T leads to error bars smaller than the symbol size.

Fig. 9. XRD spectra (left) and NMR spectra (right) are shown for: (a) Al_{85}Ni_{11}Y_4, as-quenched; (b) Al_{85}Ni_{11}Y_4, 200°C 40 min; (c) Al_{85}Ni_3Y_6, as-quenched; (d) Al_{86}Ni_{10}Y_4, as-quenched. XRD spectra show the presence of a shoulder at \(\approx 44°\) where the (2 0 0) diffraction
peak for fcc $\alpha$-Al is expected. Corresponding NMR spectra do not always indicate the presence of fcc $\alpha$-Al configurations even though atomic fractions as low as 3.9 at.% can be readily detected by NMR as shown in (a).