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# A Crystallization Study of Al-Y-Ni Glasses

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A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

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For my parents, who made me who I am. They are the First to Acknowledge. Abstract

Previous studies on  $Al_{85}Y_rNi_{15-r}$  glasses established a correlation between crystallization mode (pure growth versus nucleation and growth) and crystallization product. Glasses with approximate compositions x = 5, 7, 8, 10 were studied in order to accurately ascertain the nature of the structural variance which gives rise to different crystallization modes and the identity of the resulting crystallization products. The glasses were characterized by isochronal and isothermal mode Differential Scanning Calorimetry, X-ray diffraction and Transmission Electron Microscopy. Glasses with x = 5, 10 have a clear distinction: x = 5 contains quenched-in Al nanocrystals which act as nucleating centers leading to  $\alpha$ -Al as the first crystalline product; equilibrium crystalline phases are  $\alpha$ -Al, Al<sub>3</sub>Ni and a stacking variation of Al<sub>4</sub>YNi. x = 10 is a homogeneous glass which undergoes a glass transition prior to crystallization; first crystalline product is an unstable FCC structure which breaks down via Al segregation; equilibrium phases are  $\alpha$ -Al,  $\beta$ -Al<sub>3</sub>Y and Al<sub>16</sub>YNi<sub>3</sub>. x = 7.8 share these characteristics: x = 7 contains quenched-in Al-nanocrystals and follows the initial x = 5 pattern of primary Al crystallization; however it undergoes a glass transition prior to first stage crystallization and equilibrium phases are  $\alpha$ -Al.  $\beta$ -Al<sub>3</sub>Y and  $Al_{16}YNi_3$ . x = 8 crystallizes by nucleation and growth yet has identical crystallization products as the corresponding x = 7 crystallization stages. Isothermal annealing prior to first two crystallization stages of x = 8 yields  $\alpha$ -Al and the unstable FCC structure. Isothermal crystallization is complex, frequently involving the overlap of multiply nucleating phases and the sequential nucleation of successive crystallization stages at the same annealing temperature. The results of these crystallization studies imply that Al-Y-Ni glasses obey the cluster model (Al-Y versus Al-Ni clusters) where cluster-cluster correlation establishes the degree of medium-range order and presence or absence of Al nanocrystals.

Résumé

Des études précédentes ont établi une corrélation pour les verres de type  $Al_{85}Y_rNi_{15-r}$ entre le mode de cristallisation (croissance pure ou nucléation et croissance) et les produits de cristallisation. Des verres avec des compositions approximatives x =5, 7, 8, 10 ont été étudiés pour déterminer exactement la nature de la variation structurale qui est responsable pour les différents modes de cristallisation, et la composition des produits de cristallisation. Les verres sont caractérisés par les modes "isochronal" et "isothermal" d'un DSC (calorimètre différentiel à balayage), par diffraction par rayons-X et par le TEM (microscopie de transmission d électrons). Les verres x = 5, 10 sont clairement différencié: x = 5 contient des nanocristaux de Al dans l'état de verre, ces nanocristaux se présentent comme des centres pour le nucléation, donc  $\alpha$ -Al est le prémier produit de cristallisation; les produits cristallins d'équilibre sont  $\alpha$ -Al, Al<sub>3</sub>Ni et une variation d'empilation de Al<sub>4</sub>YNi. x = 10 est une verre homogène qui montre une transition de vitrification avant la cristallisation; le premier produit cristallin est une structure FCC instable qui se dissipe par la ségrégation de Al; les produits d'équilibre sont  $\alpha$ -Al,  $\beta$ -Al<sub>3</sub>Y et Al<sub>16</sub>YNi<sub>3</sub>. x = 7, 8partagent ces caractéristiques: x = 7 contient des nanocristaux de Al dan l'état de verre et suit la formule initiale de x = 5, cristallisation primaire de Al; mais il montre une transition de vitrification avant cette première étape et les produits d'équilibre sont  $\alpha$ -Al,  $\beta$ - Al<sub>3</sub>Y et Al<sub>16</sub>YNi<sub>3</sub>. x = 8 cristallise par nucléation et croissance mais ses produits de cristallisation correspondent à ceux de x = 7. Un recuit avant les premiers deux stages de cristallisation de x = 8 forme les produits cristallins  $\alpha$ -Al et la structure instable FCC. Cristallisation par un recuit est compliquée, fréquemment il y a un chevauchement des phases de nucléation multiples, et la nucléation en ordre consécutif des étapes de cristallisation, mais à la même température de recuit. Les résultats de ces études impliquent que les verres de type Al-Y-Ni obéissent au "cluster model" (grappes formées par Al-Y et Al-Ni) où la corrélation entre les grappes individue établit l'ordre moyen et la présence où l'absence des nanocristaux de Al.

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1

## 1.1 Metallic Glasses: an overview

Metallic glasses are materials, in the solid or condensed matter state, possessing no long range atomic order. This means there exists no distinctive correlation between two atoms separated by more than several atomic spacings. The density-density correlation function  $\langle \eta_1(\vec{r_1})\eta_2(\vec{r_2}) \rangle$  is defined as the probability of finding atom type 1 (with density distribution  $\eta_1$ ) at position  $\vec{r_1}$  and atom type 2 (with distribution  $\eta_2$ ) at position  $\vec{r_2}$ . In crystalline systems this function exhibits periodic behavior (along certain directions) as a function of the distance  $d = |\vec{r_2} - \vec{r_1}|$ . In gases there appears practically no correlation outside an atomic diameter, while in liquids it may exist up to a few atomic spacings (see fig.1.1). Glasses have correlation functions similar (or slightly enhanced) to liquids, and are thus recognized as literally being frozen liquids, i.e. liquids whose viscosity coefficient has been increased from  $10^{-2}$  poise (typical liquids at room temperature) to  $10^{13}$  poise (typical glasses)(note: 1 poise = 1 g/cm/s)[10]. Glasses are also known as non-crystalline or amorphous solids.

Metallic glasses have unique properties resulting from the amorphous structure. In particular, some glasses are very soft magnetic materials, have high electrical resistivity and corrosion resistance, and tend to display extremely high tensile strengths [11]. In particular, Al-rich alloys such as the Al-Y-Ni system have been found to exhibit unusually high specific strengths [12]. A rigorous discussion of glass state metastability and the consequent desire for carrying out a crystallization study is given, followed by a brief summary on the history of metallic glass production and the discovery of



Figure 1.1: Different material phases and associated correlation function  $g(r) = \langle \eta_1(\vec{r_1})\eta_2(\vec{r_1}+\vec{r}) \rangle$ [1]. Note the enhancement of g(r) in glass (amorphous) versus liquid phases.

Al-rich glasses. Section 1.2 summarizes the work done on the Al-Y-Ni system to date and what new contribution this thesis brings to the ongoing study of this system.

### 1.1.1 Rapid Quenching and Metastability

As stated above, the key difference between the liquid and glass state is that in the liquid state atoms are still free to move, this means all system configurations remain physically available for the system to transform into. Quite literally, a very small probability exists for a liquid to take on a crystalline configuration. However, due to the physical parameters and system temperature, being a liquid means thermal fluctuations are sufficiently large to never allow the system to remain in a crystalline configuration for any noticeable period of time, and the more energetic configurations where the system will be observed (over a perceptible period of time) will be those

with short-range order. This means that a liquid is indeed a phase in thermodynamic equilibrium. The crystalline phase is also in thermodynamic equilibrium, when the thermal fluctuations are far too low to access the liquid phase configurations. Now, the glass state is defined as being *not* in thermodynamic equilibrium, and is a metastable state. Simply put, at a given temperature, thermodynamic equilibrium is defined as the minimization of the Gibbs free energy [13]. In glasses, the temperature at which they exist requires the system to have a crystalline structure, in order to satisfy the Gibbs criterion, not amorphous. As will be explained in chapter 2, metastable states are stable against small thermal fluctuations, but are *not the absolute Gibbs minimum for the given temperature*. But how is this achieved? How are glasses formed, if they are not thermodynamic systems? They are formed by cooling a liquid by means of a non-equilibrium process, what is called *rapid quenching*.

In rapid quenching, the temperature of a liquid is reduced at a dramatic rate. The ergodic theorem states ensemble averaging is equivalent to time averaging, i.e. left to itself, the liquid over time explores the different system configurations available to it in phase space (these configurations include the crystalline configuration, as mentioned above). Now, the physical correspondence to exploring phase space is the movement, or diffusion, of atoms in the liquid (i.e. the system kinetics). The thermal fluctuations, which allow the liquid to acquire its different configurations, are limited by the response time of the system kinetics. If the system temperature can be reduced at a rate faster than the system kinetics response, the system will be trapped in an energetically costly state, one which is stable against the *now reduced* (in magnitude) thermal fluctuations.

### 1.1.2 Why do a Crystallization Study

A crystallization study of a glass is the action of slowly (with respect to system kinetics) raising the system temperature until the thermal fluctuation magnitudes are large enough to allow the system to escape from its metastable state to a more stable, crystalline state.

The study carried out in this thesis concerns itself with the activation energy,

system kinetics and reaction products involved in crystallization. Such quantitative analysis characterizes glass thermal stability, establishes an indirect understanding of glass-forming behavior, and the identity of early stage crystallization structures is indicative of short-range chemical order in the glassy state. Prior work on this system has also revealed that a partially crystallized glass has favorable effects on increasing material tensile strength[14]. From the standpoint of thermodynamics, there is no fundamental merit in studying the crystallization behavior of a particular glass; however, from a materials science perspective, the crystallization mechanisms and product of Al-Y-Ni glasses display composition dependent behavior [15] [16]. These observations, combined with prior studies of this system, has helped elaborate a greater structural understanding of such glasses. Hence, before addressing the results of the current study, a brief review is presented of past Al-Y-Ni studies in section 1.2.

### 1.1.3 A Brief History of Metallic Glasses

As mentioned above, the key to forming glasses is rapid quenching. Rapid quenching of molten silicates, borates, or organic polymers is relatively easy in comparison to metals because directional bonding between long-chained molecules places a severe limit on the rate of atomic rearrangements necessary in order to establish thermodynamic equilibrium. With a lower quenching rate limit of  $10^{-2} K/s$ , such materials end up in the amorphous state by simply air-cooling! In contrast, the effectively nondirectional *atom-atom* bonding in metals dramatically speeds up system kinetics, to the point that quenching rates in excess of  $10^5 K/s$  are required in order to solidify in the amorphous state.

The first historical reports of amorphous metal solid production were made by Kramer in 1934 (from vapor deposition) and Brenner in 1950 (electrodeposition of nickel-phosphorus alloys), who observed a single broad, diffuse X-ray scattering peak. It was not until 1960 that Duwez et al. established a technique for preparing metallic glasses by *rapid quenching from the melt*: splat cooling. In this technique a drop of molten metal was either propelled onto or squeezed between two large, cooled surfaces.

The result would be a cooling rate of ~  $10^6 K/s$ , producing thin amorphous films. However, it was Pond and Maddin's establishment of the melt-spinning technique in 1969 which made large scale production of glass ribbons a viable option, and opened the doors to metallic glass studies [11]. This is the rapid quenching technique of choice for the present work, as outlined in chapter 3. At present alternative rapid quenching techniques are water quenching, injection of liquid into a copper mold, and arc-melting on a copper hearth. Amongst these techniques, it is melt-spinning which produces the most effective quench, but the resulting glasses have thicknesses on the order of tens of microns, and thus cannot be classified as bulk glasses. Today, a broader range of techniques are classified as quenching techniques, such as solidification from the vapor state (quenching rate of  $10^{13} K/s$ ), deposition from a chemical solution or electrolyte, and ion/neutron bombardment of crystals [10].

The question arises what metals would be good glass-formers for continuous cooling from the melt, and it was found that alloys are good glass-formers over a *limited* composition range. This range corresponds to the presence of a eutectic in the alloy's phase diagram. A good glass-former is defined by it's undercooling temperature range: how far below the equilibrium crystallization temperature an alloy must be cooled before any noticeable nucleation of crystals occurs. The reason undercooling is observed is due to the activation energy required for crystal nucleation (discussed in chapter 2). The poor glass-forming ability of pure metals (having close or densely packed crystal structures) stems from the fact that crystallization of such a glassy phase from the melt requires relatively less structural adjustment, and hence comparatively less activation energy. The effect of adding solute atoms to a pure metal, most notably if they differ in size or chemistry, requires a significant diffusive rearrangement for crystallization to occur, hence increasing the activation energy and stabilizing the molten (glassy) structure. The effect of size mis-match and enthalpy of mixing will then enhance glass stability over an appropriate compositional range, indicated on the alloy phase diagram by the aforementioned eutectic. The glass transition temperature  $T_g$  is defined as the undercooling temperature at which the liquid's

atomic configuration departs equilibrium and homogeneously freezes, while the liquidus and solidus temperatures are the boundary temperatures separating completely liquid or completely solid phase regions from co-existing regions on a phase diagram. In the area of a eutectic  $T_g$  increases and liquidus temperature decreases, narrowing the temperature range over which cooling is necessary to effect rapid quench. This in turn greatly facilitates glass-forming ability. It should be noted that crystal growth rates in molten metals are very rapid once nucleation has occurred, leading to the problem of recalescence (agglomeration of heat flow) if heat extraction rate (i.e. rapid quenching) is relatively small in comparison to growth rate [10].

Recently theorists have been able to quantize the mis-match effect, establishing the universal glass criterion for glass forming behavior. However, Al-rich ternary alloys were found to display very good glass-forming ability for abnormally low solute concentration [17]. Such small concentrations do not explain glass-forming behavior according to the universal criterion. Egami has suggested that clusters (of Al and solute atoms) should be used in testing for the local topological instability [18] criterion, as opposed to single atoms of Al and solute. This modification of the universal criterion explains the very small solute content in the glasses discovered by Masumoto and Schiflet's groups [17] [19]. Egami's theory and its application to the Al-Y-Ni system will be discussed in chapter 4. Table 1.1 gives a summary of size mis-match and enthalpy or heat of mixing (as calculated from Miedema's model [16]) of Al, Y and Ni atoms.

atom	Radius (Å)	Enthalpy of mixing with Al $(kJ/mol)$		
		liquid	solid	
Al	1.43	0 0		
Y	1.78	-66 -54		
Ni	1.24	-47 -33		

Table 1.1: Atomic radii and enthalpy of mixing with Al (Miedema model).

# 1.2 The Al-Y-Ni System: discovery and current conclusions

Since aluminum-based metallic alloys have great engineering importance, there has been an effort for quite some time to make Al-based glasses. From 1965 to 1976, various groups reported the co-existence of an amorphous phase with a crystalline phase in binary Al-X (X=Si,Ge,Cu,Ni,Cr and Pd), but it wasn't until 1981 when Masumoto's group at Tohoku University discovered a homogeneous Al-(Fe,Co)-B glass [20], followed by the discovery of Al-Fe-(Si.Ge) homogeneous glasses by Shingu et al. in 1983 [21]. However, these ternary alloys were extremely brittle and displayed tensile strengths as low as 50 - 150 MPa. Masumoto's group, led by Akihisa Inoue, continued exploring ternary candidates and discovered Al-based amorphous alloys with good ductility in 1987 [17]. They focused on Al-Si-X and Al-Ge-X (X=Cr, Mn, Fe, Co, Ni) glasses and discovered that while Al-Si and Al-Ge are insoluble, the addition of an X-element renders the ternary a glass former, so that conceivably the X element's role was to alter the nature of the Al-Si/Al-Ge bond. X=Ni produced the most ductile glasses, attributed to a weak bonding between Al-Ni and Si-Ni/Ge-Ni. These glasses had 75 - 80% Al. Masumoto's group studied Al-Y-M and Al-La-M (M=Fe, Co, Ni, Cu) [22], and concluded Ni had the effect of producing the greatest compositional range for glasses, while increasing the amount of Al, relative to Y. decreased the crystallization temperature. Inoue was the first to put the spotlight on the Al-Y-Ni system [12] [23] when he measured a dramatically high tensile fracture strength of 1140 MPa, and a composition-dependent glass transition temperature  $T_q$ . Coupled with its low density, Al-Y-Ni thus has a dramatically large specific strength (see table 1.2).

In 1988, Poon and Shiflet independently discovered ductile Al-rich ternary glasses of the form Al-Fe-X, Al-Ni-X, Al-Co-X, Al-Rh-X (X=Ce,Gd,Y), with the Al-Fe-Gd glass a high specific strength candidate [19][24]. They were the first to make interesting structural observations such as heat treatment effect on tensile strength, and comment on nearest-neighbor distances and high Al-content of such glasses, whether the

Metal	tensile	density	specific strength
	strength (MPa)	$g/cm^3$	$10^3 m^2/s^2$
low carbon steel	395	7.86	50.25
stainless steel	552	7.5	73.6
high carbon steel	615	7.84	78.44
Al (99.5%)	69	2.71	25.46
Al 2014 (heat	485	2.8	173.21
treated, wrought)			
Al-rich glass [16]			
Al <sub>85</sub> Y <sub>8</sub> Ni <sub>7</sub>	777	3.28	236.89
Al <sub>85</sub> Y <sub>7</sub> Ni <sub>8</sub>	819	3.22	254.35

Table 1.2: Comparison of tensile strength versus density for several metal alloys.

glass is truly amorphous or randomly ordered micro(quasi)-crystallites, and isothermal and activation energy studies [25].

Thus, from 1989 onwards several groups began to pose more detailed structural questions about the Al-Y-Ni system. Matsubara and Waseda concluded (by anomalous X-ray scattering) that the Y atoms in  $Al_{87}Y_8Ni_5$  glass do not have Y nearest neighbors [26].

In 1991, Kwong et al. and Cao et al. did a crystallization study on  $Al_{85}Y_{10}Ni_5$  and  $Al_{88.5}Y_{6.5}Ni_5$ , respectively [27] [28]. Kwong discovered the alloy had several crystallization stages, their number and enthalpy being dependent on heating rate; isothermal annealing of the first stage showed the presence of two crystallized phases. One of the two phases was an FCC Al solid solution of Y and Ni, and the other was unidentified, but grew at the FCC Al solid solution-amorphous matrix interface. Any quenched-in nucleating centers existing in the glass were determined to be of diameter less than 1 nm. Crystallization products were suggested to be  $Al_3(Y,Ni)$ ,  $Al_2(Y,Ni)$ and  $AlY_2$ . No glass transition was observed in any of the DSC scans; they were the first to compute activation energies and suggest Al-Y or Al-Ni clustering. Cao con-

firmed multiple crystallization stages, observed a broad primary crystallization peak, calculated activation energies and identified the crystallization product at each stage as being

- (1) glass +  $\alpha$ -Al(Y,Ni)
- (2)  $\alpha$ -Al(Y,Ni) + Al<sub>3</sub>Y
- (3)  $\alpha$ -Al + Al<sub>3</sub>Y + AlYNi
- (4)  $\alpha$ -Al + Al<sub>3</sub>Y + Al<sub>3</sub>Ni

Cao claimed in the third stage metastable AlYNi precipitates out of supersaturated  $\alpha$ -Al, only to decompose at the next stage into Al<sub>3</sub>Ni and Al<sub>3</sub>Y.

In 1992 Kamiyama et al. [29] studied first stage isothermal crystallization in  $Al_{85}Y_{10}Ni_5$  by small angle scattering, and concluded first stage precipitates grew for 5.4 ks, stabilizing to a diameter of approximately 200 Å, with a well defined interface. First stage crystallization products were identified as FCC Al, Al<sub>3</sub>Ni and an unidentified non-equilibrium phase. The presence of multiple precipitates is in agreement with Kwong, hence the precipitate diameter is some sort of weighted calculation.

In 1993 Goyal et al. [15] made the first report of systematic variation in DSC scans: Al<sub>83</sub>Y<sub>10</sub>Ni<sub>7</sub> has a glass transition and Al<sub>80</sub>Y<sub>10</sub>Ni<sub>10</sub> does not. Their results did *not* concur with Kwong et al.'s assertion of heating rate effect on number of crystallization stages, and Kwong didn't see a glass transition. Crystallization products at each stage were identified as being

- (1) amorphous  $+ \alpha$ -Al
- (2)  $\alpha$ -Al + Al<sub>3</sub>Y
- (3)  $\alpha$ -Al + Al<sub>3</sub>Y + AlYNi
- (4)  $\alpha$ -Al + Al<sub>3</sub>Y + Al<sub>3</sub>Ni

the same for *both* compositions. At this time, Li, Johnson, Johansen and Sarholt-Kristensen [30] discovered that the chemical short-range order and amorphicity of Al-Fe-Y glasses varied with rapid quenching process parameters. This work gave possible credence to Kwong's observation of no glass transition and heating rate crystallization

variability, by suggesting crystallization product or mechanism variation as a function of rapid quenching parameters (the technique used to cool into the glassy state). Thus the discrepancies between Kwong's and Goyal's findings may be resolvable.

In 1994, independent of Goyal's findings, Sabet-Shargi, Altounian and Muir [16] did a systematic study of tensile strength, Young's Modulus, and DSC characteristics, as function of sample composition. DSC scans of first crystallization stage was either a glass transition or broad exothermic peak, (their temperature locations some 100Kapart)depending on composition. X-ray diffraction showed the broad exothermic DSC peak corresponded to primary Al crystallization. For Al content fixed at 85%, for the ratio of Y:Ni > 1, a glass transition was observed ("Y-rich" glass). A glass transition was also observed for Al content less than 85%, when the Y:Ni content is kept at a constant ratio of 8 : 7. By itself, these two observations leave more than one interpretation of the relation between amorphous short-range order and crystallization behavior. X-ray diffraction of the series of glasses made indicated a correlation length of 5.74 Å, which can be satisfied by Y atoms separated by a single shell of Al atoms. This is in agreement with the Y-Y nearest-atomic neighbor conclusions of Matsubara and Waseda[26]. A prepeak is observed in X-ray diffraction, which can subscribe to more than one glass-structure theory. Apart from the prepeak, a main peak and a shoulder (for compositions with primary Al crystallization) were observed. Isothermal studies established for the first time that compositions with primary Al crystallization had quenched-in nucleating centers in the amorphous state. Hence Sabet-Shargi et al. proposed these nucleating centers to be Al nanometer-scale crystals. The shoulder seems to originate from some Al-Al correlation, sensitive to the Ni content. Some activation energies and Avrami exponents were calculated, and first crystallization stage product for glass transition compositions produced a complicated, unidentified diffraction pattern. Sabet-Shargi's results agreed with Goyal's findings except for crystallization product identity.

Since then several groups have been researching particular aspects of the Al-Y-Ni system. Latuch, Matyja and Fadeeva [31] [32] [33] have carried out crystallization studies independent of Goyal's and Sabet-Shargi's results. In  $Al_{90-x}Y_{10}Ni_x$  (x = 2, 5, 8) crystallization occurs in 5 stages, with product (for x = 5)

(1) Al(Ni,Y) + Al<sub>3</sub>Ni(Y)
 (2), (3), (4) Al(Ni,Y) + Al<sub>3</sub>Ni(Y) + Al<sub>3</sub>Y(Ni)
 (5) α-Al + β-Al<sub>3</sub>Y + Al<sub>16</sub>YNi<sub>3</sub>

Only the x = 5 composition displayed glass transition behavior. x = 2 and x = 8 differ in crystallization product by the presence of intermediate Al<sub>2</sub>Y and absence of intermediate Al<sub>3</sub>Y(Ni), respectively. The have also observed variation in the number of crystallization stages of x = 5 with heating rate, in agreement with Kwong.

In 1996, Chang et al. [34] verified for the first time the presence of quenchedin Al nanocrystals by high resolution TEM in  $Al_{85}Y_5Ni_{10}$ . They also claimed to observe a quenching rate dependence on the pattern of DSC scans of  $Al_{85}Y_{10}Ni_5$ . They observed isothermal crystallization products of  $\alpha$ -Al,  $Al_3Y$ ,  $Al_3Ni$  and AlYNi; this is not in agreement with Latuch et al. but consistent with Goyal et al. and Cao et al.

Lindsay Greer's group [14] [35] [36] [37] at Cambridge have chosen to focus on the effect of partial crystallization on tensile strength in compositions that have quenchedin Al nanocrystals. They claim precipitating some Al leaves behind a relatively Yenriched amorphous matrix, leading to material hardening. The precipitated Al crystallites have homogeneous distribution and an average diameter of 5-12 nm. Since an Y-enriched matrix would render the material brittle (consistent with Y-rich glasses), they have hypothesized the Al-crystallites have a ductilizing effect [36]. The effect of isothermal anneals as opposed to continuous heating on the Al nanocrystal leads to the establishment of a metastable equilibrium with the amorphous matrix, retarding Al crystal growth and leading in turn to a smaller volume fraction crystallized (as a result of the Gibbs-Thomson effect) [14]. In their most recent publication they have also claimed to detect nucleation and growth at the first crystallization stage of alloys containing quenched-in Al nanocrystals [37].

Freitag, Altounian et al. have done a mechanical study on the series first studied by

Sabet-Sharghi [6]. Their conclusions are that the Young's modulus is correlated with crystallization temperature and product, implying a dependence of mechanical properties on the short-range order in the glass state. Electron transport measurements [38] on these same series have established that whereas glasses with quenched-in Al nanocrystals are consistent with the free electron picture, those with a glass transition have a discrepancy which may in turn be due to an increase in s-d orbital scattering from the partially filled d-bands at the Fermi level of Ni atomic sites.

At present Altounian, Saini, Mainville and Bellissent have concluded a neutron diffraction study of  $Al_{85}Y_xNi_{15-x}$  [5], the result of which indicates x = 10 glass has non-negligible atomic density-density correlations up to 12 - 15 Å, whereas x = 5 has such noticeable correlations only up to 8 - 10 Å. Good statistics due to high neutron flux permitted an accurate measurement of nearest neighbor distances, from which it was concluded glasses with  $x \ge 8$  are far more homogeneous than x < 8 glasses.

## 1.2.1 The Al-Y-Ni System: the goal of the present study

Each of the many studies on the Al-Y-Ni system brings a part of the puzzle determining the fine connection between glass composition. structure and crystallization behavior. However, not all the above conclusions are consistent with each other, and some of the published data raises more questions than answers. The attempt with the work represented in this thesis was to do a systematic, accurate characterization of  $Al_{85}Y_xNi_{15-x}$  glasses (x = 5, 7, 8, 10). The work involved three major components: isothermal and isochronal calorimetry analysis (done by DSC). Xray diffraction, and Transmission Electron Microscopy (TEM). Calorimetry measurements determined the enthalpy, crystallization temperatures, activation energies, and a thorough Avrami exponent characterization of the multiple crystallization stages. Variance of DSC scan characteristics as a function of rapid quenching parameters was also investigated in an attempt to resolve the disparate conclusions of different groups in the past. X-ray diffraction was carried out on both isochronally and isothermally annealed samples, establishing for the system, for the first time, a smooth consistency between the identity of crystallization products achieved by both heat

treatment techniques. TEM studies were essential to completing the understanding of the crystallization process in terms of identifying reaction processes, number of crystallized phases, and selected area diffraction. The technique complemented and enhanced X-ray diffraction conclusions and expanded on some of Kwong's [27] initial findings.

Chapter two of this thesis is a brief review of phase transformation theory and the derivation of Kissinger's equation for activation energy and the Johnson- Mehl-Avrami equation. Chapter three describes the experimental and data analysis techniques involved in determining a quantitative characterization of the glasses. Chapter four is the results and discussion section, and chapter five summarizes our findings.

# 2

# Theoretical Background

## 2.1 Phase Transformations in Metals

As mentioned in the introduction, the amorphous, or glassy, state in condensed matter systems is a metastable state. System configurations are classified as either stable, metastable, or unstable; fig. 2.1 gives an example of all three cases. The thermodynamic limit of finite statistical mechanical systems states that, at constant temperature T and pressure P, thermodynamic systems in equilibrium have a minimum Gibbs free energy, G (G = U + PV - TS, where U is the internal energy, V is the volume and S is the entropy) [39]. Unstable states are defined as having zero first order and negative second order derivatives of G, with respect to two thermodynamic variables (also known as reaction coordinates). Stable and metastable states have zero first-order and positive second-order Gibbs free energy derivatives. Only stable or metastable states are observed in our thermodynamic reality, as their positive Gcurvature establishes a restoring force against against thermal or particle fluctuations [40].

The metastable (and in our case glassy) state is then identified as not having the absolute minimum value of G. The second law of thermodynamics indicates our metastable system will have the tendency to try and minimize *absolutely* it's Gibbs free energy, and this tendency is quantitatively identified as the Gibbs free energy difference  $\Delta G = G_I - G_F$  between the particular initial metastable state  $G_I$  our system is currently trapped in, and the absolute final stable equilibrium state  $G_F$ (see fig. 2.1).  $\Delta G$  is referred to as a driving force for the transformation from the

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Figure 2.1: The change in free energy of a system as it undergoes a phase transition from an initial metastable state  $G_I$  to a final stable state  $G_F$ . An activation free energy  $G_A$  is required to pass through the unstable transition state  $G_A^{\bullet}$  in order to complete the reaction.  $\Delta G = G_F - G_I$  is the thermodynamic driving force for this reaction, and the reaction coordinate is the thermodynamic variable whose variation is changing G [2].

metastable state to the stable phase [39].

At a nanometer scale, phase transitions imply an atomic rearrangement, be it structural or chemical. Appendix 1 details the different structural changes occurring during a phase transformation. For this study, for almost all cases transformation occurs by a diffusion controlled nucleation and growth or pure growth mechanism.

Nucleation and growth processes are either interface-controlled (linear dimension of transformed region proportional to time at constant temperature) or diffusioncontrolled (linear dimension proportional to square-root of time) transformations. In a phase transformation from the metastable state to a stable state, three possible reactions may occur: primary, eutectic and polymorphous. Primary reactions produce a new phase whose chemical composition differs from the parent phase; such a segregation of aluminum is observed upon crystallizing certain Al-Y-Ni glasses. Eutectic reactions produce two or more new phases of differing chemistry, such that the chemical identity of the parent phase remains intact (i.e. there is no perceived segregation in the parent phase). Polymorphous reactions produce a new phase with identical chemistry as the parent phase. It should be kept in mind that segregation transformations in all likelihood are diffusion-controlled processes.

Due to the presence of segregation in certain Al-Y-Ni glasses, a brief detailing of particle diffusion and it's influence on isothermal analysis is discussed in Appendix 1.

# 2.2 The Arrhenius Equation and Activation Energy

Since a metastable state can effectively be considered an equilibrium state, normal thermodynamics and statistical mechanics can be applied to both it and of course the stable state. However, the configurations the system passes through during phase transformation cannot strictly be evaluated by such methods. The ideal would be to treat the system as a multi-body particle dynamics problem, or develop an irreversible thermodynamics theory which contains an equilibrium limiting condition, however these proposed solutions prove to be quite intractable in complex heterogeneous reactions. An alternative which works quite well with experimental results is the quasi-equilibrium theory [13] [41].

Since the metastable state is a local minimum, if the system evolves through a continuous series of intermediate configurations during its phase transition, it stands to reason that the system will pass through an intermediate state which is unstable (i.e. a local maximum), as indicated in fig. 2.1. This intermediate state is defined as the activated complex, or transition state. The energy component of the Gibbs free energy difference between the initial  $G_I$  and transition state  $G_A^*$  is defined as the activation energy  $G_A = G_A^* - G_I$  of the phase transition. The transition state is not observed experimentally. The quasi-equilibrium picture describing nucleation's connection to the transition state is discussed in Appendix 1.

The derivation of the Arrhenius equation requires the critical assumption of quasiequilibrium: treating the transition state as a thermodynamic state. Thus the probabilities of the system being in the initial state  $P_I$  and the transition state  $P_A$  are derived from equilibrium statistical mechanics, using the equilibrium partition function. Now, applying the Metropolis transition rule, we write  $P_A = p_T P_I$ , where  $p_T$ 

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is the probability of the system transitioning from state I to state A. Solving for  $p_T$ in this equation thus gives  $p_T = e^{-G_A/k_BT}$ , where  $G_A$  is the activation free energy and  $k_B$  is the Boltzmann constant. The reaction rate then would be the product of the probability of reacting with the frequency with which particles in the initial state attempt to transform,  $\nu$ , giving us  $\frac{dx}{dt} = \nu e^{-G_A/k_BT}$ , where x(t) is the fraction transformed at time t. This is the Arrhenius equation, which we can rewrite in terms of internal energy U and cast in a logarithmic form

$$ln(dx/dt) = ln(A) - \frac{U_A}{k_B T}$$
(2.1)

where A is called the frequency factor [13]. It should be noted that  $U_A$  is the activation energy difference between the ground states of the initial and activated complexes. In a grand-canonical system we should worry about higher energy state occupations, however for a negligible change in heat capacity during such a reaction, the ground state calculation is a good enough approximation.

In a phase transformation, while the Gibbs driving force  $\Delta G$  must always be negative, the change in internal energy may be positive (endothermic reaction) or negative (exothermic reaction). In the crystallization of some Al-Y-Ni glasses, there is an endothermic reaction called the glass transition. It is physically characterized by a sudden lowering of the viscosity coefficient, which may be thought of as a manybody response to a solid system where diffusion processes cannot help surmount the activation energy barrier. The entire structure relaxes its rigidity in order to give its constituent atoms enough degrees of freedom to establish an activated complex.

Eyring, Wigner, Polanyi et al. [41] have developed a more general reaction theory known as the Transition State or Absolute Reaction Rate Theory. The theory derives the reaction rate by applying a Maxwell-Boltzmann (and hence still quasi- equilibrium framework) distribution to the transformation of activated complexes into the final state and derives an expression for an equilibrium constant (ratio between equilibrium concentrations of activated and initial state). The theory's significant contribution is trying to give an expression for the characteristic frequency of initial state transformation attempts,  $\nu = \frac{k_BT}{h}$ , where h is Planck's constant [13] [42]. For the record, there exist far more complex nucleation theories such as the Volmer and Becker-Doring theories[41].

Given the Arrhenius equation, Kissinger has established a technique for experimentally determining activation energies of phase transformations [43]. His proof proceeds in two steps. First, he establishes that in a continuous heating rate process (constant heating rate, what is termed in calorimetry an isochronal scan) the exothermic/endothermic peak maxima corresponds to the temperature at which the reaction rate.  $\frac{dx}{dt}$  is a maximum. Chapter 3 explains in detail what is experimentally acquired in an isochronal scan: a plot of power released by the phase transition reaction, per unit mass, versus temperature (for a constant heating rate). The temperature distribution of the sample holder in our calorimeter device obeys the heat flow equation

$$\frac{dT}{dt} - \frac{\kappa}{\rho c}T = \frac{1}{\rho c}\frac{dq}{dt}$$
(2.2)

where  $\kappa$  is the thermal conductivity,  $\rho$  the density, c the specific heat and  $\frac{dq}{dt}$  the rate of heat generation due to chemical reaction (in our case a metastable state crystallizing into a stable state). Since the reference holder in our calorimeter has no irreversible reactions, it obeys the above equation with  $\frac{dq}{dt} = 0$ . Using an ansatz of  $T = T_0 + \phi t$ , where  $T_0$  is the initial temperature and  $\phi$  is the constant heating rate, the temperature at the center of the reference sample  $T_r$  is solved to be

$$T_r = T_0 + \phi t - \frac{\phi \rho c a^2}{4\kappa}$$
(2.3)

where a is the radius of the sample holder. Now, since  $\frac{dy}{dt}$  is a function of temperature, equation (2.2) is a non-linear partial differential equation, and thus can't be solved by typical analytic methods. However, if we make the plausible assumption that the same ansatz holds for the sample holder, we may conclude that the temperature at the center of the sample holder  $T_s$  is of the form

$$T_s = T_0 + \phi t - f(\frac{dq}{dt}) \tag{2.4}$$

where  $f(\frac{dq}{dt})$  is a function of the reaction rate. The time derivative of the temperature

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difference  $\theta = T_r - T_s$  between the two holders will then be

$$\frac{d\theta}{dt} = f'(\frac{dq}{dt})\frac{d^2q}{dt^2}.$$
(2.5)

 $\theta$  is a maximum when the above derivative is zero, which occurs if  $\frac{d^2q}{dt^2} = 0$  i.e. if the rate of heat generation is a maximum. Since the rate of heat absorption is proportional to the rate of reaction, this means that the maximum temperature discrepancy between the two calorimeter holders (which corresponds to the peak maximum in an isothermal scan) occurs when the reaction rate  $\frac{dx}{dt}$  is a maximum.

The second step to Kissinger's derivation then takes the time derivative of the Arrhenius equation (where the time dependent variable is  $T = T_o + \phi t$ ) and sets it equal to zero for  $T = T_x$  (where  $T_x$  is the isochronal exothermic peak maximum); isolating some terms and taking the the natural logarithm of both sides gives us the Kissinger equation:

$$\ln(\frac{\phi}{T_x^2}) = \ln(\frac{k_B}{A \cdot U_A}) - \frac{U_A}{k_B} \frac{1}{T_x}.$$
 (2.6)

Hence a plot of  $\ln(\phi/T_x^2)$  versus  $1/T_x$  should give a straight line with slope proportional to the activation energy.

### 2.3 Nucleation and Growth

Isothermal scans, or constant temperature annealing, forms the second half of the calorimetric analysis in this thesis. The derivation for the Arrhenius equation imposes a simplistic physical framework on the phase transformation process. It is concerned with the creation of nucleating centers and not the subsequent complications which accompany the growth of these nuclei. The simplest example is that, dependent upon nucleation density and volume of the initial phase, eventually these nucleating centers will grow (either isochronally or isothermally) large enough to start impinging on each other, and depending on the models describing these nucleating phases, that result may incur anisotropic growth, merging of nuclei, or an abrupt stop in further growth. The situation further complicates if the nucleating centers are a primary reaction or subject to a diffusion-limited process; the resulting drain of solute atoms from the
remnant amorphous matrix, as the nuclei grow, will eventually alter the concentration of solute atoms available to a given nuclei for further growth. This is referred to as *soft impingement*, as opposed to the previously mentioned *hard impingement*. In annealing a system at a fixed temperature, the transformation process is slowed down, and in some sense experimental data acquires a finer resolution with respect to all the varying physical factors which contribute to affecting the fraction transformed.

An outline is given of the simple derivation for isothermal crystallization put forth by Avrami et al. [44] The more complicated physical effects. their effect on different variables and the two Avrami parameters is then briefly discussed in order to motivate an Avrami exponent analysis for the Al-Y-Ni system.

At constant temperature exothermic peaks measured in calorimetric scans are proportional to the fraction of the phase crystallized. Consider the formation of a nuclei after a characteristic time  $\tau$ , defined as the inverse of the nucleation frequency. Then the expression for the volume of such a spherical nucleus as a function of time is

$$v_{\tau} = \frac{4\pi}{3} [\gamma(t-\tau)]^3 \text{ for } t > \tau$$
$$v_{\tau} = 0 \qquad \text{ for } t < \tau$$

where  $\gamma$  is the isotropic growth rate. If the initial and final phases are labeled  $\alpha$  and  $\beta$ , respectively, one would think the number of new  $\beta$  regions nucleated in the time interval between  $\tau$  and  $\tau + d\tau$  is  $I^{\nu}V^{\alpha}d\tau$ , where  $I^{\nu}$  is the nucleation rate per unit volume and  $V^{\alpha}$  is the total initial phase volume. Not quite. During the time  $d\tau$ , when  $V^{\beta} = I^{\nu}V^{\alpha}d\tau$  new transformed regions are formed,  $I^{\nu}V^{\beta}d\tau$  of this transformed region is subject to transformation also. In other words, we have not accounted for the fact that transformed volume can't be used when determining nucleation content. If we imagined that in fact nucleation occurs in these transformed regions, these extra nuclei are defined by Avrami as phantom nuclei, and accounting for them in the analysis allows us to satisfy the condition that the act of nucleation, described by  $I^{\nu}$ , is homogeneous, i.e. occurs at random positions and is technically not dependent on the phase identity of the volume in which it occurs (i.e. history independent). This is

a subtle point to consider, but it implies  $I^{\nu}$  is independent of hard impingement. The total volume that has transformed into this new greater volume  $(I^{\nu}V^{\alpha}d\tau + I^{\nu}V^{\beta}d\tau, \text{ in time } d\tau)$ , dubbed the "extended" volume  $V_{e}^{\beta}$ , is  $dV_{e}^{\beta} = v_{\tau}I^{\nu}Vd\tau$  (where  $V = V^{\alpha} + V^{\beta}$ ), for times between  $\tau$  and  $\tau + d\tau$ . We thus get the expression

$$V_{e}^{\beta} = \frac{4\pi V}{3} \int_{\tau=0}^{t} I^{\nu} \gamma^{3} (t-\tau)^{3} d\tau.$$
 (2.7)

A second point to consider for this expression,  $V_e^{\beta}$ , is that all nucleating regions, be they physical or phantom, continue to grow irrespective of each other's presence, i.e. they grow through each other. Thus hard impingement is not an issue to consider for  $V_e^{\beta}$ , since  $I^{\nu}$  and  $\gamma$  both have no dependence on it (however, soft impingement does indeed have effect on  $\gamma$  with time).

Now once a relation is established between the actual volume transformed and  $V_e^{\beta}$ , an expression for the fraction transformed can be acquired. Consider a small random region, of which a fraction  $1 - V^{\beta}/V$  remains untransformed at time t. After a further time dt, the extended volume of  $\beta$  will increase by  $dV_e^{\beta}$ , and the true volume by  $dV^{\beta}$ . Of the regions making up  $dV_e^{\beta}$ , a fraction  $1 - V^{\beta}/V$  on average lies in previously untransformed phase, thus contributing to  $dV^{\beta}$  i.e.  $dV^{\beta} = (1 - V^{\beta}/V)dV_e^{\beta}$ ; which gives  $V_e^{\beta} = -V \ln(1 - V^{\beta}/V)$ . Substituting this expression in the previous equation and reworking it gives

$$r(t) = 1 - \exp(-\frac{4\pi}{3} \int_0^t I^{\nu} \gamma^3 (t-\tau)^3 d\tau)$$
 (2.8)

where x(t) is the fraction  $V^{\beta}/V$  transformed at time t. Provided any time dependence of the nucleation rate  $I^{\nu}$  or growth rate  $\gamma$  established, once the integral in the above expression is evaluated we have an equation of the form

$$x(t) = 1 - e^{-kt^{n}} = 1 - e^{-(\frac{t}{\tau})^{n}}$$
(2.9)

where  $\tau$  is a different characteristic time constant and n is defined as the Avrami exponent.

In the simplest case, both nucleation and growth rates are constant, giving an Avrami exponent of 4, 3 or 2 for three, two or one-dimensional growth, respectively.

Time dependence of the nucleation rate in the form of an exponential decay (an alternative assumption by Avrami) can possibly lower the exponent value by as much as 1 (i.e.  $3 \le n \le 4$  for three-dimensional growth). Further complications to the functionality of the growth rate variable may be due to an extra amount of heterogeneous nucleation occurring on the surfaces, edges and corners of presently growing nuclei (i.e. when nuclei are not spherical in geometry).

Further, growth rates are either interface or diffusion-controlled processes. The growth of a nucleus is a two-step process. involving a) diffusion of atoms towards a nucleus, and b) the requirement for these atoms to overcome the activation energy posed by the nucleus' surface in order to combine with the nucleus. Both processes transpire at rates independent of each other, giving rise to two possible growth scenarios: interface and diffusion-controlled growth. In interface-controlled growth, the reaction of atoms next to the nucleus interface occurs at such a slow rate that there is always a steady supply of atoms before the nucleus interface; solute concentration and growth rate are constant, possibly of the form  $\nu e^{-\Delta g/k_B T}$  ( $\nu$  is the Eyring characteristic frequency and  $\Delta g$  is the driving force for growth of the nuclei). This driving force has concrete physical meaning as it ends up being proportional to the velocity of the growing interface. In diffusion-controlled growth, the reaction of atoms next to the nucleus interface occurs at such a high rate that the local region before the growing nucleus gets drained of solute atoms, until more such atoms can diffuse to this location from other regions in the matrix. This gives a time dependence to the growth rate, linked to the time dependence of the solute-matrix diffusion coefficient. To summarize, in interface-controlled growth the growth rate is influenced by the growth activation energy, which remains constant throughout the reaction (hence a constant growth rate). In diffusion-controlled processes, the growth rate is influenced by the matrix's diffusion coefficient for the atoms of interest, which in the soft impingement situation will very much depend on time. Whenever multiple reaction rates are involved in a transformation process, it is the slowest rate which determines the overall rate of the process.

Such complications manifest themselves in deviations of the Avrami exponent values from d+1, where d is the dimensionality of growth, only because the complications are some functionality of time. Any such evolution of nucleation or growth rates with time can be considered a geometrical modification of the initial transformation scenario. This is because all other system parameters (such as temperature) have no time dependence. The key to the argument is recognizing that in the simple case of a constant nucleation and growth rate, n = d + 1 because nucleus volume has a cubic dependence on its radius, and the radius in this case varies linearly with time (the constant of proportionality being the growth rate). Thus any temporal variation in the growth constant affects the time-radius relation, and hence the exponent the time variable has in the integral is altered. Any such nucleation rate temporal variation can be buried into the time factor due to nucleus growth in a mathematically non-distinguishable way. This means annealing at different temperatures prior to the onset of a given transformation has negligible effect on n. The time constant  $\tau$ , however, is very much dependent on the nucleation or growth rate having a temperature dependence. The most striking example of this being diffusion- controlled growth, where  $\tau$  is a function of the diffusion constant D, which in turn depends on T.

Christiansen has compiled a thorough table characterizing different values of n as a means to infer the kinetics of heretofore unknown processes, reproduced in table. 2.1.

## (a) Polymorphic changes, discontinuous precipitation, eutectoid reactions, interface

n
> 4
4
3 - 4
3
2
1

Conditions	n
All shapes growing from small dimension, increasing nucleation rate	> 2.5
All shapes growing from small dimension, constant nucleation rate	2.5
All shapes growing from small dimension, decreasing nucleation rate	1.5 - 2.5
All shapes growing from small dimension, zero nucleation rate	1.5
Growth of particles of appreciable initial volume	1 - 1.5
Needles and plates of finite long dimensions, small in comparison	1
with their separation	
Thickening of long cylinders	1
Thickening of very large plates	0.5
Precipitation on dislocations (very early stages)	$\sim \frac{2}{3}$

Table 2.1: Physical interpretation of different Avrami exponent values [8].

# 3

# **Experimental Techniques**

This chapter discusses sample preparation and characterization techniques. In addition, analysis techniques for data processing and error estimation are discussed.

## 3.1 Sample Preparation

### 3.1.1 Alloy Preparation

Al-Y-Ni alloys were prepared from 99.99% pure Al (in pellet form), 99.9% pure Y (rough chunks stored at 500 *mtorr* pressure) and 99.99% pure Ni (pellet form). Masses were cut to exact size, within an error of  $\pm 0.3mg$ . For each alloy, the amounts of masses required for each element were calculated using the atomic percentages of each element in the alloy and the element's atomic molar mass. Table 3.1 lists the elements' atomic molar masses and other pertinent arc-melting characteristics.

Element	Atomic molar	melting	boiling	Thermal	Electrical
(Structure)	mass (g/mol)	point (K)	point (K)	Conductivity	Conductivity
				at $300K$	at 300K
				$(cal/cm^3/K/s)$	$(\mu\Omega^{-1})$
Al (FCC)	26.982	933	2723	0.5	0.382
Y (HEX)	88.91	1782	3200	0.035	0.019
Ni (FCC)	58.71	1726	3003	0.22	0.145

Table 3.1: Some physical characteristics of the elements of interest [9].

Three different techniques were attempted to produce the Al-Y-Ni alloys: arcmelting, induction melting with an Ar background and induction melting under high vacuum.

As for induction melting under Ar or high vacuum (< 10 mtorr), while negligible mass was lost in the melting process, inhomogeneous alloys were produced. The principle behind induction melting is to induce AC currents inside the bulk of the individual elements by placing them within an alternating EM field, generated by an AC solenoid. The resulting currents then heat dissipate and melt the individual elements until they merge and mix. The problem occurs in the mixing process. The surface tension of the individual metals was far too strong (for the range of power at our disposal) to allow the elements to break through and mix successfully with one another. The presence of surface oxidation, notably in Al pellets, compounds this problem.

Sample homogeneity being a priority, the arc-furnace was chosen for preparing the alloys. In arc-melting the heat dissipation due to a DC current passing through the elements melts them. Arc-melting all three elements altered the alloy composition by several percent, however samples were consistently homogeneous. The reason for such high composition deviation is that Al pellets are tremendously difficult to melt due to their high surface to volume ratio, a readily oxidizable surface and high electrical and thermal conductivity (see table 3.1). This necessitated the use of current settings at which non-negligible portions of Y and Ni were vaporized (Y and Ni have higher melting points than Al, but the much smaller amounts of Y and Ni versus Al made their relative percentage loss due to vaporization at a given current a nonnegligible effect). Large sized Al chunks were pre-formed and used instead, giving homogeneous alloys with less than 0.3% atomic deviation in most cases, with an occasional deviation by as much as 0.5%. The arc-furnace chamber is evacuated by mechanical pump and back- filled with Ar gas three times, in order to ensure a clean atmosphere. The chamber is finally evacuated to a pressure of 60 - 80 mtorr and a partial Ar gas atmosphere of 175 torr is introduced. A Ti getter is heated for 1.5-2minutes at 50 A current in order to remove as much residual oxygen as possible. Y pieces were pre-melted at a current setting of 50 A for  $\sim 3 s$  in order to diffuse any oxides (accumulated along the surface of cracks in the Y chunks) to the surface. Al

chunks were pre-formed by melting pellets at 120 A for 3 s. Any surface oxidation was peeled away and the exact Al content required was cut down to size. Y and Ni were melted together at 25 A for 5 – 10 s, forming a binary alloy. This binary alloy was then melted with the Al chunk at 100 A for 5 s. The small surface to bulk ratio of the Al chunk makes the piece very easy to melt and once the reaction begins with the Y-Ni alloy the difficult Al characteristics drastically decrease. The resulting alloy was turned over and re-melted 3 to 4 times at 75-100 A for 30, 90 and 120 s. in order or ensure sample homogeneity. Total mass lost was systematically  $\sim 2\%$  ( $\sim 50 - 90 \ mg$  for a  $\sim 2 \ g$  ingot), corresponding to a compositional deviation of  $\sim 0.5\%$ , as determined by electron microprobe. Nominal compositions were then chosen to account for systematic composition deviation. The resulting microprobeevaluated and nominal identities are tabulated in table 3.2.

Nominal	Mass lost	Microprobe
Composition	in melt (%)	Composition
Al <sub>85</sub> Y <sub>5</sub> Ni <sub>10</sub>	$\sim 1.5\%$	Al <sub>86.0</sub> Y <sub>4.7</sub> Ni <sub>9.2</sub>
Al <sub>85.5</sub> Y7Ni7.5	$\sim 1.5\%$	Al <sub>85.8</sub> Y <sub>6.8</sub> Ni <sub>7.4</sub>
Al <sub>84.5</sub> Y <sub>8.5</sub> Ni <sub>7</sub>	$\sim 1.5\%$	Al <sub>84.7</sub> Y <sub>8.2</sub> Ni <sub>7.0</sub>
Al <sub>85</sub> Y <sub>10</sub> Ni <sub>5</sub>	$\sim 1.5\%$	Al <sub>85.6</sub> Y <sub>9.5</sub> Ni <sub>4.9</sub>

Table 3.2: Deviation in composition as a result of arc-melting.

### 3.1.2 Rapid Quenching

In order to produce amorphous Al-Y-Ni alloys, a rapid technique of heat extraction was required where the quenching reservoir had a high thermal conductivity, in order to avoid recalescence in the alloy. The single roller melt-spinning technique was chosen since past documentation has shown it to achieve cooling rates of  $10^6 K/s$ , making it a very effective technique for producing metallic glasses. The ~  $20\mu m$  thickness of Al-Y-Ni ribbons and high thermal conductivity of the melt-spinning copper wheel ensured a rapid quench without risk of recalescence.

0.5-0.7g pieces were broken off the alloys and placed in a quartz crucible with an orifice of 0.45-0.5mm diameter. Larger sized pieces could not be completely ejected, upon melting, from the crucible. This is because upon melting the alloy would be in good thermal contact with the quartz crucible, and Al's high thermal conductivity contributed to rapidly cooling the molten alloy while still in the crucible. The result was that in the time roughly 0.5g alloy would be ejected, the remaining alloy in the crucible had cooled down to near its solidification point.

The chamber was evacuated by mechanical pump and back-filled with He gas twice, bringing the pressure down to 100 *mtorr*. A partial He gas atmosphere of 380 *torr* was introduced. (It was observed that using He as the background gas produced ribbons with well defined edges, while with Ar background gas ribbon edges were frayed.) The alloy piece was melted by induction melting and ejected through the crucible opening by an Ar gas overpressure of 380 *torr*. The ejected molten alloy formed a puddle on a rotating copper wheel. Wheel diameter was 9 *cm*. Tangential velocity at the site of the molten puddle was approximately 60 *m/s*. The quartz crucible opening was positioned 2 - 3 mm above the wheel surface, and the ribbon came tangentially off the wheel surface. Fig. 3.1 shows an example of melt-spinning Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub>, and the orientation of the melt-spun ribbon with respect to the meltspinning wheel. The resulting metallic ribbons were consistently amorphous, with dimensions being a width of 1 - 2 mm, thickness ~ 25  $\mu m$ , and lengths varying from 0.5 - 3 m.

### 3.1.3 Electron Microprobe Characterization

As stated above, actual alloy composition was characterized by a wavelength dispersive electron microprobe, JEOL 8900-L. The melt-spun ribbons were mounted on double-sided carbon sticky tape and coated with a 20 nm layer of carbon (under a vacuum  $\approx 10^{-5}$  torr). Carbon is the choice of coating as it has a minimal effect on the X-ray spectrum both in terms of low attenuation of incident electrons or emergent X-rays. Its effect on spectra peak intensities is calculated to be of the order of 1% [45]. A wavelength dispersive spectrometer was used to determine atomic composi-



Figure 3.1: Melt-spinning in action on Al84.5 Y8.5 Ni7.

tion counts, which guarantees finer wavelength (and hence composition) resolution but poorer statistics for unit collection time compared to an energy-dispersive spectrometer. X-rays emerging from the sample were dispersed through a lithium-fluoride crystal and the count of a particular wavelength's photons was detected by a Bragg angle sweep using an Ar(90 %)-methane(10 %) gas filled proportional counter. Kshell photons for Al and Ni, and L-shell photons for Y were counted. K-shell photons for Y were not accessed as their high energy ionizes the Al and the associated electron beam penetrates too deep into the sample, drastically increasing the large absorption correction for emitted x-rays. High count rates saturate the detector, leading to a depression in the pulse height (photon count); therefore, to avoid this problem from high energy X-rays (which ionize Ar atoms and initiate an avalanche effect, and thus high count rate), only first order dispersed X-rays are admitted to the counter. Poisson statistics models the random emission of X-ray photons and subsequent probability of its ionizing an Ar atom, hence these statistics govern the error analysis for the pulse heights which are proportional to the photon count for a given wavelength [46]. The Castaing approximation gives sample concentration for an atom A,  $c_{sample}^{A}$ , as

$$c_{sample}^{A} = \frac{I_{sample}^{A}}{I_{std}^{A}} c_{std}^{A}$$
(3.1)

where  $I_{sample}^{A}$  and  $I_{std}^{A}$  are the spectra intensity for atom A in sample and standard, and  $c_{std}^{A}$  is its concentration in the standard [47]. This simple calculation is then subject to complicated "matrix effects" or ZAF (Z for atomic number (affects electron beam penetration and backscattering), A for absorption, F for fluorescence) corrections. Peak positions need not be the same for a given atom in the sample versus the standard, since slight shifts may occur as a result of the chemical bond. Hence in our detection of Al content, an Al oxide was used as the standard, as opposed to a "pure" Al standard. Incident electron beam had a  $1 - 5 \ \mu m$  diameter. and an accelerating voltage of 15 kV. The net intensity measurement for a given spectral peak is a weighted subtraction of background intensity on either peak side from the peak maximum intensity value. A standard deviation calculated from statistical fluctuation gives an uncertainty of  $\pm 0.5\%$  on atomic percent of composition detected. The microprobe was also used in a Scanning Electron Microscope mode to develop high contrast images (electron micrographs) of the ribbon topology, as shown in fig. 3.2.

## 3.2 Sample Characterization

### 3.2.1 Differential Scanning Calorimetry (DSC)

In order to quantitatively determine the enthalpy, activation energy and Avrami exponent of each crystallization stage in the Al-Y-Ni systems studied, a Perkin-Elmer Differential Scanning Calorimeter DSC-2C was used. In contrast to other calorimetric analysis techniques, such as classical or Boersma Differential Thermal Analysis DTA, the DSC is ideally suited for acquiring enthalpy measurements. In the DTA, both sample and reference holders (defined below) are in thermal contact with the same heat reservoir. For a given heating rate, the temperature difference between a sample and reference holder is monitored. This temperature difference is sensitive to any change in enthalpy  $\Delta H$ , heat capacity (at constant pressure)  $C_p$  and resistance to heat flow R in the sample versus the reference holder. Thermal resistance occurs because of poor physical contact (hence poor thermal contact) between sample and



Figure 3.2: (a) SEM micrograph of an Al-Y-Ni melt-spun ribbon ( $\times$ 40; (b) & (c) are micrographs of an Al-Y-Ni ribbon ( $\times$ 100) (b) wheel-side (c) free side.

Al pan or between Al pan and sample holder. Foreknowledge of both  $C_p$  and R are required in order to determine the enthalpy of reaction. In a DSC there are *individual* heat reservoirs for each holder. This allows for a precise system response to reactions taking place in the sample holder, the response being temperature controlled by a feedback mechanism using the reference holder as a standard of comparison (explained in detail in Appendix 2) [48].

The vertical axis of a DSC plot is the unit power (mcal/s/mg) difference, input to the sample holder (by difference it is meant subtracting with respect to the unit power input to the reference holder); the horizontal axis represents (in the isochronal mode) the temperature of the reference holder (and thus the temperature the sample holder

is brought to by thermocouple feedback). In isothermal mode the axis represents time. Now, when the sample reaches a phase transition temperature, the reaction is either exothermic (in our case crystallization) or endothermic (glass transition). In such an instance there is a heat flow excess or deficit in the sample holder, and secondary control will appropriately reduce or increase the sample heater's power, and this results in a peak deflection from the baseline; there may or may not be a change in heat capacity contribution. In most instances there is a negligible change in  $C_p$ , noted by the fact that after reaction, the DSC scan returns to almost the same baseline (see figure in Appendix 2). In such a case the area under any such "exothermic" or "endothermic" peaks observed in DSC plots is proportional to the enthalpy (because of constant pressure) of the reaction (effectively equal to the energy term in the Gibbs free energy difference between initial and final states for this given phase transformation).

Perkin-Elmer DSC models guarantee a maximum sensitivity of 0.1 mcal/s for a full-scale peak deflection, requiring only milligrams of sample [48]. Thermal resistance between sample holder and thermocouple are certified as being minimum, and good thermal contact between sample and Al pan is insured by tightly crimping the Al pans shut in order to minimize sample volume and maximize sample to pan surface contact. A new Al pan was used for each sample analyzed ensuring no thermal resistance contribution from reacted pans. Hence the only significant contribution to thermal resistance comes from the Al pan to sample holder contact. A constant flow of pre-purified Ar gas was maintained at 1000 torr in both holders in order to minimize oxidation.

### Isochronal mode analysis

The presence of a fine layer of evaporated samples in the sample holder (produced from the vaporization of samples over years of DSC runs) gives an extra temperaturevarying heat capacity contribution. This produces large curvature backgrounds in isochronal DSC plots, and is removed by repeating the same heating history once the Al-Y-Ni glass has crystallized to its equilibrium concentration (at which point

the alloy's specific heat will remain effectively constant over the temperature range of interest), and subtracting this second run as a background from the initial crystallization run. Crystallization  $T_x$  and glass transition  $T_g$  temperatures on a DSC scan is open to different interpretations by different groups. We have chosen the convention that exothermic peak maximum is  $T_x$ , and endothermic peak onset is  $T_g$ .

The thermal resistance between Al pan and sample holder causes a time lag, where the temperature scanned and recorded by the DSC at a given instant differs from the actual temperature of the sample. Since thermal lag is a function of the heating rate, for each heating rate a calibration is performed using a pure zinc standard, determining a correction offset which must be added to all  $T_x$  or  $T_g$  measurements. The details of this correction are presented in Appendix 3.

Since the temperature readings in an isochronal plot are at a constant heating rate, dividing temperature readings by the heating rate gives a plot of unit power versus the time over which this power is coming out (exothermic) or going into (endothermic) this system. Hence integrating any such peaks gives the energy, or enthalpy, of the reaction. In some DSC plots exothermic peaks overlapped to the point that an accurate enough integration of the peaks could not be performed. These peaks were fitted by pseudo-Voigt functions, whose individual areas in turn were evaluated. This point is discussed in detail in Appendix 3. A pseudo-Voigt function is a linear combination of a Gaussian and Lorentzian, and hence is a more general shape fit than a pure Gaussian. The pseudo-Voigt function is discussed in the X-ray diffraction section of this chapter.

Isochronal peak maximas were determined using the DSC peak analysis function. Care was taken to carry out all such determinations with no curved background, since this can shift  $T_x$  by as much as 1 K in broad DSC peaks.

### Isothermal mode analysis

Since the DSC-2C does not come with an explicit isothermal analysis software package, these studies were accomplished by setting the DSC upper and lower hardware temperature limits at the annealing temperature value. Upon heating the DSC up to

this temperature, the hardware settings would then maintain the annealing temperature. Picking corresponding heating rates and temperature ranges on the software allowed to then program the DSC with an annealing time over which to gather data.

It order to anneal at some temperature above room temperature, the DSC needs to be heated up at some heating rate. It was found that approaching an annealing temperature at higher heating rates produced a more noticeable artefact in the collected isothermal data. This artefact comes in the form of a peak at the start of the isothermal anneal, lasting typically for about 30s. Fig. 3.3.a shows examples of such artifacts generated due to transitions between specific heating rates. Great care was taken to reproduce systematically the heating rate history with which annealing temperatures were approached. There is an inherent danger in perceiving such artefacts as being part of, or in fact wholly a reaction process (see Fig.3.3.b), and care must be taken to test such a possibility by either a) X-raying the sample for any new phases, once such a dubious peak has formed as a function of time, or b) annealing systematically at lower and lower temperatures, in which case any genuine physical reaction will occur at a later time in the anneal, while the artefact will still occur at time t = 0.

Any genuine nucleation peak observed in isothermal scans corresponds to nucleation and growth (a clearly defined peak), or pure growth (a decaying plot); fig. 3.3b shows examples of both processes. These peaks, both representing exothermic processes, are quantified by fitting them to the Avrami function. Since the heating evolved with time is proportional to the fraction crystallized x(t), we obtain x(t) by doing partial area integrals of nucleation and growth peaks from a time  $t_0$ , at which it appears there is no exothermic process observed above the background error bar, to a time t within the peak, and dividing these partial areas by the total area under the peak. This then results in exactly the fraction crystallized for this process at a time  $t - t_0$ , i.e.  $x(t - t_0)$ . A plot then of  $ln(ln(\frac{1}{1-x}))$  versus ln(t) yields a straight line with the Avrami exponent as it's slope. In some crystallization stages, more than one isothermal reaction occurred within a period of time such that there was enough



Figure 3.3: DSC isothermal scans demonstrating (a) peak artifacts, the result of discontinuous changes in the heating rate [ (i)  $10 - 20 \ K/min$  (ii)  $20 - 40 \ K/min$  (iii)  $40 - 80 \ K/min$  (iv)  $80 - 0 \ K/min$ ] and (b) comparison of DSC scans [ (i) artefact dues to heating rate discontinuously changing to zero (ii) pure growth + artefact (iii) nucleation and growth + artefact]; care must be taken not mistake the artefact for a nucleation and growth peak (see inset of (b)).

overlap between their respective exothermic peaks to hinder a quantitatively precise area integration (see chapter 4). In such cases an attempt was made to directly fit the experimental data with the derivative of the Avrami equation. The results and difficulties of fitting with this function are discussed in chapter 4 and Appendix 3.

### 3.2.2 X-ray Diffraction

The Al-Y-Ni systems studied were partially crystallized in the DSC, at a constant heating rate of 40 K/m, just past each crystallization stage and analyzed to determine the identity and structure of compositions formed. X-ray diffraction is ideally suited to this task, and all such measurements were done using an automated Nicolet-Stoe L11 powder diffractometer with  $K\alpha$  copper radiation (weighted wavelength 1.5418 Å). The diffractometer is made up of a 2.2kW Cu tube source and a detector-analyzer assembly consisting of a a photo-tube and a graphite analyzer crystal[49]. Fig.3.4 is a schematic diagram of the diffractometer, set up in a non-dispersive reflection geometry mode. Diffraction scans spanned a  $2\theta$  range of  $10^\circ - 80^\circ$ , using a stepping scan of  $0.1^\circ$  (in  $2\theta$ ). At each scan step, diffraction data was collected for 50s.



Figure 3.4: Diffractometer setup for the X-ray diffraction experiments [3].

The X-ray beam forms a rectangular window, about 1 cm in height, at the sample holder position. The window width W is given by

$$W = R \times \frac{\sin(\alpha)\cos(2\theta)}{\cos(\alpha)\sin(\theta)}$$
(3.2)

where  $R = 17.9 \ cm$  is the diffractometer's Rowland radius and  $\alpha = 0.6$  is the equatorial divergence of the incident beam at the sample [50]. W is largest for smallest value of  $2\theta$ ; in our case  $W = 2.12 \ cm$  and 1.01 cm for  $2\theta = 10^{\circ}$  and 20°, respectively.

### Diffraction corrections

Glassy ribbons that were partially crystallized in the DSC have a typical length of approximately 5 mm. Hence many such 5 mm ribbons were tiled next to each other, forming a roughly 1  $cm^2$  area of sample. To hold the ribbons in place, they were tiled on top of double-sided sticky tape, mounted in turn on a glass-slide. X-ray scans of both sides of crystallized ribbon showed no perceptible difference. Calculated absorption coefficient for typical Al-Y-Ni compositions studied gives an absorption length of ~ 20  $\mu$ m; typical ribbon thicknesses are 20 - 25  $\mu$ m. The tape and slide

produced a collective background contribution at low scan angles  $10^{\circ} < 2\theta < 30^{\circ}$ . The complete background correction formula is

$$I_{theo}(2\theta) = \frac{I_{expt}(2\theta) - e^{-2t\mu/\sin(2\theta)}I_b(2\theta)}{2\mu(1 - e^{-2t\mu/\sin(2\theta)})}$$
(3.3)

where  $I_{theo}$  is the theoretically calculated intensity from single scattering, absorption corrected;  $I_{expt}$  is the experimentally acquired diffraction data,  $\mu$  is the absorption constant and t the sample thickness. The denominator represents the sample's selfabsorption correction. The  $\frac{1}{2\mu}$  factor was not applied to data correction, since it only modifies the data by a constant factor.

Selected powder diffraction and rocking  $\omega$ -curves were done on some of the Al-Y-Ni systems in order to ensure texturing did not affect relative intensities for a crystallizing phase. This was done by rocking the detector-sample angle while maintaining the sample-source angle fixed at a  $2\theta$  angle corresponding to an observed Bragg peak.

### Bragg peak broadening

Instrumental broadening was estimated from an annealed Al standard's powder diffraction, seen in Appendix 3. The large sized, strain-free Al crystals will produce a diffraction pattern whose peak broadening is effectively due to instrumentation effects. Broadening was quantified by calculating the peak integral breadth,  $\eta$ , defined as the diffraction peak area divided by peak maximum intensity. A given peak's integration was calculated between  $2\theta$  limits where, contrasting against background noise, the peak appears to be of negligible height. Artefact Bragg peaks occur, due to Cu- $K\beta_1$  and W-  $L\alpha_1$  radiation, however their magnitudes are small (see Appendix 3 for details).

X-ray diffraction Bragg peak broadening was fit with three purposes in mind: the determination of crystallizing Al's lattice parameter and peak integral breadth, and the peak maxima location of any remaining amorphous peak contribution to the diffraction pattern. All parameters were determined by fitting pseudo-Voigt functions to the diffraction data. Diffraction intensity is proportional to the magnitude squared of the form factor (also known as the atomic scattering amplitude), which itself is

defined as the Fourier transform of the scattering density. In the case of X-rays this is the electronic density of the sample.

Crystal size effect, under rigorous theoretical considerations, produces a Lorentzian broadening effect. Appendix 2 discusses the mathematical origin of peak broadening from the size effect. The presence of anisotropic strains in a system (the *strain effect*) may be modeled by an inherent fuzziness in the location of atoms within the crystal lattice, and Wilson has exhaustively show the strain effect to produce Gaussian peak broadening. He has also shown that the cumulative effects and size and strain can collectively be modeled by fitting the experimental diffraction peak to a *convolution* of the Gaussian and Lorentzian function [51].

Such a convolution of Gaussian and Lorentzian functions, defined the Voigt function, is a mathematically complicated function [52] to achieve experimental data fits with. Another point to keep in mind is that the initial choice of fitting parameter values may place the fitting process in a region of parameter space where locally a better fit can not be discerned; the fitting process may get stuck in a sort of metastable selection of parameter values (i.e. values which appear locally stable but do not absolutely minimize the fit to data). A discussion is presented on the goodness of fitting in Appendix 2. This means initial choice of parameter values may have crucial effects on the outcome of the fit, and the parameters in a Voigt function have a somewhat complicated graphical interpretation, leaving the experimenter hard-pressed to suggest good initial parameter fit values. An alternative is to use the pseudo-Voigt fitting function, defined as a weighted *sum* of a Gaussian and a Lorentzian

$$\Phi(q) = \Phi(0) \left[ \eta \frac{w^2}{w^2 + q^2} + (1 - \eta) \pi \ln(2) e^{-\ln(2)q^2/w^2} \right]$$
(3.4)

where  $0 \le \eta \le 1$  is the weighting fraction and w is the full width at half maximum (FWHM), and setting it equal for both Lorentzian and Gaussian terms introduces the ln(2) factor in the Gaussian term. It has been observed experimentally that the pseudo-Voigt does just as effective a job at determining crystal size and strain, given the error bars of the problem [53]. It should be noted that crystal size effects determined by diffraction profile fitting produces a volume-weighted average grain

size, whereas TEM real space imaging gives us a number-weighted average grain size [51].

With the pseudo-Voigt function it is far easier to fit with starting parameter values closer to the parameter phase-space absolute minima. Because of its linear sum and identical FWHM of both Lorentzian and Gaussian, simple quantitative approximation of experimental peak maxima location and FWHM have direct correspondence. This allows for very good educated guesses as to starting values of pseudo-Voigt fitting parameters.

There exists one more complication to diffraction peak profiles: instrumental broadening. The finite size of the X-ray source and slit width introduce two major modifications to diffraction profiles. Appendix 2 gives a brief review of the physical origin to the different instrumental broadening contributions.

There are three different breadths describing the shape of Voigt functions, either of which may characterize peak broadening. These are the FWHM, integral breadth (defined as the peak integral divided by peak maxima) and the peak variance [54]. Out of these the FWHM is the least susceptible to background error, however it has no direct theoretical relevance. The variance is an ideal quantity to use, since it has been mathematically proven that any instrumental correction to variance can be removed without knowledge of the functional form of instrumental weighting correction. However, the variance has no analytically established connection to theory. It is the integral breadth,  $\beta$ , which has a simple relation to grain size and strain. The unfortunate problem in making instrumental corrections to integral breadth is that a functional form must be chosen for the instrumental correction. Years of experimental experience have decided on the cumulative instrumental correction having an approximately Gaussian correction, which means that the experimental integral breadth  $\beta_{exp}$ , instrumental breadth  $\beta_{inst}$  and sample breadth  $\beta_{sample}$  are related by the relation  $\beta_{exp}^2 = \beta_{inst}^2 + \beta_{sample}^2$ . Now, in determining  $\beta_{exp}$ , instead of integrating the experimental intensity and involving background error, we note that determining  $\beta_{exp}$  from our pseudo-Voigt function gives a relation between  $\beta_{exp}$  and fitted FWHM

w, hence doing a pseudo-Voight fit (acquiring a value for w) will give a  $\beta^{exp}$  of

$$\beta^{exp} = [\eta \pi + (1 - \eta) \frac{\pi}{\ln(2)}]w.$$
(3.5)

Wilson has shown that the  $2\theta$  strain broadening dependence [55] is given by

$$\beta^{strain} = 4e \tan(\theta) \tag{3.6}$$

where e is an approximate inhomogeneous strain upper limit and is related to the rootmean-square inhomogeneous strain  $\langle \epsilon^2 \rangle^{1/2}$  by  $\langle \epsilon^2 \rangle^{1/2} = \frac{4}{5}e$ . The Debye intensity approximation for grain-size broadening gives in turn the well-known Scherrer grainsize formula

$$\beta^{size} = \frac{\lambda}{d\cos(\theta)} \tag{3.7}$$

where  $\lambda$  is the X-ray wavelength, and d the average grain size. By making the coordinate transformation to s-space (s-space differs from reciprocal space by a constant factor of  $2\pi$ ) the  $\beta^{strain}$ ,  $\beta^{size}$  expressions are recast as

$$(\delta s)^{strain} = 2es \tag{3.8}$$

and

$$(\delta s)^{size} = \frac{1}{d}.\tag{3.9}$$

Now we establish a relation between the Voigt function integral breadth (denoted as the experimental integral breadth  $(\delta s)^{exp}$  in the equation below) and Gaussian  $(\delta s)^G$  and Lorentzian  $(\delta s)^L$  integral breadths. Remember, in doing a pseudo-Voigt fit we demanded the Gaussian and Cauchy function to have the same FWHM, but this implies nothing about their respective integral breadths! The integral breadth relation is a complicated one, but is well approximated by

$$\frac{(\delta s)^L}{(\delta s)^{exp}} = 1 - \left[\frac{(\delta s)^G}{(\delta s)^{expt}}\right].$$
(3.10)

Since in our approximation  $(\delta s)^L = (\delta s)^{size} = 1/d$  and  $(\delta s)^G = (\delta s)^{strain} = 2es$ , a bit more massaging gives us

$$\left[\frac{(\delta s)^{exp}}{s}\right]^2 = 4e^2 + \frac{1}{d}\left[\frac{(\delta s)^{exp}}{s^2}\right].$$
 (3.11)

Thus a plot of  $[(\delta s)^{exp}/s]^2$  versus  $(\delta s)^{exp}/s^2$  is a straight line with intercept giving e and slope giving average crystal grain size.

The fitting of Al-peaks was done by fitting a value for the FCC lattice parameter that would produce peaks which had the best match against experimental data. Error bars in intensity profiles, for a given scattering angle, are the square root of the intensity at that angle; this is an exact result derived from Poisson distribution error statistics.

### 3.2.3 Transmission Electron Microscopy (TEM)

While X-ray diffraction proves to be a very powerful tool for materials characterization at the atomic scale, there is a broad range of questions X-ray diffraction leaves unanswered in complicated condensed matter systems. Questions such as phase microstructure, selected area analysis, accurate determination of grain size and chemical identification are effectively answered by electron microscopy techniques. Together. X-ray diffraction and electron microscopy form largely complimentary techniques (indeed X-ray diffraction is a reciprocal-space analysis, whereas for the most part electron microscopy is real-space analysis); for complex multiple crystallization systems such as the Al-Y-Ni alloys studied, it has very much helped to establish a more complete understanding of the crystallization process.

A Philips CM20 Transmission Electron Microscope was used in analyzing the initial crystallization stages in some Al-Y-Ni systems. A hot tungsten filament generates free electrons which are in turn accelerated by a  $V = 200 \ keV$  potential difference. Most electrons undergo multiple scattering due to the strong electrostatic scattering potential generated by the sample's bounded atoms. While it would be technically proper therefore to apply a multiple-beam dynamical analysis of acquired data, kinematic single scattering theory provides an adequate interpretation of diffraction features. In simplest terms, a TEM is comprised of three focusing Einzel lenses. After a wave scatters off an image (in this case the Al-Y-Ni sample), its propagation through free space has the physical interpretation of undergoing a Fourier transform, where in fact the Fourier transform of the image is generated at infinity (Fraunhoffer

diffraction). Of the three "lenses" used in a TEM, the first and third play the role of magnification and focus, whereas it is control of the focal length of the second lens which determines whether the final image will be the Fraunhoffer diffraction pattern of the finite sample area which was illuminated by the incident electron beam (selected area diffraction), or whether the final image will in fact be the Fourier transform of the Fraunhoffer pattern (i.e. a real-space image of the illuminated sample area) [56].

The more effective real-space contrast of electron microscope crystallite images (in comparison to optical illumination) is chiefly due to Bragg diffraction. Crystal grains with an orientation satisfying strong Bragg scattering will appear dark since diffracted electrons will not pass through the aperture. This allows for dark field imaging (see  $Al_{85}Y_{10}Ni_5$  in the next chapter), by allowing only a particular Bragg spot to pass though an aperture opening (in diffraction mode), and then imaging this spot in real-space. The image shows grains contributing to the Bragg spot as bright, those that do not appear dark [56].

The incident illuminated sample area is typically a few microns. This, along with third-order spherical aberration in the focusing lenses make a geometric contribution to instrumental resolution. Thermal smearing introduces an electron beam energy spread of  $\frac{\Delta E}{E} = 10^{-5}$ , assuming a stability in accelerating potential of  $10^{-5}$ . While stray fields and mechanical vibrations limit magnification to a factor  $\approx \times 10^2$ , additional lenses provide a magnification as high as  $\times 10^6$  (used in High Resolution Electron Microscope HREM of Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub>).

Samples for TEM analysis were prepared by ion-beam milling, using a Gatan model 600 Ar beam mill [3]. Applied beam was 6kV and oriented at an angle of 14° with respect to the sample.

# 4

# **Results and Discussion**

## 4.1 From Glassy Order to Equilibrium Crystals

As first mentioned in chapter one, glasses have short-range order (SRO). Such compositional correlation has been observed in  $Al_{85}Y_5Ni_{10}$  and  $Al_{85}Y_{10}Ni_5$  in a study by Altounian et al. [5]. The glass phase is a non-equilibrium configuration, one that had begun the process of establishing crystalline equilibrium order before loosing significant atomic mobility. In thermodynamic terms, we might envisage such a non-equilibrium stage as a liquid phase configuration which has a *lowered* activation barrier separating it from the equilibrium crystalline state. This stems from the idea that the SRO serves as a structural template, or chemical catalyst, which selects a path of transformation for the metastable state, given sufficient thermal fluctuation. Thus is the nature of the thermodynamic driving force for transformation in such glasses. The structural template established by the SRO will lead to the equilibrium crystallized phases. In other words, while the liquid was cooling and in the process of establishing long range crystalline order by SRO enhancement, it froze. Heating up the glass then will continue this halted process, leading to the equilibrium crystallization products identified in the Al-Y-Ni phase diagram for the appropriate chemical composition (see Fig.4.1).

However, the crystallization process suffers from a possibly competing mechanism: atomic diffusion and growth of partially crystallized phases. The thermodynamic driving force favors the energetically least costly phase transformation, and in the case of primary or eutectic transformations, such a process has a dependence on the diffusive



Figure 4.1: Local corner of Al-Y-Ni phase diagram [4]. Two bars show the compositions prepared and studied by Altounian et al. [5] [6]. Compositions studied in this thesis are highlighted as points on the bars. Al<sub>3</sub>Y(HT2) is the high temperature phase known also as  $\beta$ -Al<sub>3</sub>Y. Stoichiometric composition Al<sub>4</sub>YNi is identified by the number 7 on this diagram.

ability of the different atomic species. The diffusion coefficient of solute atoms in the glass is independent of the activation energy for nucleation or pure growth of a crystal phase and dependent on the amorphous matrix. Hence a phase that is energetically less favorable to occur during isochronal crystallization may crystallize in relatively larger amount during an isothermal process. This sort of competition between different crystallizing phases is referred to as a competition between the thermodynamic driving force and diffusion.

Nonetheless, the identity of crystallized phases should be *local* to the region of the phase diagram where the initial glass compositions are. These locations on the phase diagram for the four glasses studied ( $Al_{85}Y_5Ni_{10}$ ,  $Al_{85.5}Y_7Ni_{7.5}$ ,  $Al_{84.5}Y_{8.5}Ni_7$  and  $Al_{85}Y_{10}Ni_5$ ) are marked in Fig.4.1 as points.  $Al_{85}Y_5Ni_{10}$  and  $Al_{85.5}Y_7Ni_{7.5}$  are the first two points immediately above the Al-Al<sub>4</sub>YNi tie-line.  $Al_{84.5}Y_{8.5}Ni_5$  and  $Al_{85}Y_{10}Ni_5$  are the two points immediately below this tie-line. We have also marked  $Al_{85}Y_3Ni_{12}$  (point lying just above the Al-Al<sub>16</sub>YNi<sub>3</sub> tie-line) and  $Al_{76}Y_{12.8}Ni_{11.2}$  (point lying closest to the Al<sub>4</sub>YNi stoichiometric position) glass compositions, since their equilibrium product was also studied in order to answer pertinent questions. Hence we should be expecting crystallization product of the type Al,  $\beta$ -Al<sub>3</sub>Y, Al<sub>4</sub>YNi, Al<sub>16</sub>YNi<sub>3</sub>, and

possibly even Al<sub>2</sub>Y, Al<sub>3</sub>Ni, Al<sub>7</sub>Y<sub>2</sub>Ni<sub>3</sub> or Al<sub>3</sub>Ni<sub>2</sub>. In the following sections we follow the crystallization process of the four glasses at a heating rate of 40 K/min. Goodness-of-fits to X-ray diffraction data are quantified by a normalized  $\bar{\chi}^2$  parameter, defined in Appendix 2.

## 4.2 $Al_{85}Y_5Ni_{10}$

Fig.4.2 shows X-ray diffraction plots of the glass and each crystallization stage in  $Al_{85}Y_5Ni_{10}$ ; each crystallization stage corresponds to heating the glass at 40 K/min to just past a corresponding exothermic peak (i.e. up to temperatures  $T_1$ ,  $T_2$  and  $T_3$ ). Al lattice parameter, grain size, main and shoulder amorphous peak maxima, their positions and goodness of fit  $\bar{\chi}^2$  are presented in table 4.1 and Fig.4.3. The strain effect on Al crystals was found to be negligible. Crystallization temperature (at 40 K/min isochronal scan), enthalpy and activation energy for each stage are presented in table 4.2. Fig. 4.4 shows pseudo-Voigt fits to the 40 K/min isochronal scan, from which the crystallization enthalpies were determined. Avrami exponents, determined by isothermal crystallization, are also summarized in table 4.2, where r refers to the fraction of stage crystallized.

 $Al_{85}Y_5Ni_{10}$  reaches equilibrium crystallization in three stages. The first two stages. at  $T_1$  and  $T_2$ , produce  $\alpha$ -Al, with an apparently negligible change in crystal grain size (in addition, the second stage nucleates a relatively smaller amount of what will be identified below as an  $Al_4YNi$  phase-variant). This indicates that the first two stages

Cryst.	Al lattice	Al grain	Main & shoulder amorphous peak	$\bar{\chi}^2$
stage	parameter (Å)	size (Å)	intensity, position $(I_{max}, 2\theta_{max})$	
1	4.04619	$166 \pm 42$	237(38.3°), 65.7(44.74°)	2.79
2	4.04179	$138 \pm 51$	180.7(37.3°), 63.6(44°)	6.38
3	4.03821	$164 \pm 11$	-	33.98

Table 4.1: Al lattice parameter, crystal grain size, main and shoulder amorphous peak intensity and positions, and goodness of fit  $\bar{\chi}^2$  from X-ray diffraction of Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> crystallization stages.



Figure 4.2: X-ray diffraction of Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> at each crystallization stage.

represent separate Al segregation events. TEM images support this conclusion (see Figs.4.5.a and 4.8.a). The amorphous halo in the large area diffraction in Fig.4.5.b confirms the co-existence of an amorphous matrix. The average crystal grain size calculated from Bragg peak broadening (table 4.1) are in relatively good agreement with TEM images (Fig.4.5c). Isothermal DSC analysis reveals that the first stage is a pure growth process (see Fig.4.6.a). The presence of a broad peak for the first stage in the isochronal DSC scan also supports this conclusion. X-ray diffraction of isothermally annealed first stage (Fig.4.7.a) shows only Al pure growth. Hence it



Figure 4.3: Fits of  $Al_{85}Y_5Ni_{10}$  X-ray diffraction data corresponding to the different stages from table 4.1. (a) first stage, (b) second stage.

appears that the as-made glass contains quenched-in nucleating centers, most likely made of Al. The Al lattice constant for the first stage crystallization is less than for pure Al, however this discrepancy is just outside the fitting error bar (see Appendix 3 for details). The decrease is not likely genuine, as it can only be explained by Ni substitution at Al sites, and the miscibility limit of Ni in Al is 0.1% at eutectic temperature and a maximum of 7.7% in rapidly quenched Al rich glasses. As expected, only a fractional (i.e. < 1) Avrami exponent can fit the isothermal pure growth curve.

Cryst.	Cryst.	Enthalpy	Activ.	Avrami
stage	Temp.	(kJ/mol)	Energy	Exponent(s)
	(K)		(eV)	
I	508	0.954	1.89	< 1
2	612.6	1.567	2.76	< 1, 2.84, 3.37
3	643.5	1.6663	2.32	$4.54 \ (0.02 < x < 0.13)$
				$5.2 \ (0.13 < x < 0.63)$

Table 4.2: Crystallization temperature (at 40 K/min heating rate), enthalpy, activation energy and Avrami exponent for each crystallization stage of Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub>. x is the fraction of stage crystallized.



Figure 4.4: Pseudo-Voigt fits (solid line) to isochronal 40 K/min DSC scan (dotted line) of Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub>.

Greer et al. [36] have claimed to detect a small nucleation peak at the first stage, if the annealing temperature is approached at a rapid heating rate. However, reproduction of their annealing technique has revealed that what appears as a small nucleation peak is in fact the combination of the pure growth peak with a power spike artefact (due to the sudden change in heating rate from 400 to 0 K/min as the annealing temperature is reached). This artefact was discussed in chapter 3.

Isochronally heating a glass after first stage annealing gives a scan where there still remains a broad first stage exothermic peak, but at a higher first stage crystallization temperature  $T_{x_1}$  and with less enthalpy (see Fig.4.6.b). This indicates that the first stage growth of Al crystals is a dynamic process: isothermally, the mobility of Al atoms in the amorphous matrix is governed by a diffusion coefficient, leading to some level of efficiency for Al atoms to travel across the amorphous matrix, happening upon a quenched-in Al-crystal, and then overcoming the interfacial barrier and bonding to its crystalline structure. Growth of these crystals will not assist the transformation process, because segregating some Al out of the matrix reduces the mobility of the remaining amorphous state Al atoms (this is why  $T_{x_1}$  is higher after annealing). The required diffusive ability for more pure growth now requires a





Figure 4.5: TEM images of first stage crystallization in  $Al_{85}Y_5Ni_{10}$ . (a) Al crystals co-existing with amorphous matrix; (b) large area diffraction gives  $\alpha$ -Al Debye Scherrer rings and amorphous halo; (c) average Al crystal grain size of  $5 - 10 \ nm$ .

higher temperature, and this is why isochronal scans, done after an anneal prior to first crystallization stage, have a higher  $T_{x_1}$ . Hence the isothermal process of first stage Al crystal growth is limited by a dynamically decreasing diffusion coefficient. When heating an as-quenched glass at a constant rate, the ever-increasing temperature versus the dynamically increasing difficulty of moving through the Al-drained



Figure 4.6: Isothermal annealing of  $Al_{85}Y_5Ni_{10}$ . (a) Annealing at temperatures prior to first and second stage crystallization onset; (b) isochronal scan of a glass after it has undergone these anneals.



Figure 4.7: (a) X-ray diffraction of glass after first, second and third stage isothermal anneals. (b) Avrami plot of third stage crystallization, showing change in slope during different amounts of total fraction crystallization, x.

matrix results in a net greater diffusive ability, until the matrix is drained of a critical amount of Al, and the exothermic reaction trails off, not to resume for approximately another 100 K, where a new, independent Al crystallization stage occurs.

The interesting point to note is that at heating rates as high as 160 K/min, there

still remains a well defined temperature difference of about 100 K between the first and second crystallization stages. This indicates that after the first stage, the matrix is drained of excess Al to a point where the mobility of Al atoms in the amorphous phase comes to an effective halt. The activation energy for further transformation should therefore be significantly higher, and this is verified by the experimentally determined activation energies for the first versus second stages. The as-quenched Al nucleating centers may therefore be considered catalysts which lower the activation barrier, but the process of first stage transformation dynamically raises that barrier again (due to the heavy Al-depletion of the amorphous matrix).

At the second crystallization stage, isothermal analysis indicates the presence of *both* pure growth and nucleation and growth. In fact, as Fig. 4.6.a shows, there are at least two nucleation peaks occurring at the second stage. The possibility of one of them being an artefact is ruled out since both occur after a finite anneal time. The second nucleation peak is believed to be crystallization of a small amount of Al<sub>4</sub>YNi-variant phase (this phase is discussed below in third stage crystallization analysis). At this higher temperature the Al-drained matrix now has sufficient activation energy to segregate more Al from the system. But, this causes a critical breakdown of the amorphous matrix. Hence, while some of the now mobile Al atoms contribute to pure growth of the first stage crystals, *most* Al atoms combine with newly nucleating centers. TEM imaging (see Fig.4.8.a) and X-ray diffraction (see table 4.1) determined no perceptible difference between grain sizes of crystals from the first versus second stage, supporting the idea that most Al atoms liberated at the second stage form new crystals.

As a result of this critical matrix breakdown, the Al<sub>4</sub>YNi-variant phase nucleates in a relatively much smaller amount. This is evidenced by very broad peaks in second stage diffraction scans (see Fig.4.7.a), which don't correspond to  $\alpha$ -Al, and TEM imaging of this stage doesn't show any crystals morphologically differing from  $\alpha$ -Al. An attempt was made to fit the isothermal second stage peaks in Fig.4.6.a, in order to determine the Avrami exponents. The error associated with such a fit





Figure 4.8: TEM images of second stage crystallization in  $Al_{85}Y_5Ni_{10}$ . (a) Al crystals co-existing with very little amorphous matrix; (b) large area diffraction gives less intense amorphous halo.

is discussed in Appendix 3. Fitted Avrami exponent values were 2.84 and 3.37 for the two nucleation peaks, with corresponding time constants of 284 s and 258 s. The Avrami exponents, for a diffusion controlled process, indicate arbitrary shaped crystallites growing with an *increasing* nucleation rate. This confirms the idea that many Al nuclei form at the second stage, as evidenced by TEM images (see Fig.4.8.a). The increase in isochronal enthalpy of the second stage versus the first also indicates

that a much larger number of Al nuclei form at the second stage. Fig.4.8.b shows a large area diffraction, where the presence of a weaker amorphous halo (in comparison to first stage crystallization, Fig.4.5.b) confirms alongside X-ray fitting (see Fig.4.3 and amorphous peak intensities in table 4.1) the existence of an amorphous matrix which is decreasing at each successive crystallization stage.



Figure 4.9: Equilibrium crystal phases of (a)  $Al_{85}Y_5Ni_{10}$  and (b)  $Al_{85}Y_3Ni_{12}$ . The phase labeled "unknown" is suggested to be an  $Al_4$ YNi-variant. Most small sized peaks above  $2\theta = 50^\circ$  are not indexed due to artefact Bragg peaks (see Appendix 3 for artefact discussion).

The third crystallization stage presents interesting results both from an isochronal and isothermal perspective. X-ray diffraction of the third stage reveals the presence of three phases:  $\alpha$ -Al, Al<sub>3</sub>Ni and an indeterminate phase (see Fig. 4.9.a). The presence of Al<sub>3</sub>Ni is unambiguously clear in the equilibrium crystallization of Al<sub>85</sub>Y<sub>3</sub>Ni<sub>12</sub> (see Fig. 4.9.b, Bragg peaks between 20° < 2 $\theta$  < 30°, 40° < 2 $\theta$  < 50°), and comparison against Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> shows that the indeterminate phase is present in a relatively *lower* amount. The aforementioned phase diagram suggests the equilibrium phases of Al<sub>85</sub>Y<sub>3</sub>Ni<sub>12</sub> and Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> to be  $\alpha$ -Al, Al<sub>3</sub>Ni, Al<sub>16</sub>YNi<sub>3</sub> and  $\alpha$ -Al, Al<sub>4</sub>YNi, Al<sub>16</sub>YNi<sub>3</sub>, respectively. During the course of establishing this phase diagram, Rykhal et al. [4] discovered Al<sub>16</sub>YNi<sub>3</sub> and identified its Bragg peaks on the equilibrium crystallization diffraction plot of Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub> (see Fig.4.39). Al<sub>16</sub>YNi<sub>3</sub> is orthorhombic and differs in lattice constants from  $Al_4YNi$  only along the c-axis by an approximate factor of 4. Hence  $Al_{16}YNi_3$  appears to be a stacking variant of  $Al_4YNi_5$ , yet their diffraction peaks noticeably differ. The indeterminate phase in the equilibrium diffraction plots of both Al<sub>85</sub>Y<sub>3</sub>Ni<sub>12</sub> and Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> has characteristics of both Al<sub>4</sub>YNi (peaks on either side of the Al-(111) peak, the low angle peak higher in intensity than the high angle one) and Al<sub>16</sub>YNi<sub>3</sub> (peaks at  $2\theta = 30.58^\circ, 36.03^\circ$ ). The telling absence of the Al<sub>4</sub>YNi low angle Bragg peak at  $2\theta = 11.46^{\circ}$  suggests that this unknown phase may be a stacking variant of  $Al_4YNi$ , different from  $Al_{16}YNi_3$ . It may be that this structure forms as a result of our approach to equilibrium from metastability: the segregation of a notable amount of Al atoms may give Y a dominant role in establishing the stacking order of Al<sub>4</sub>YNi. The fact that  $Al_{85}Y_3Ni_{12}$  and  $Al_{85}Y_5Ni_{10}$  have this third phase and  $Al_3Ni_4$ . while being on opposing sides of the Al-Al<sub>16</sub>YNi<sub>3</sub> tie-line, may be explained by Alsegregation as well. The resulting Al-depleted matrix of  $Al_{85}Y_3Ni_{12}$  and  $Al_{85}Y_5Ni_{10}$ may cross or may sit on this tie-line (see Fig.4.1). Attempts to heat isochronally or isothermally just into the third crystallization stage have been unable to establish the order of crystallization of the unknown and Al<sub>3</sub>Ni phases. Hence the process may be eutectic or two very closely occurring primary crystallizations. It is certain however that at least two phases are forming at the third stage since the diffraction plots of equilibrium Al<sub>85</sub>Y<sub>3</sub>Ni<sub>12</sub> versus Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> show a slight difference in the relative intensities of the Al<sub>3</sub>Ni and remaining (excluding  $\alpha$ -Al) Bragg peaks.

Isothermal annealing just prior to the second stage reveals something interesting: at the same annealing temperature (579 K), a nucleation and growth peak, representing third stage transformation, is observed over the course of a one hour anneal (see Fig. 4.6.a, crystallization product in Fig.4.7.a). The second stage crystallization of Al leaves behind a less metastable amorphous matrix, hence the second stage annealing temperature is now high enough to break down this matrix. This explains the adjacency of second and third stage isochronal exothermic peaks. This has also been verified by performing an isochronal scan on a glass which has been annealed past the second stage and then cooled to room temperature. The resulting plot shows a reduced third stage crystallization temperature of 629.15 K and an enthalpy of 1.611 kJ/mol (see Fig.4.6.b), which is equal to the third stage isochronally measured enthalpy (when the glass is directly crystallized up to equilibrium at a constant heating rate in one shot). A  $ln(ln(\frac{1}{1-r}))$  versus ln(t) graph gives a line with changing slope (see Fig.4.7.b), giving Avrami exponents which noticeably change with fraction crystallized (see table 4.2). The high third stage values for the Avrami exponents occur in explosive transformation processes, which is believed not to be the case here since annealing at appropriately lower temperatures smoothes out the nucleation and growth peak over a larger time span. Such high Avrami exponents during the bulk crystallization fraction can only be indicative of the overlap of two separate nucleation and growth peaks, representing the formation of Al<sub>3</sub>Ni and the Al<sub>4</sub>YNi stacking-variant phase. Hence the processes are individually primary, not eutectic.

### Summary of $Al_{85}Y_5Ni_{10}$ Crystallization:

Stage	Isochronal Product	Comments
1	glass + $\alpha$ -Al	diffusion controlled, primary pure growth
2	glass + $\alpha$ -Al + Al <sub>4</sub> YNi-variant	2 primary nucleation (diffusion controlled.
		increasing nucleation rate) & pure growth
3	$\alpha$ -Al + Al <sub>3</sub> Ni + Al <sub>4</sub> YNi-variant	2 primary nucleation

- isochronal and isothermal crystallization product are in agreement for all stages
- quenched-in Al nanocrystal stabilize the amorphous matrix at first stage
- 2nd and 3rd stage nucleate (isothermal) at the same annealing temperature

## 4.3 Al<sub>85.5</sub> Y<sub>7</sub>Ni<sub>7.5</sub>

Fig.4.10 shows X-ray diffraction plots of the glass and each crystallization stage in Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub>; each crystallization stage corresponds to heating the glass at 40 K/min to just past a corresponding exothermic peak. Al lattice parameter, grain size, main and shoulder amorphous peak maxima, their positions and goodness-of-fit  $\bar{\chi}^2$  are presented in table 4.3 and Fig.4.11. Once more calculated strain on Al-crystals is negligible. Crystallization temperature (at 40 K/min isochronal scan), enthalpy and activation energy for each stage are presented in table 4.4. Fig. 4.12 shows the pseudo-


Figure 4.10: X-ray diffraction of  $Al_{85.5}Y_7Ni_{7.5}$  at each crystallization stage.

Voigt fits to the 40 K/min isochronal scan, from which the crystallization enthalpies were determined. Avrami exponents, determined by isothermal crystallization, are also summarized in table 4.4.

Unlike  $Al_{85}Y_5Ni_{10}$ ,  $Al_{85.5}Y_7Ni_{7.5}$  reaches equilibrium crystallization in four stages. The first two stages produce once more  $\alpha$ -Al. However, with this composition Bragg peak fits indicate a marked increase in Al crystal grain size between these two stages. DSC isochronal scan (Fig.4.10) shows that the first and second stages have the same characteristics as  $Al_{85}Y_5Ni_{10}$ , namely a broad primary peak and sharp secondary



Figure 4.11: Fits of Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> X-ray diffraction data corresponding to the different stages from table 4.3. (a) first stage, (b) second stage.

peak. While the crystallization temperatures of the second stage peaks are in close agreement between the two compositions, the first stage of  $Al_{85.5}Y_7Ni_{7.5}$  occurs at a noticeably higher temperature. The higher Y content possibly stabilizes the glassy phase, requiring a higher temperature for sufficient Al atom diffusion in order to start the pure growth process. This enhanced stability of the glass becomes obvious at higher heating rates, where a very weak glass transition is resolved from the first DSC peak (see Fig.4.14.a). In comparison to an Y-richer composition like  $Al_{84.5}Y_{8.5}Ni_7$  (see table 4.6), the activation energy for this glass transition is consis-

Cryst.	Al lattice	Al grain	Main & shoulder amorphous peak	$\bar{\chi}^2$
stage	parameter (Å)	size (Å)	intensity, position $(I_{max}, 2\theta_{max})$	
1	4.04483	$93 \pm 3$	171.6(37.88°), 11.1(45.2°)	4.25
2	4.0512	$143 \pm 47$	$210.3(37.03_{\circ}), 34.8(43.91^{\circ})$	4.01
3	4.04483	$214 \pm 114$	-	19.68
4	4.04163	-	-	32.780060

Table 4.3: Al lattice parameter, crystal grain size, main and shoulder amorphous peak intensity and position, and goodness-of-fit  $\bar{\chi}^2$  from X-ray diffraction of Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> crystallization stages.



Figure 4.12: Pseudo-Voigt fits (solid line) to isochronal 40 K/min DSC scan (dotted line) of Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub>.

Cryst.	Cryst.	Enthalpy	Activ.	Avrami
stage	Temp.	(kJ/mol)	Energy	Exponent
	(K)		(eV)	
T <sub>g</sub>	-	-	2.91	< 1
1	525.1	0.889	2.81	2.66 $(0 < x < 0.2)$
				$6.31 \ (0.2 < x < 0.89)$
				$3.28 \ (0.89 < x < 1.0)$
2	607.6	2.11	3.38	$2.34 \ (0 < x < 0.13)$
				$5.27 \ (0.13 < x < 0.81)$
				$3.57 \ (0.81 < x < 1.0)$
3	650.8	1.267	2.44	2.61 ( $0 < x < 0.81$ )
				$3.75 \ (0.81 < x < 1.0)$
4	763.4	0.214	1.89	-

Table 4.4: Crystallization temperature (at 40 K/min heating rate), enthalpy, activation energy and Avrami exponent for each crystallization stage of Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub>. x is the fraction stage crystallized.

tently smaller. The higher first stage enthalpy of  $1.142 \ kJ/mol$  at higher heating rate indicates that this glass transition is buried in the primary peak of the 40 K/minscan, hence the peak's measured enthalpy is an underestimate. Therefore, in comparison to Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub>, first stage crystallization has a higher enthalpy, and comparing grain sizes, this higher enthalpy implies more Al nuclei at the first stage, as opposed to larger sized nuclei. Isothermal analysis at the first stage gives a pure growth curve (see Fig.4.13.a), supporting the idea of quenched-in Al nucleating centers. However, the presence of a buried glass transition is a very interesting discovery: a portion of the materials science community defines glasses as materials exhibiting glass transitions, with the idea that the glass will be a homogeneous mix of its constituent atoms. However, for this composition, in spite of the quenched-in Al nuclei, a glass transition is observed at high isochronal heating rates.

Isochronally scanning the glass after annealing (Fig.4.13.b) at the first stage produced the same conclusions as with the  $Al_{85}Y_5Ni_{10}$  glass: higher stage crystallization temperatures and enthalpies remain constant. For these two glasses, isochronal and isothermal processes are consistent, hence there is no critical competition between the thermodynamic driving force and diffusion. X-ray diffraction of glasses annealed at these two stages support this conclusion (see Fig.4.17.a).

Compared to  $Al_{85}Y_5Ni_{10}$ , the second stage occurs at a slightly lower temperature and has a higher enthalpy. A notable increase in crystal grain size is observed from Bragg peak fitting. The grain size is comparable to that of the second stage in  $Al_{85}Y_5Ni_{10}$ . The activation energy is consistently higher for the second stage compared to the first. Table 4.4 shows the Avrami exponents computed for the different stages. The exponent for the second stage changes with time, indicative of a multiple nucleation process. Similar to  $Al_{85}Y_5Ni_{10}$ , the crystallization product at this stage is  $\alpha$ -Al and a very small amount of what has been labeled an  $\alpha$ -Al<sub>3</sub>Y-variant phase (see below for details). Once more, isothermal and isochronal crystallization product are consistent (see Fig.4.17.a).

The higher temperature of the third stage, relative to Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub>, indicates the



Figure 4.13: Isothermal annealing of  $Al_{85.5}Y_7Ni_{7.5}$ . (a) Annealing at temperatures prior to first and second stage crystallization onset; (b) isochronal scan of a glass after it has undergone these anneals.



Figure 4.14: (a) Heating  $Al_{85.5}Y_7Ni_{7.5}$  at 160 K/min resolves a glass transition prior to the first stage exothermic peak; (b) annealing second stage at different temperatures modifies isothermal time constant, leading to "explosive" looking peaks.

amorphous matrix of the two glasses may differ at this point, and this is verified by the difference in crystallization products (see Fig.4.15.a). The sum of third and fourth stage enthalpies differs distinctly from the  $Al_{85}Y_5Ni_{10}$  third stage enthalpy, also indicating a deviation in crystallization product. The third stage products have peaks



Figure 4.15: Crystal phases of Al<sub>85.5</sub>Y<sub>7.5</sub>Ni<sub>7</sub> at (a) third stage (relative intensities of unlabeled peaks have  $\alpha$ -Al<sub>3</sub>Y pattern, but  $2\theta$  positions do not match), (b) fourth (equilibrium) stage.

characteristic of  $\alpha$ -Al<sub>3</sub>Y, however the discrepancy in Bragg peak locations corresponds to a d-spacing deviation of anywhere from 9% and 3.7%. This is too large a structural strain to be realistically possible; also, the discrepancy is due to an expansive strain, something which can not be explained by  $\alpha$ -Al<sub>3</sub>Y(Ni). However the high temperature conjugate,  $\beta$ -Al<sub>3</sub>Y, is part of the fourth stage crystallization product. Hence this third stage phase has been labeled as an  $\alpha$ -Al<sub>3</sub>Y-variant. The asymmetric broadening on the low angle side of the  $2\theta = 36.8^{\circ}$  peak and a small peak at  $2\theta = 22.9^{\circ}$  suggest a small amount of Al<sub>16</sub>YNi<sub>3</sub> may have crystallized at the third stage as well. The presence of two crystallization products at this stage is proved by isothermal analysis (discussed below). Isochronal and isothermal crystallization product are in agreement (see Fig.4.16.b).

The lower activation energy of the third stage, compared to the second stage, indicates the heavily Al-depleted amorphous matrix, which is left after second stage crystallization, is a relatively less stable glass. While this may sound initially counterintuitive (since glasses with relatively lower Al versus Y content seem to be better glass formers), it indicates there exists a lower critical Al content, below which is more favorable for the matrix to break down into stoichiometric compositions. This stability observation is consistent with the third crystallization stage of Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub>. In fact, as Fig.4.14.b demonstrates, annealing prior to the second stage is sufficient to activate the third stage product as well. Fig.4.14.b also shows what appears to be an explosive response in second stage nucleation, for annealing at 575 K. This should not be confused with genuine explosive nucleation (characterized by Avrami exponents as high as 9), since annealing 5 K earlier has a marked affect on the nucleation peak profile. This dependence of nucleation peak profile on annealing temperature is due to the isothermal time constant's dependence on temperature. X-ray diffraction seems to indicate that after the third stage there is none or very little amorphous matrix left. The abnormal increase of second stage main and shoulder amorphous peaks in X-ray diffraction reflects the presence of broad Bragg peaks associated with the nucleation of a second crystal phase. Indeed, the distended shape of the isothermal crystallization peak on the later times side (see Fig.4.14.b) strongly indicates two phases are indeed nucleating, the second in a smaller quantity than the first. This second nucleating phase may be the small amount of Al<sub>16</sub>YNi<sub>3</sub>. X-ray diffraction of an isothermal anneal past the third stage gives the same crystallization product (see Fig.4.16.b). A corresponding Avrami plot (see Fig.4.17.b) shows two fractional crystallization regimes where the exponent non-negligibly changes, indicative of multiple peak overlap. In both cases, the exponent is indicative of an increasing nucleation rate in a diffusion controlled process.

In diffraction scans past the fourth crystallization stage, the  $\alpha$ -Al<sub>3</sub>Y-variant has disappeared and  $\beta$ -Al<sub>3</sub>Y grows, and there is a greater portion of Al<sub>16</sub>YNi<sub>3</sub> (see Fig.4.15.b).

Equilibrium products are thus  $\alpha$ -Al,  $\beta$ -Al<sub>3</sub>Y and Al<sub>16</sub>YNi<sub>3</sub>. In the context of the Al-Y-Ni phase diagram, it seems the earlier segregation of Al from the matrix during the first two stages moved the remaining amorphous matrix composition across the Al-Al<sub>4</sub>YNi tie-line. However, Al<sub>4</sub>YNi is not one of the equilibrium phases, rather Al<sub>16</sub>YNi<sub>3</sub> is. This point will be elaborated upon in the next section. Isothermal analysis of the fourth stage proved inconclusive; a broad monotonically increasing DSC



Figure 4.16: (a) Isothermal annealing of  $Al_{85.5}Y_7Ni_{7.5}$  at third and fourth stage. Third stage peak is an overlap of two nucleation peaks. (b) Corresponding X-ray diffraction of annealed crystalline product.



Figure 4.17: (a) X-ray diffraction of  $Al_{85.5}Y_7Ni_{7.5}$  glass after annealing at first and second stage. (b) Avrami plot of third stage crystallization, showing change in slope during different stages of total fraction crystallized, x.

scan is obtained (see Fig.4.16.a), which does not crest even after two hours of annealing. Isothermal crystallization product remains consistent to isochronal product (see Fig.4.16.b). The activation energy for this stage is the lowest amongst all the stages. Summary of Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> Crystallization:

Stage	Isochronal Product	Comments
1	glass + $\alpha$ -Al	diffusion controlled, primary, pure growth
2	glass + $\alpha$ -Al + $\alpha$ -Al <sub>3</sub> Y-variant	2 primary nucleation
3	$\alpha$ -Al + $\alpha$ -Al <sub>3</sub> Y-variant + Al <sub>16</sub> YNi <sub>3</sub>	2 primary nucleation
4	$\alpha$ -Al + $\beta$ -Al <sub>3</sub> Y + Al <sub>16</sub> YNi <sub>3</sub>	indeterminate

- isochronal and isothermal crystallization product in agreement for all stages
- quenched-in Al nanocrystal stabilize the amorphous matrix at first stage
- glass transition co-exists with quenched-in Al nanocrystals
- 2nd and 3rd stage nucleate (isothermal) at the same annealing temperature

# 4.4 $Al_{84.5}Y_{8.5}Ni_7$

Fig.4.18 shows X-ray diffraction plots of the glass and each crystallization stage in Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub>; each crystallization stage corresponds to heating the glass at 40 K/min to just past a corresponding exothermic peak. Al lattice parameter, grain size, main and shoulder amorphous peak maxima, their positions and goodness of fit  $\bar{\chi}^2$  are presented in table 4.5. Once more, calculated Al crystal strain was found to be negligible. Crystallization temperature (at 40 K/min isochronal scan), enthalpy and activation energy for each stage are presented in table 4.6. Fig. 4.19 shows the pseudo-Voigt fits to the 40 K/min isochronal scan from which the crystallization enthalpies were determined. Avrami exponents, determined by isothermal crystallization, are summarized in table 4.6.

Cryst.	Al lattice	Al grain	Main & shoulder amorphous peak	$\bar{\chi}^2$
stage	parameter (Å)	size (Å)	intensity, position $(I_{max}, 2\theta_{max})$	
1	4.04993	$127 \pm 88$	175.9 (37.42°), 13.4 (44.95°)	4.63
2	4.04638	112 ± 19	211.7 (36.8°), 36.5 (43.35°)	6.641461
3	4.04272	$182 \pm 95$	-	28.9
4	4.05406	-	-	9.11

Table 4.5: Al lattice parameter, crystal grain size, main and shoulder amorphous peak intensity and position, and goodness of fit  $\bar{\chi}^2$  from X-ray diffraction of Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> crystallization stages.



Figure 4.18: X-ray diffraction of Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> at each crystallization stage.

 $Al_{84.5}Y_{8.5}Ni_7$  reaches equilibrium crystallization in four stages. At the onset of the first stage there is now a clearly defined glass transition, one which is observable even at heating rates as low as 10 K/min. The stability of this transition is evident by its high activation energy (in comparison to first stage activation energy of  $Al_{85.5}Y_7Ni_{7.5}$ ). The first stage crystallization temperature is consistently higher, supporting the picture of a very stable glass structure (already implied by the presence of a glass transition). First stage enthalpy is significantly higher than the first stage of  $Al_{85.5}Y_7Ni_{7.5}$ , however the sum of first and second stage enthalpies of the two



Figure 4.19: Pseudo-Voigt fits (solid line) to isochronal 40 K/min DSC scan (dotted line) of Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub>.

compositions is approximately the same, and the crystallization product is in large majority Al: at the end of the second stage, roughly the same amount of Al therefore has segregated from the amorphous matrix in both compositions. Second stage

Cryst.	Cryst.	Enthalpy	Activ.	Avrami
stage	Temp.	(kJ/mol)	Energy	Exponent
	( <i>K</i> )		(eV)	
T <sub>g</sub>	538	-	5.53	
1	563.2	1.642	3.06	$2.29 \ (0.01 < x < 0.42)$
				$1.35 \ (0.42 < x < 0.93)$
2	611.8	1.715	2.31	*2.6 $(0 < x < 0.93)$
				** $3.01 \ (0.13 < x < 0.81)$
3	656.4	1.259	2.31	$2.58 \ (0 < x < 0.89)$
4	751	0.601	2.62	-

Table 4.6: Crystallization temperature (at 40 K/min heating rate), enthalpy, activation energy and Avrami exponent for each crystallization stage of Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub>. x is fraction of stage crystallized. The Avrami exponents labeled with prefix \* and \*\* for second stage are determined from isothermal anneals where the annealing temperature was approached at 10 and 40 K/min, respectively.



Figure 4.20: Fits of  $Al_{84.5}Y_{8.5}Ni_7$  X-ray diffraction data corresponding to the different stages from table 4.5. (a) first stage, (b) second stage.

crystallization temperature is within 5 K of the corresponding stage temperature in  $Al_{85.5}Y_7Ni_{7.5}$ .



Figure 4.21: Isothermal annealing of  $Al_{84.5}Y_{8.5}Ni_7$ . (a) Annealing at temperatures prior to first and second stage crystallization onset; (b) X-ray diffraction and isochronal scan of a glass after it has undergone these anneals. Approaching the annealing temperature at slow heating rates enables the nucleation of a new phase, labeled as X phase.

Crystallization product at the first stage of  $Al_{84.5}Y_{8.5}Ni_7$  is Al grains of roughly the same or larger size as the first stage Al grains of  $Al_{85.5}Y_7Ni_{7.5}$ . The lattice con-



Figure 4.22: Isothermal annealing of  $Al_{84.5}Y_{8.5}Ni_7$ . (a) Isochronal scan after annealing at first stage. (b) X-ray diffraction after annealing at this new first crystallization stage.

stant is approximately that of pure  $\alpha$ -Al. Isothermal analysis of the first stage shows the process to be nucleation and growth (see Fig.4.21.a) where the changing Avrami exponent (with crystallization fraction) (table 4.6) indicates the process is a superposition of two nucleation peaks. Assuming a diffusion controlled process, the early crystallization is most likely an increasing nucleation rate. The second nucleation event may be a constant or decreasing nucleation, most probably due to the effects of soft impingement.

The presence of two phases at first stage is in contrast to  $Al_{85.5}Y_7Ni_{7.5}$ : this second nucleation event only appears to occur during isothermal crystallization (since first stage isochronal crystallized diffraction pattern shows only  $\alpha$ -Al). X-ray diffraction of a first stage isothermally annealed glass indeed shows a novel development:  $\alpha$ -Al has crystallized, but so has an additional phase (see Fig.4.21.b). This is a fascinating new development: the absence of quenched-in nucleating centers has a notable effect on the competition between diffusion and the thermodynamic driving force. While the thermodynamic driving force still has the tendency to form Al crystals, constant temperature annealing opens the possibility via enhanced (due to the glass transition) atomic diffusion for the atoms to assemble into an alternate crystalline phase.

Performing an isochronal scan after this anneal *still* produces four exothermic peaks, and a notably absent glass transition (see Fig.4.22.a). The second and higher stage peaks have shifted to higher temperatures, and a new first stage peak, which itself appears to be the overlap of two peaks, appears around 608 K.

Annealing just before this anneal-altered first stage produces greater amounts of the new phase (see Fig.4.22.b), which is labeled X phase. Hence the short range order of melt-spun Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> differs sufficiently from that of Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> so that an alternate, possibly Al-Y composition is realizable a good 90 K earlier. This X phase differs significantly from the Al<sub>4</sub>YNi-variant equilibrium crystallization product of Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> glass. Isochronal crystallization of the anneal-altered stages produces an increase in the amount of Al and X phase, then the X phase transforms into the  $\alpha$ -Al<sub>3</sub>Y-variant phase at the third stage.

However, in an isochronal analysis, Al84.5Y8.5Ni7 matches Al85.5Y7Ni7.5 crystallization product at all stages. As mentioned above, at 40 K/min heating rate, second stage crystallization product is more Al and a small amount of the  $\alpha$ -Al<sub>3</sub>Y-variant. In Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> second stage activation energy is higher than first, however the converse holds true here. The very important glass transition allows for a large number of nucleation events (as evidenced by the relatively larger first stage enthalpy), significantly draining the amorphous matrix far past a possibly critical content of Al. leaving it relatively unstable (just as was discussed for Al<sub>85.5</sub>Y<sub>7.5</sub>Ni<sub>7</sub> after its second crystallization stage). What is interesting to note is that with increasing Y content, a lower amount of Al appears to crystallize, as evidenced by comparison of Al Bragg peak intensities of Al84.5 Y8.5 Ni7 versus the previous two glasses. Hence the presence of nucleating centers remains more effective than a glass transition in terms of segregating  $\alpha$ -Al from the amorphous matrix. In contrast, the quenched-in nucleation centers in  $Al_{85.5}Y_7Ni_{7.5}$  allowed for a roughly 30 K earlier first stage segregation of Al, but this segregation was pure growth, which did not increase the number of nuclei and against which the matrix was able to dynamically stabilize itself.

Isothermal analysis of the second stage confirms the presence of both a nucleation

peak and a pure growth decay (see Fig.4.21.a). But there is also a second nucleation event present, revealed by X-ray diffraction to be the X phase phase once more. An interesting observation has been made of second stage isothermal annealing: if the annealing temperature is approached at a high heating rate, the resultant anneal produces *only* Al crystallization product (see Fig.4.21.b). Hence the new phase's appearance is possibly a glass structural order lingering after the first stage, one which diffusional processes can pick up upon when approaching the annealing temperature at a slower rate. In any case, Avrami exponents derived for either heating history are indicative of increasing nucleation rate in a diffusion controlled process.



Figure 4.23: (a) Isothermal annealing of  $Al_{84.5}Y_{8.5}Ni_7$  glass at third and fourth stages. (b) X-ray diffraction after annealing.

The occurrence of third stage crystallization at approximately the same temperature in both  $Al_{84.5}Y_{8.5}Ni_7$  and  $Al_{85.5}Y_7Ni_{7.5}$  indicates both transformations must surmount relatively similar *free energy* activation barriers, and hence are subject to almost identical thermodynamic driving forces, but  $Al_{84.5}Y_{8.5}Ni_7$  nonetheless has a lower *energy* activation barrier. Third stage enthalpy of both  $Al_{84.5}Y_{8.5}Ni_7$  and  $Al_{85.5}Y_7Ni_{7.5}$  are comparable, and the crystallization product is once more  $\alpha$ -Al\_3Yvariant (see Fig.4.24.a). Intensity ratios of the  $\alpha$ -Al\_3Y-variant peak versus the  $\alpha$ -Al (111) peak indicates there is relatively more  $\alpha$ -Al\_3Y-variant in  $Al_{84.5}Y_{8.5}Ni_7$  than in



Figure 4.24: Crystal phases of Al<sub>54.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> at (a) third stage (relative intensities of unlabeled peaks have  $\alpha$ -Al<sub>3</sub>Y pattern, but  $2\theta$  positions do not match), (b) fourth (equilibrium) stage.

Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub>. Unlike the previous two compositions, isothermal annealing prior to the second stage (when the second stage is approached at 40 K/min!) very weakly resolves nucleation from third stage crystallization (see Fig.4.21.a and Fig.4.23.a). Third stage nucleation appears to be a superposition of two such peaks, in agreement with Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub>, and X-ray diffraction reveals the crystallization product to be indeed  $\alpha$ -Al<sub>3</sub>Y-variant and Al<sub>16</sub>YNi<sub>3</sub>; thus as of third stage stage crystallization the competition between diffusion and thermodynamic driving force has now turned wholly in favor of the latter. Since the nucleation peaks are superimposed the Avrami exponent has dubious physical interpretation.

Fourth stage crystallization represents the same process observed in the corresponding stage for Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub>:  $\alpha$ -Al<sub>3</sub>Y-variant transforms into  $\beta$ -Al<sub>3</sub>Y and more Al<sub>16</sub>YNi<sub>3</sub> is formed (see Fig.4.24.b). Intensity ratios of  $\beta$ -Al<sub>3</sub>Y Bragg peaks versus Al<sub>16</sub>YNi<sub>3</sub> peaks indicates there is more  $\beta$ -Al<sub>3</sub>Y than Al<sub>16</sub>YNi<sub>3</sub> in Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> crystallized glass than in Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> crystallized glass. The relatively higher fourth stage enthalpy thus indicates its contribution comes mainly from the  $\alpha$ -Al<sub>3</sub>Y-variant to  $\beta$ -Al<sub>3</sub>Y phase transformation. The significantly higher activation energy (compared to the corresponding Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> stage) indicates this transformation is energetically more costly a transformation than  $Al_{16}YNi_3$  or  $\alpha$ -Al growth. Isothermal analysis yields the same inconclusive observation as with the corresponding stage in  $Al_{85.5}Y_7Ni_{7.5}$  (see Fig.4.23).a.



Figure 4.25: Equilibrium crystallization product of Al<sub>76</sub>Y<sub>12.8</sub>Ni<sub>11.2</sub>.

Both Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> and Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> have equilibrium phases  $\alpha$ -Al,  $\beta$ -Al<sub>3</sub>Y and Al<sub>16</sub>YNi<sub>3</sub>, but not Al<sub>4</sub>YNi. As promised at the end of the previous section, we now elaborate on this observation. This suggests that perhaps on the Al-Y-Ni phase diagram, an unconfirmed tie-line exists between Al<sub>16</sub>YNi<sub>3</sub> and Al<sub>3</sub>Y. If so, equilibrium crystallization product of Al<sub>76</sub>Y<sub>12.8</sub>Ni<sub>11.2</sub> (which would be on the opposing side of this tie-line) should contain Al<sub>4</sub>YNi; it does not (see Fig.4.25). This reaffirms the earlier assertion in the Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> section, of a non-equilibrium crystallization process for the Al-Y-Ni glass. In the case of Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> and Al<sub>76</sub>Y<sub>12.8</sub>Ni<sub>11.2</sub>, this non-equilibrium process yields Al<sub>16</sub>YNi<sub>3</sub> crystallization product; in the case of Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> this process yields a stacking variation of Al<sub>4</sub>YNi, one which can possibly order at a much higher temperature.

Summary of Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> Crystallization:

Stage	Isochronal Product	Comments
1	glass + $\alpha$ -Al	diffusion controlled, primary, nucleation
		and growth of $\alpha$ -Al and X phase
2	glass + $\alpha$ -Al + $\alpha$ -Al <sub>3</sub> Y-variant	2 primary nucleation
3	$\alpha$ -Al + $\alpha$ -Al <sub>3</sub> Y-variant	2 primary nucleation
	+ Al <sub>16</sub> YNi <sub>3</sub>	
4	$\alpha$ -Al + $\beta$ -Al <sub>2</sub> Y + Al <sub>1</sub> eYNi <sub>2</sub>	indeterminate

4 | α-Al + β-Al<sub>3</sub>Y + Al<sub>16</sub>Y Ni<sub>3</sub> | indeterminate
isochronal and isothermal crystallization product are not in agreement for first
two stages: get extra X phase (see Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub> section for details about X-phase)

• strong glass transition, isochronally have *identical* crystallization product as  $Al_{85.5}Y_7Ni_{7.5}$ 

• quenched-in nucleating centers seem more effective than glass transition at segregating  $\alpha$ -Al from amorphous matrix

• 2nd and 3rd stage nucleate (isothermal) at the same annealing temperature

• Note: equilibrium crystallization product of  $Al_{76}Y_{12.8}Ni_{11.2}$  is  $\alpha$ -Al,  $\beta$ -Al<sub>3</sub>Y and  $Al_{16}YNi_3$ ; there is *no* non-equilibrium tie-line connecting  $Al_{16}YNi_3$  and  $\beta$ -Al<sub>3</sub>Y on the Al-Y-Ni phase diagram.

# 4.5 $Al_{85}Y_{10}Ni_5$

Fig.4.26 shows X-ray diffraction plots of the glass and each crystallization stage in  $Al_{85}Y_{10}Ni_5$ ; each crystallization stage corresponds to heating the glass at 40 K/min to just past a corresponding exothermic peak. Al lattice parameter, grain size and goodness-of-fit  $\bar{\chi}^2$  are presented in table 4.7. Calculated strain on Al crystals was found to be negligible. Crystallization temperature (at 40 K/min isochronal scan), enthalpy and activation energy for each stage are presented in table 4.8. Fig. 4.27.a shows the pseudo-Voigt fits to the 40 K/min isochronal scan, from which crystallization enthalpies were determined. Avrami exponents, determined by isothermal analysis, are also summarized in table 4.8.

Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub> reaches equilibrium crystallization in five stages, where the last stage



Figure 4.26: X-ray diffraction of Al85 Y10Ni5 at each crystallization stage.

occurs in a two step process. The crystallization process of this composition drastically differs from the previous three glasses studied. While glass transition onset and activation energy, first stage crystallization temperature, enthalpy and activation energy, are all comparable to those of  $Al_{84.5}Y_{8.5}Ni_7$ , the first stage crystallization product is completely different.

First stage crystallization product has  $\alpha$ -Al, but it is now co-existing with a complex structure, as evidenced by the many Bragg peaks in Fig.4.33. None of the Al-Y, Al-Y-Ni, or Al-Ni compositions in the local area of interest in the Al-Y-Ni phase dia-

gram have corresponding diffraction patterns. TEM imaging (see Fig.4.28) shows the presence of a phase, defined as the X phase, with Al crystals growing on its surface. Fig.4.28.a, imaged during the beginning of the first stage isochronal crystallization process, shows an amorphous matrix still present. Image (Fig.4.28.b), taken at the end of the first crystallization stage, shows little or no amorphous phase left. This is in stark contrast to the previous glasses, which retained an amorphous matrix at least

Cryst.	Al lattice	Al grain	$\bar{\chi}^2$
stage	parameter (Å)	size (Å)	
1	4.056	$31.2 \pm 10$	12.48
2	4.057	$44 \pm 6.2$	17.77
3	4.044	$78.9 \pm 17$	10.92
4	4.042	$172 \pm 126$	17.05
5	4.041	-	13.01
6	4.041	-	14.00

Table 4.7: Al lattice parameter, crystal grain size and goodness of fit  $\bar{\chi}^2$  for each crystallization stage X-ray diffraction plot for Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub>.

	Carlo Car			
Cryst.	Cryst.	Enthalpy	Activ.	Avrami
stage	Temp.	(eV/mol)	Energy	Exponent
	(K)		(eV)	
$T_g$	542.4	-	5.92	
1	565.5	1.865	2.96	2.3, 3.32, 2.3
2	606.1	0.433	4.18	(< 1)
3	630.2	0.488	2.32	$3.79 \ (0 < x < 0.81)$
				$3.27 \ (0.81 < x < 1.0)$
4	649.4	0.704	2.03	2.45 $(0 < x < 0.93)$
5		0.282	2.98	
6	702.7	0.127	2.53	

Table 4.8: Crystallization temperature (at 40 K/min heating rate), enthalpy, activation energy and Avrami exponent for each crystallization stage of Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub>. x is fraction of stage crystallized.



Figure 4.27: (a) Pseudo-Voigt fits (solid line) to isochronal 40 K/min DSC scan (dotted line) of Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub>. (b) Isochronal 40 K/min scan of a second melt-spun batch; mild composition fluctuation has a significant effect on amount of second stage crystallization.



Figure 4.28: TEM imaging of first stage crystallization in  $Al_{85}Y_{10}Ni_5$ . (a) Beginning of crystallization: co-existence of Al and another crystalline phase with amorphous matrix. (b) End of crystallization: little or no amorphous matrix left.

until the onset of the third crystallization stage. Selected Area Diffraction (SAD) of the X phase crystals confirms they are not  $\alpha$ -Al (see Fig.4.29). Fig.4.36.b shows an X-ray diffraction of a partially annealed first crystallization stage sample. The near negligible Al Bragg peaks confirm it is not the phase to nucleate during first stage.



Figure 4.29: Selected Area Diffraction of X phase in  $Al_{85}Y_{10}Ni_5$  first stage crystallization product. (a) FCC symmetry (Beam direction = [011]). (b) Cubic symmetry (Beam direction = [112]).



Figure 4.30: High resolution TEM of  $Al_{85}Y_{10}Ni_5$  first crystallization stage: direct evidence of stacking in the X phase. The highlighted *d*-spacing is ~ 8.9 Å.

Lattice constant fitting of  $\alpha$ -Al Bragg peaks indicate pure  $\alpha$ -Al crystals within measurement error. Fig.4.29 shows SAD of a crystalline region. The Bragg spots in Fig.4.29.a indicates an FCC symmetry and the first three d-spacings measured are 8.92 Å for (hkl) = (111), 7.725 Å for (200), and 5.462 Å for (220). For an FCC symmetry, these spacings correspond to a lattice constant of 15.42 Å. Bragg peaks generated for such a structure are superposed on the first stage X-ray diffraction plot and matching peaks are labeled in Fig.4.33. While there are many good matches between generated and experimental Bragg peaks, there are some experimental peaks which are not accounted for by the FCC structure, and most importantly, the 8.92 Å and 7.725 Å spacings, corresponding to  $2\theta$  positions of 9.9° and 11.44°, do *not* have any experimentally observed Bragg peaks. The only explanation is that TEM imaged a local region that was perhaps a more ordered X phase, while X-ray diffraction, which averages over the entire sample volume, sees overall much more of the disordered than ordered X phase.



Figure 4.31: High resolution TEM of the first crystallization stage: stacking variation may be origin of W phase (Note evolution of lattice fringe shape from cubic to non-cubic in traveling across an arbitrary row, from right to left).

Fig.4.30 is a high resolution micrograph of the X phase showing some sort of "double structure", allowing for stacking variation. The stacking of mirror image



Figure 4.32: (a) Large area electron diffraction pattern of  $Al_{85}Y_{10}Ni_5$ . (b) Dark field image of  $Al_{85}Y_{10}Ni_5$  taken using 7.7 Å reflection.

units depicted in Fig.4.30 gives a Bragg peak d-spacing of  $\sim 8.9$  Å. Restacking such mirror units back to back, instead of face to back, will introduce a different periodicity in the system. High resolution micrographs of the X phase lattice fringes does indeed show the co-existence of another phase. Traveling across a lattice row in Fig.4.31 from right to left, it appears that lattice symmetry is changing from cubic to non-cubic. This altered structure, which may be due to the above mentioned restacking scenario, is thus a structural variation of the X phase, and is identified as the W phase. Large area electron diffraction (see Fig.4.32.a) for this crystallization stage shows extra Debye-Scherrer rings whose sequence (with respect to the FCC 15.42 Å (X-phase) rings) and d-spacing ratio suggests a possible W phase to be close to a simple cubic lattice of 7.7-7.8 Å. The Debye-Scherrer rings for FCC 15.42 Å (X-phase) are quite spotty, indicative of a small amount of large crystals. In contrast, the extra Debye Scherrer rings are smooth and broad, suggesting the interpretation there are relatively many small randomly oriented W phase crystals. Dark field imaging of the early first stage crystallization product was done, selecting beam spots corresponding to the FCC 15.42 Å (X-phase) d-spacings of 7.725 Å and 8.92 Å; the resulting image was indeed the large sized crystal (see Fig.4.32.b). This confirms the X phase crystallizes

before the W phase, not vice versa, and the W phase proceeds to grow from the X phase. Fig.4.33 shows the match between data and Bragg peaks generated for an 8.2 Å simple cubic structure; there is good agreement with the peaks unaccounted for by the FCC structure. Keeping in mind the implication of a slightly deformed cubic symmetry as suggested by high resolution TEM (see Fig.4.31), we suggest the simple cubic structure as a close approximation to the W phase. The W and X phases may be stacking variations of each other, so the possibility exists that they may in fact represent order-disorder phases, respectively (for example lattice constants for phases X and W,  $a_X$  and  $a_W$ , may be related by  $a_X \approx \frac{1}{2}a_W$ ).



Figure 4.33: Match between generated Bragg peaks and first crystallization stage of  $Al_{85}Y_{10}Ni_5$ . Unidentified peaks can be due either to the FCC or simple cubic phases.

Despite the promising fit of this simple cubic structure, this does not unambigu-



Figure 4.34: (a) First stage isothermal crystallization of two different melt-spun batches of  $Al_{85}Y_{10}Ni_5$ . (b) Corresponding X-ray diffraction scans. Peaks at angles higher than  $2\theta = 45^{\circ}$  are not identified since it was not possible to differentiate between the X and W phases.

ously state whether all Bragg peaks accounted or unaccounted for by the FCC structure belong to the same phase (i.e. the X-phase). To determine if the non-FCC Bragg peaks do indeed all belong to the same phase, isothermal analysis was performed. Sure enough, Fig.4.34 ("first batch" where the annealing temperature has been approached at 10 K/min) shows a clear cut difference: isothermal anneals encourage far more growth of a particular phase, one whose Bragg peaks match our FCC structure (i.e. the X phase). In contrast, Fig.4.34 also shows isothermal anneals done on a second, separate melt-spun batch (one that came from a separately prepared  $Al_{85}Y_{10}Ni_5$  ingot), where the annealing temperature has been approached at 5 K/min. The corresponding Bragg peaks not associated with the FCC structure (i.e. the W-phase) have higher intensity, and in fact the relative intensity of Bragg peaks is approaching the isochronally crystallized diffraction pattern distribution. It also appears that as a function of either melt-spinning parameters, compositional fluctuation, or heating rate approach to annealing temperature, first stage isothermal crystallization is able to resolve individual nucleation peaks from the W phase and  $\alpha$ -Al phase (see Fig.4.34.a). DSC isochronal scan (see Fig.4.27.b) of the second batch

shows a more pronounced second crystallization stage (and hence relatively more Wphase). In such a situation, the crystallization fraction of the W and  $\alpha$ -Al phases, versus the X phase, increases as well. We have made the remark that the W phase is growing from the X phase; this is justified only if second stage crystallization does indeed produce more of this phase. As we will see below, this is indeed the case.



Figure 4.35: (a) Second, third and fourth crystallization stages of  $Al_{85}Y_{10}Ni_5$  all can occur at the same annealing temperature, 581 K. (b) Corresponding X-ray diffraction of crystallization product.

A second verification that indeed, FCC-fitted Bragg peaks belong to the X-phase, comes from the diffraction data of isothermal first stage crystallization of  $Al_{84.5}Y_{8.5}Ni_7$ (see Fig.4.22.b). Comparison of the X phase Bragg peaks with those of the isothermal first stage crystallization of  $Al_{84.5}Y_{8.5}Ni_7$  reveals that both are the same phase. We thus suggest that the X phase is a non-equilibrium phase whose structural template is stored in the short-range order of the glass. In  $Al_{84.5}Y_{8.5}Ni_7$ , the weakness of this order is unable to match the thermodynamic driving force in an isochronal process, however in an isothermal process atomic diffusion enables the glass to crystallize into this nonequilibrium metastable state. Successive heating of the phase has it eventually break down into the  $\alpha$ -Al<sub>3</sub>Y-variant. In  $Al_{85}Y_{10}Ni_5$ , on the other hand, the above mentioned short-range order is enhanced, so that even in an isochronal process the phase is still able to manifest itself. And of course an isothermal crystallization of this glass will



Figure 4.36: (a) Variable heating rate effect on enthalpy of second and higher crystallization stages in  $Al_{85}Y_{10}Ni_5$ . (b) X-ray diffraction of partial isothermally crystallized product indicates Al is the least crystallized quantity

again largely favor the formation of the X phase. The key to enhancing this shortrange order would seem to be the relative Al versus Y content, and this leads to our conclusions about the Al-Y-Ni glass structure in the next section.

The two individual nucleation peaks in Fig.4.34.a indicate W and  $\alpha$ -Al phase formation to be primary processes, and X phase formation may be either primary or polymorphic (X phase is probably a primary formation since it nucleated in the isothermal first stage crystallization of Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> as well). Despite their individual resolvability in isothermal scans, isochronal scans are unable to resolve the first stage peak into three individual exothermic peaks. Al grain size computed from Bragg peak broadening suggests a size distinctly smaller than that observed at the first stage of the previous glasses; TEM imaging indicates a smaller Al grain size as well.

As mentioned earlier, only High resolution TEM (HRTEM) was able to distinguish the W phase from the X phase. The W phase appears to be growing within the bulk of the X phase, in contrast to  $\alpha$ -Al which segregates to the surface. This is explained by the fact that the lattice constant fit to Bragg peaks indicates the  $\alpha$ -Al to be pure, hence any interface it shares with the X phase will be subject to great structural

stress. Free energy minimization thus dictates the Al atoms will diffuse to the X phase surface and coalesce into Al crystals there. By the same token, this means the W phase is not too dissimilar from the X phase, supporting the idea they are stacking or perhaps order-disorder variations of one another.

As mentioned earlier, both  $Al_{84.5}Y_{8.5}Ni_7$  and  $Al_{85}Y_{10}Ni_5$  have similar activation energies for glass transition and first stage crystallization. This indicates the  $Al_{84.5}Y_{8.5}Ni_7$  glass is at a very critical composition with respect to glass structure. The rate at which a transformation is pressed can either produce a glass structure breakdown similar to  $Al_{85.5}Y_7Ni_{7.5}$  or  $Al_{85}Y_{10}Ni_5$ . The activation energy for Al crystallization in  $Al_{84.5}Y_{8.5}Ni_7$  is much higher than that for initial crystallization in  $Al_{85}Y_{10}Ni_5$ . At constant temperature, the short range order in  $Al_{84.5}Y_{8.5}Ni_7$  thus opens an alternate transformation path with lower activation energy, possibly comparable to that of the first stage in  $Al_{85}Y_{10}Ni_5$ .

Avrami exponents for the first stage were determined by fitting the three first stage nucleation peaks of the 5 K/min annealing temperature approach in Fig.4.34.a. Fitted values are tabulated in table 4.8. Avrami exponents for second and third nucleation peaks, considered diffusion controlled processes, are indicative of increasing and constant nucleation rate for W and  $\alpha$ -Al phases, respectively. This makes sense as the W phase will continue to grow at the second stage crystallization (see below), while Al segregation, as discussed earlier, must diffuse through the bulk of the X phase. Being forced to nucleate on the surface of the X phase strongly suggests that the nucleation rate would be roughly constant.

While the crystallization temperature of the second stage is comparable to the corresponding stage in Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub>, enthalpies are significantly different, since different crystallization processes are at work. The second stage diffraction scan is almost identical to the first stage, except for the intensity decrease of a peak at  $2\theta = 40^{\circ}$ and intensity increase of a peak at  $2\theta = 30^{\circ}$ , corresponding to the W phase. TEM imaging of this phase shows growth of the W phase, emerging from the X-phase (see Fig.4.37.a). Fig.4.37.b is a magnification of the W phase showing stacking character



Figure 4.37: High Resolution TEM of the second crystallization stage. (a) Direct evidence of W phase pure growth (emerging from the X phase). (b) Magnification of W phase shows stacking character.

similar to that observed in Fig.4.31. This definitively supports the presence of the W phase in first stage crystallization. Isothermal analysis confirms that this is a pure growth stage (see Fig.4.35.a). Hence this confirms that the first stage large crystal imaged by TEM (and from which the FCC 15.42 Å structure was proposed) is consistently the X phase; the W phase nucleates inside the X phase (second nucleation peak in Fig.4.34) and proceeds to grow through the X phase (as we had postulated earlier on) at the second crystallization stage. Coming back to another unanswered question, second stage TEM imaging indicates Al does not segregate from the W phase, since the W phase is continuing to grow. It is more likely Al segregates from the X phase. It is clear that W phase growth seriously hinders Al segregation, as the Al (220) and (222) peaks in this glass have very low intensity, relative to the previously discussed glasses. The very large activation energy of the second stage indicates it is getting very difficult to further break down the X phase into the W phase at this point.

Annealing prior to second stage not only brings about second stage crystallization, but also third and fourth stage crystallization (see Fig.4.35.a), verified by X-ray diffraction at each annealing step (see Fig.4.35.b). Isochronal crystallization of the third stage gives X-ray diffraction peaks which indicate the W and X phase are break-



Figure 4.38: (a) Crystallization phases matching  $Al_{85}Y_{10}Ni_5$  third stage data. (b) Crystallization phases matching fourth stage data.

ing down into Al<sub>4</sub>Y and Al<sub>16</sub>YNi<sub>3</sub> (see Fig.4.38.a). The notable absence of peaks at  $2\theta = 19^{\circ}, 22^{\circ}$  indicate that the X phase is breaking down, and no peak at  $2\theta = 25^{\circ}$ , 38.6° indicates the W phase is also breaking down. The Bragg peaks at  $2\theta = 23.1^{\circ}$ , 35.5°, and 43.1° belong to Al<sub>4</sub>Y. Isothermal crystallization of the third stage is consistent. Activation energy is smaller for this stage compared to the previous stages.

During fourth stage isochronal crystallization a significant amount of  $Al_4Y$  appears, however the presence of a nucleation peak in isothermal analysis (see Fig.4.35.a)rules out the possibility of pure growth of the  $Al_4Y$  formed during third stage. The Avrami plot seems characteristic of a single phase transformation and yields an Avrami exponent of 2.45, which under diffusion controlled processes represents a constant nucleation rate.

Interestingly, at high heating rates, the enthalpies of third and fourth stage crystallizations drastically change, the former decreasing and the latter increasing (see Fig.4.36.a). This possibly indicates that at high heating rates most of the  $Al_4Y$ nucleation gets shunted to the fourth stage.

Fifth stage crystallization actually breaks into two stages (5.1, 5.2) over a broad temperature range, where in stage 5.1  $\beta$ -Al<sub>3</sub>Y has probably nucleated from Al<sub>4</sub>Y.



Figure 4.39: Equilibrium phases of crystallized Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub>.

Isothermal analysis is unable to image any nucleation and growth peak or pure growth peak above the background noise. Stage 5.1 gives the equilibrium crystallization product,  $\alpha$ -Al, $\beta$ -Al<sub>3</sub>Y and Al<sub>16</sub>YNi<sub>3</sub> see (Fig.4.39). Once again, these products do not tally with the Al-Y-Ni phase diagram. The possibility exists these are not the equilibrium crystallization products, and that at higher temperatures will finally transform the Al<sub>16</sub>YNi<sub>3</sub> phase into Al<sub>4</sub>YNi. Stage 5.2 is probably growth of Al<sub>4</sub>Y and Al<sub>16</sub>YNi<sub>3</sub>.

Summary	of	Al <sub>85</sub> \	10Ni5	Crystal	lization:
1					1

Stage	Isochronal Product	Comments
1	$X + W + \alpha$ -Al	3 nucleation peaks (X, W and $\alpha$ -Al)
2	$X + W + \alpha$ -Al	pure growth of W
3	$\alpha$ -Al + Al <sub>4</sub> Y +	2 primary nucleations
	$Al_{16}YNi_3 + X + W$	
4	$\alpha$ -Al + Al <sub>4</sub> Y + Al <sub>16</sub> YNi <sub>3</sub>	primary nucleation
5.1	$\alpha - \mathrm{Al} + \beta - \mathrm{Al}_3 \mathrm{Y} + \mathrm{Al}_{16} \mathrm{YNi}_3$	probably primary nucleation.
5.2	$\alpha - \mathrm{Al} + \beta - \mathrm{Al}_3 \mathrm{Y} + \mathrm{Al}_{16} \mathrm{YNi}_3$	pure growth?
difford	nt isochronal crystalligation n	achanism compared to provious glasses

- different isochronal crystallization mechanism compared to previous glasses
- X,W crystallize before  $\alpha$ -Al, little or no amorphous matrix left
- X phase also observed in Al84.5 Y8.5 Ni7 isothermal crystallization
- W phase is possibly stacking variant of X or they are order-disorder pair

• 2nd, 3rd and 4th stages nucleate (isothermal) at same annealing temperature

• X phase is Al(Ni,Y) FCC with 15.42 Å lattice parameter; despite low miscibility of Ni in Al, Al-Ni clustering (see next section) may allow for higher Ni content to be in the X phase

- compared to previous glasses less  $\alpha$ -Al crystallized
- equilibrium phases don't match phase diagram

# 4.6 An Interpretation of Al-Y-Ni Glass Structure

It is suggested the formation of X phase in first stage crystallization of  $Al_{85}Y_{10}Ni_5$  is close to or a polymorphic process because both W phase and Al have been established to emerge from X, and at the end of the first crystallization stage there appears no amorphous matrix to be left. This being the case, it implies that perhaps the short range order of the glass is in fact *conserved*, to some degree, during this polymorphic transformation, and is the cause of the giant, complex basis set this FCC structure seems to have. Neutron diffraction experiments [5] have established this glass as having enhanced correlations up to a radial distance of about 15 Å. The size of the X phase unit cell is about 15 Å; there may be a connection between glassy correlation and X phase unit cell size. FCC symmetry is probably established as a result of the relatively large amount of Al in this system. However, this FCC structure is unstable, and immediately orders into W (homogeneously throughout its bulk) followed by  $\alpha$ -Al (diffusing to the surface).

The glass structure proposed here for  $Al_{85}Y_{10}Ni_5$  is a random collection of glassy units, on the order of 15 Å in diameter. When this glass is cooled from the melt, liquid short range order favors formation of sub-units of (i.e. the glassy unit is made up of these sub-units) Al clustering about Y and Ni atoms, due to the high enthalpy of mixing (as computed by the Miedema model, tabulated in chapter 1) and size mismatch. Riaz et al.[16] concluded the nearest neighbor Y atoms were in fact separated by Al atoms, supporting the result of Waseda et al. [26] that Y atoms had no nearest Y neighbors in  $Al_{85}Y_{10}Ni_5$ . Hence these 15 Å glassy units may be made up of such

sub-units, or clusters, and the larger range 15 Å SRO may in fact then be due to the relative absence of Al-Ni clusters. Ni's role in such glasses has never been clearly established, other than it made a poor glass (Al-Y) into a very good glass former.

With  $Al_{85}Y_5Ni_{10}$ , the higher Ni content will produce more Al-Ni clusters, weakening some possible longer range ordering effect due to the Y or Al-Y cluster content. The result is that while the sub-units of Al clustered about Y is maintained, the larger 15 Å glassy unit now is unstable, and breaks along its sub-unit boundaries during the process of rapid cooling from the melt. The mobile atoms at these glass sub-unit boundaries would be most likely Al, which end up forming  $\alpha$ -Al nanocrystals at the sub-unit boundaries. This then would be the origin of the quenched-in Al nanocrystals in  $Al_{85}Y_5Ni_{10}$  and  $Al_{85.5}Y_7Ni_{7.5}$ .

Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> and Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> share intermediate characteristics to these two extremes. While Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> contains quenched-in nuclei, they may be either fewer in content or smaller in size (note the reduced enthalpy of first stage crystallization compared to Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub>). As a result of the competition between Al diffusion and the thermodynamic driving force, a glass transition occurs, which makes the  $\leq 15$ Å glass units soften up (i.e. Al-Y correlations cannot maintain the structure against thermal fluctuations) and start to break-up at their edges. Al atoms, thus liberated, crystallize onto the quenched-in Al nanocrystals. By contrast the Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> glass has no quenched-in Al nanocrystals. The relatively higher Y content has a net effect of maintaining the structure of the  $\leq 15$  Å glassy unit. So a glass transition is required to soften up the glass units, and Y content is still low enough to allow Al atoms to break away from sub-unit peripheries, diffuse, and combine to form  $\alpha$ -Al crystals.

The more pronounced glass transition required to break these more stable glassy units, in comparison to the glassy units of  $Al_{85.5}Y_7Ni_{7.5}$ , liberates Y (and possibly Ni) atoms from their Al-Y (Al-Ni) sub-unit, allowing crystallization of the X phase during isothermal processes. Since the X phase would be less favorable, as it requires the diffusion of atoms other than Al, it is not surprising that it is only observed

isothermally in first and second stage anneals. For  $Al_{85}Y_{10}Ni_5$ , heating up such a glass brings about a very pronounced glass transition which softens the 15 Å glassy units, but the higher Y content enables the sub-units to maintain the glass unit's integrity, and rather than Al atoms breaking away from the sub-units, the glassy units collectively agitate and settle into a 15.42 Å FCC lattice, where each unit becomes part of a crystal basis unit. Hence the basis unit retains some memory of the SRO of the glass. But this structure proves to be unstable, and immediately breaks down into W and  $\alpha$ -Al phases.

Recent work by T. Egami [18] indirectly supports such a picture of the Al-Y-Ni glass structure. The Hume-Rothery rule for alloying elements states that when their atomic sizes differ by more than 15%, crystalline solid solutions are possible over very limited composition ranges. Egami established a relationship between this size factor and the minimum solute concentration  $c_{min}^s$  required to destabilize the crystal structure:

$$c_{min}^{s} \frac{|\nu_{s} - \nu_{m}|}{\nu_{m}} = 0.1 \tag{4.1}$$

where  $\nu_s$  and  $\nu_m$  are solute and matrix (i.e. solvent) atomic volumes, respectively.

The proof of this expression stems from what Egami describes as a universal criterion for glass formation: local topological instability. Using an expression for nearest neighbors derived by a glass model of atoms with Johnson potentials, he derived an expression for the critical amount by which a solute radius must change in order to change the number of nearest neighbors by one: the local topological instability criterion. Translating this condition into an elemental solid instability (now originating from uniform expansion), Egami proceeds to establish a relation between critical volume strain and fractional atomic volume change. A formula by Eshelby [57] relates the above size factor-critical concentration product to the critical strain, for which Egami has already calculated a number by using the topological instability criterion; this in turn leads to his equation.

However, Egami's equation gives too high a critical solute concentration for Alrich glasses, compared to what has been observed experimentally (in our case as little as 15% solute renders Al glass forming, a stunning effect if one stops to think of it as 15 atoms of Y and/or Ni affecting 85 atoms of Al). Experiments have established that Al bonds covalently to transition metals TM (in our case Ni), producing an Al-TM distance less than the sum of their radii, probably due to strong hybridization of TM 3d-states with the Al 3s and 3p orbitals. Egami proposes that this strong bonding is *intact* in the liquid structure as complex aggregates, and it is these aggregates which attempt to form a crystal structure during cooling, not the individual atoms! This then requires the modification of atomic volumes in the above equation to aggregate. or *cluster*, volumes, which in turn successfully predicts critical solute concentrations of 0.15.

The experimental observation of strong Al clustering about Y atoms has established similar Al-Y clusters to exist. In fact, if 6 Al atoms cluster about an Y atom and 4 Al atoms cluster about a Ni atom, for 8 Y and 7 Ni atoms this will account for 76 Al atoms.Now the absence of Y or Ni from Al-Y-Ni gives a poorer glass former: the co-existence of the two impurities, and hence their interaction (most likely indirect as opposed to direct) is a requirement. The postulate put forth by this work is that a non-random correlation between these Al-Y and Al-Ni clusters (what we referred to also as sub-units) in turns leads to larger scale superclusters: what we have referred to as the glassy unit. Altering relative content of the 3 elements, so that more Al is left over than what is required for both the Al-Y and Al-Ni clusters, may then create pockets of Al within the supercluster or at its boundaries; this would be the origin of the quenched-in Al nanocrystals.

# 4.7 Consistency: a comparison against past findings

We now compare the results of our crystallization findings for Al-Y-Ni glasses against those of Kwong[27], Cao[28], Goyal[15], Latuch[31][32][33], Greer[35][36][37] and Chang[34].

Consistent with Goyal and the combination of Kwong and Cao's work, Sabet Sharghi et al.[16] established the variation of DSC isochronal and isothermal scans with composition. This was re-confirmed by the present work, however there are sev-
#### 4: Results and Discussion

eral key disagreements on the nature of the crystallization products. Cao claimed to observe Al<sub>3</sub>Y at second stage isochronal crystallization of Al<sub>88.5</sub>Y<sub>6.5</sub>Ni<sub>5</sub>, a glass with Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> type DSC isochronal scan. Since Cao did not include second crystallization stage and higher diffraction plots, we cannot comment on this discrepancy; we observed very broad Bragg peaks possibly belonging to an  $\alpha$ -Al<sub>3</sub>Y-variant phase. The crystallization of Al<sub>3</sub>Y at second stage may suggest that the non-equilibrium path to crystallizing is affecting by rapid quench parameters (they melt-spun in a nitrogen background). Their suggestion that this phase forms as a eutectic process with  $\alpha$ -Al is highly doubtful; no irrefutable proof has been presented. While Al<sub>3</sub>Y is one of the equilibrium crystallization products of Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> glass, Cao et al. also claim to observe the co-existence of Al<sub>3</sub>Ni. Given the phase diagram established by Rykhal et al., this seems highly unlikely. Cao was probably not aware of the Al<sub>16</sub>YNi<sub>3</sub> phase at the time. The segregation of AlYNi from  $\alpha$ -Al(Y,Ni) at third stage is highly unlikely (Cao et al. are possibly mis-labeling the Al<sub>16</sub>YNi<sub>3</sub> Bragg peaks).

Goyal et al. observed the crystallization of only  $\alpha$ -Al at the first stage of both Al<sub>83</sub>Y<sub>10</sub>Ni<sub>7</sub> and Al<sub>80</sub>Y<sub>10</sub>Ni<sub>10</sub>. This indicates the sudden transformation in crystallization product to the X phase for Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub> is sensitive the number of Al-Y versus Al-Ni clusters. Their observation of AlYNi and equilibrium Al<sub>3</sub>Ni does not make sense against Rykhal's phase diagram. Like Cao, it appears they were unaware of the Al<sub>16</sub>YNi<sub>3</sub> phase.

Both Kwong and Latuch have claimed to see a variation in the number of DSC isochronal scan exothermic peaks, with heating rate (for  $Al_{85}Y_{10}Ni_5$  glass). However, consistent with Goyal, we were unable to see any such variation: at most we saw a notable change in enthalpy between third and fourth stages at high heating rates. What is noteworthy is that the ribbons studied by Kwong and Latuch exhibit *no glass transition* effect, hence in all likelihood the actual composition of their glass was non-negligibly different from the nominal values. In a separate paper, Latuch studies a batch of  $Al_{85}Y_{10}Ni_5$  glass where now there is a glass transition, and DSC scans of another glass they study,  $Al_{82}Y_{10}Ni_8$ , matches Kwong's and Latuch's (heating rate

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variation paper) data. Hence  $Al_{82}Y_{10}Ni_8$  may be the critical heating rate dependent crystallizing glass. Consistent with Kwong, first stage crystallization produces an FCC solid solution Al phase (probably the X phase). The phase he left unidentified on this larger crystal's surface has now been established by this work as  $\alpha$ -Al. In addition to this, we have discovered the crystallization of a third (i.e. the W) phase. Long, 300-day anneals produced crystal structures with orthorhombic and hexagonal symmetry: most likely Al<sub>4</sub>YNi-variant (such as Al<sub>16</sub>YNi<sub>3</sub>) and  $\beta$ -Al<sub>3</sub>Y phases.

As already stated, the proposal of Al-Y clusters in the glass is supported by Waseda's anomalous X-ray scattering measurements. Kwong proposed such a structure as well, after concluding first stage crystallization (of  $Al_{85}Y_{10}Ni_5$ ) did not represent a polymorphous transformation. While nucleation of W and  $\alpha$ -Al are indeed primary processes, we have not concluded with certainty the type of process which nucleates the X phase. Kamiyama's claim of  $Al_3Ni$  crystals in first stage isothermal crystallization of  $Al_{85}Y_{10}Ni_5$  is inconsistent with its location on the Al-Y-Ni phase diagram and our observations. It may be W phase peaks have been mistaken for  $Al_3Ni$ .

Latuch et al. were the first group studying this system to make reference to the Al-Y-Ni phase diagram by Rykhal et al. The absence of a glass transition in  $Al_{88}Y_{10}Ni_2$  and  $Al_{82}Y_{10}Ni_8$  glasses can only corroborate with our picture of *both* Y and Ni content affecting the quality of the glass. They claim to observe  $Al_3Ni$  crystals at first stage isochronal crystallization. This is highly unlikely, given the location of glass compositions on the Al-Y-Ni phase diagram. Examination of their diffraction data suggests they have attributed some of the X phase peaks to  $Al_3Ni$ , as they claimed that this phase existed during the same stages as the X phase.

Chang et. al observed isothermal crystallization products  $Al_3Ni$  and AlYNi for a  $Al_{85}Y_{10}Ni_5$  glass; once more, these may by attributed to X,W phase Bragg peaks. We were unable to verify their claim of observing variation in DSC isochronal scans as a function of varying quench rate. It may be their actual composition differs from the nominal value, and in fact is closer to the  $Al_{82}Y_{10}Ni_8$  glass instead.

#### 4: Results and Discussion

Most crystallization product discrepancies can be attributed to lack of knowledge of the Al-Y-Ni phase diagram, or lack of knowledge of the existence of the X and W phases. We have established exhaustively by TEM studies, corroborated with X-ray diffraction of isothermally annealed glasses, the existence of the X and W phases in Y-rich glasses. The confidence we have in ultimately crystallizing to phase diagram products stems from the idea that in rapid quenching from the melt, SRO stores partial information concerning crystallization products. However, how this ordering information connects to Al-Y and Al-Ni clustering (from the melt, as proposed from Egami's theory) is a question beyond the scope of the present work. An accurate determination of partial radial density correlation functions should provide a definitive answer to such a question. The confidence in matching crystallization products against the Al-Y-Ni phase diagram also stems from the fact that it represents high temperature phases (1073 K), and we have always heated our glasses up to 820 K. We have concluded that as a result of much Al segregation in some of the glasses studied, amorphous matrix composition has the tendency to cross phase diagram tielines; but gross deviations, such as crystallization of  $Al_3Ni$  in an Y-rich glass (eg.  $Al_{85}Y_{10}Ni_5$ ), are unlikely. There is always an alternate explanation, which in our case are the X (Al solid solution) and W (stacking or ordering variant) phases.

Conclusion

5

The work presented in this thesis represents an attempt at an accurate study of both isothermal and isochronal crystallization processes in four Al-Y-Ni glasses:  $Al_{85}Y_5Ni_{10}$ ,  $Al_{85.5}Y_7Ni_{7.5}$ ,  $Al_{84.5}Y_{8.5}Ni_7$  and  $Al_{85}Y_{10}Ni_5$ .

DSC isochronal scans of these glasses break them into two groups:  $Al_{85}Y_5Ni_{10}$  and  $Al_{85.5}Y_7Ni_{7.5}$  have quenched-in nucleating centers, while  $Al_{84.5}Y_{8.5}Ni_7$  and  $Al_{85}Y_{10}Ni_5$  have glass transitions, indicative of a homogeneous glass. However, subtle complications blur the difference between  $Al_{85.5}Y_7Ni_{7.5}$  and  $Al_{84.5}Y_{8.5}Ni_7$ .

Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub> undergoes a glass transition prior to crystallizing, despite the presence of quenched-in Al nuclei which grow by pure growth at first stage crystallization. Al<sub>84.5</sub>Y<sub>8.5</sub>Ni<sub>7</sub> undergoes a glass transition followed by nucleation and growth, but its crystallization product is identical to that of Al<sub>85.5</sub>Y<sub>7</sub>Ni<sub>7.5</sub>, for each of their four isochronal crystallization steps. In contrast, Al<sub>85</sub>Y<sub>5</sub>Ni<sub>10</sub> has three crystallization stages, where the first stage is pure growth of Al, and Al<sub>85</sub>Y<sub>10</sub>Ni<sub>5</sub> has six crystallization stages, where the first stage nucleates an FCC structure with 15.42 Å lattice parameter, which proceeds to order/stack into a cubic 8.22 Å phase and break down by segregation of  $\alpha$ -Al.

Isochronal crystallization product of  $Al_{85}Y_5Ni_{10}$  is  $\alpha$ -Al for the first two stages, and  $Al_3Ni$  and an  $Al_4YNi$ -variant for the third stage. Isochronal crystallization product for both  $Al_{85.5}Y_7Ni_{7.5}$  and  $Al_{84.5}Y_{8.5}Ni_7$  are  $\alpha$ -Al at the first two stages,  $\alpha$ -Al<sub>3</sub>Y-variant at the third stage and  $\beta$ -Al<sub>3</sub>Y and  $Al_{16}YNi_3$  at the fourth stage. For  $Al_{85}Y_{10}Ni_5$  second stage crystallization is pure growth of the cubic 8.22 Å phase, third and fourth stages are the nucleation of  $Al_4Y$  and more nucleation of  $Al_4Y$  and  $Al_{16}YNi_3$  at the expense

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of the FCC 15.42 Å and cubic 8.22 Å phases. Fifth stage is believed to represent nucleation of  $\beta$ -Al<sub>3</sub>Y and Al<sub>16</sub>YNi<sub>3</sub> at the expense of Al<sub>4</sub>Y, however its signal is not resolvable above the background thermal noise. The same detection problem holds true for the sixth stage, which is believed to be pure growth of these two phases.

Quantitative analysis of crystallization steps by Avrami exponent analysis was attempted for the first time with this glass. However the multiple overlaps of nucleation and growth peaks made it impossible in most case to quantify individual phases. Despite this most transformations were estimated as being diffusion controlled primary processes with constant to increasing nucleation rates. The only exception was crystallization of the FCC 15.42 Å structure at the first stage of  $Al_{85}Y_{10}Ni_5$ : it may represent a polymorphic process.

While both isochronal and isothermal crystallization for  $Al_{85}Y_5Ni_{10}$  and  $Al_{85.5}Y_7Ni_{7.5}$ are consistent, isothermal crystallization of the first two stages of  $Al_{84.5}Y_{8.5}Ni_7$  yield both pure  $\alpha$ -Al and the FCC 15.42 Å phase. This indicates this glass' composition represents a critical value with regards to competing crystallization paths. The crystallizing of the FCC 15.42 Å phase only at constant temperature indicates the glass SRO contains the requisite information to establish this structure, but at finite heating rates Al atoms are unable to access this information, instead bonding to each other and forming  $\alpha$ -Al. This suggests the glass structure to be made up of glass units which contain this SRO and whose peripheries have a large number of Al atoms that link the neighboring glassy units.

Neutron diffraction experiments by Altounian et al. [5] clearly demonstrate such enhanced SRO, indicative of a glass unit, in  $Al_{85}Y_{10}Ni_5$  over a larger distance than in comparison with  $Al_{85}Y_5Ni_{10}$ . The FCC 15.42 Å phase which first forms at first stage crystallization of  $Al_{85}Y_{10}Ni_5$  suggests the basis set of this abnormally large FCC lattice to contain Al-Y and Al-Ni clusters, ordered according to the short-range order of the precursor glassy units.

Separate experiments by Waseda et al. [26] have led Sabet-Sharghi et al. to conclude Al atoms cluster about Y atoms in the glass. Egami's theoretical picture of

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Al-rich glasses suggests strong clustering of Al atoms about Ni atoms in the molten alloy, due to orbital bond hybridization between transition metals and Al 3s,3p orbitals. Hence the glass units may be populated by Al-Y and Al-Ni clusters, where in fact the correlation of these clusters and the relative number of Al-Y versus Al-Ni clusters establishes the enhancement of the SRO of the glass unit. If Al-Y clusters take up more Al than Al-Ni clusters (a good possibility due to higher size mis-match and enthalpy of mixing), a lower Y and higher Al content may free up an excess of Al atoms, which in turn may form quenched-in  $\alpha$ -Al nanocrystals. This then is the microstructure picture we have developed for the Al-Y-Ni glass system. Testing of this model is planned to be done eventually through determination of partial density-density correlation functions by anomalous X-ray diffraction.

# A.1 Phase Transformation Theory

# A.1.1 The Physical Process of Transformation

Gibbs distinguished the physical process of transformation as characteristic between two extreme types of atomic fluctuations: drastic rearrangements within small, localized volumes, versus small rearrangements over large volumes. The first type of fluctuation gives rise to distinct regions having different phases, and is thus termed heterogeneous. These tiny regions where a phase transformation has occurred are referred to as nucleating centers, and whether or not the entire volume of condensed material transforms into this new phase is the result of these nucleating centers having the ability to grow or not. Such transformations are referred to as first-order phase transitions, defined as crossing a phase boundary on an equilibrium phase diagram, or that  $\partial F/\partial R$  (R is a reaction coordinate, F = U - TS is the Helmholtz free energy ) is discontinuous [58] across this phase region.

The second type of fluctuation, involving minor atomic fluctuations over a large volume, implies the presence of nucleating centers with vanishingly small surface areas, and hence a vanishingly small nucleation barrier (nucleation barrier is defined in section A.1.3). But this would mean the transformation may in fact take place in all parts of the system simultaneously, and is thus termed homogeneous. With a vanishingly small or diffuse nucleation surface there is no abrupt change at the boundary between the new and old phases. Such transformations are referred to as second-order transitions, thermodynamically defined as crossing from one phase to another by way of circumventing a phase boundary on an equilibrium phase diagram, or  $\partial F/\partial R$  is continuous [58] across this phase region [44].

Take note that while it is a necessary condition for homogeneous transformations to be second-order, it is not sufficient. Further, in the study of heterogeneous transformations, the syntax suffers a bit of colloquial horseplay: nucleating centers formed at some position in a phase purely by statistical chance are referred to as *homogeneous*, whereas nucleating centers formed at the site of defects or impurities, etc, are referred to as heterogeneous.

That being said, heterogeneous transformations are composed of two broad, overlapping classes of transformation: *nucleation and growth* and what is colloquially referred to as *martensitic* reactions. Nucleation and growth processes require a thermal activation (defined in section A.1.3) and involve the diffusion of atoms across an interface boundary separating the metastable and stable phases. Martensitic reactions require *no thermal activation* and are diffusionless processes, characterized instead by cooperative motion of groups of atoms [44].

## A.1.2 Diffusing Around . . .

If we consider atoms diffusing between two parallel, say crystallographic planes[59] (identified by the index 1 and 2) by jumping across a distance d separating them, the number of A-type atoms per unit area on the two planes will be  $c_{A1}d$  and  $c_{A2}d$ , where  $c_{A1}$  and  $c_{A2}$  are the concentrations of A atoms per unit volume at the two planes. Defining the probability per unit time of an A atom making a jump from plane 1 to 2 or vice-versa as  $\pi_{A,12}$  and  $\pi_{A,21}$ , the net flow of A atoms will be

$$I_A = c_{A1} d\pi_{A,12} - c_{A2} d\pi_{A,21}. \tag{A.1}$$

It should be noted this current flow is called a *diffusion* current; the atoms are not moving in response to an external force (an applied current), but are rather acting to counter any concentration gradient, i.e. the particle analog of the first Law of Thermodynamics. Heat flow does not contribute to this equation for solids. The frequency of jumping,  $\pi$ , is dependent upon its chemical environment. In metals, the most common process of diffusion is by a mono-vacancy mechanism. For such a mechanism, if all atoms are chemically identical,  $\pi_{A,12} = \pi_{A,21} \equiv \pi_A$ . Thus the net

flow, or current density  $I_A$ , of A atoms is

$$I_{A} = \pi_{A}d(c_{A1} - c_{A2}) = -\pi_{A}d^{2}\frac{\delta c_{A}}{\delta x} = -D_{A}\frac{\delta c_{A}}{\delta x}$$
(A.2)

where the x-axis is perpendicular to planes 1 and 2. D is defined as the diffusion coefficient, and is a measure of the mobility of atoms in the system. It can be a function of lattice energies for crystal systems, and hence may be a function of time in phase transformations. The above equation is the simplest form of Fick's Law. and combining it with the continuity equation  $\frac{\delta c_A}{\delta t} = \vec{\nabla} \cdot \vec{I_A}$  we get the well-known diffusion equation

$$\frac{\delta c_A}{\delta t} = -D_A \nabla^2 c_A. \tag{A.3}$$

It should be noted the general derivation of a diffusion current equation for a system uses the free energy gradient.

# A.1.3 Approaching the Transition State

The transition state is not observed experimentally. In light of this, nucleation may be viewed as a two-step process: first, an infinitesimal amount of the initial phase must surmount part of the activation energy to form nuclei of radius less than a critical value (its Gibbs free energy will be somewhere between  $G_I$  and  $G_A^*$ ). This is the nucleation barrier and the requisite energy is the thermal activation energy for nucleation. These nuclei still face the possibility of decomposing back into the initial phase. This has been explained empirically as the result of a competition between the decrease in Gibbs free energy inside the bulk of this nuclei (as a result of phase transforming) versus the Gibbs free energy cost of the interface between these finite sized nuclei and the rest of the initial phase (in solid systems this would be due to elastic strain between the two different solid phases). For glasses, the leftover amorphous phase is referred to as the amorphous matrix, and the precipitated nucleus is referred to as a solute nucleus. Now in order for these nuclei's Gibbs free energies to reach  $G_A^*$ , the bulk energy decrease must cancel the interfacial energy increase. This cancellation will correspond to a critical-size nucleus radius, at which the nucleus is now considered an activated state. If the nucleus' radius is larger than this critical radius, the bulk free

energy gain outweighs the nucleus interface cost, and it is favorable for the nucleus to continue growing (and the bulk free energy term continues to dwarf the surface term more and more). However, there is still also a free energy cost for initial phase atoms to diffuse across (or bond to) this nucleus surface. This second activation energy, which determines whether the activated nucleus continues to grow, is referred to as the growth activation energy [42].

# A.2 More Experimental Techniques!

# A.2.1 DSC Measurement Principle

The DSC is composed of two platinum holders, referred to as the reference and sample holders (see Fig.A.1), connected to separate thermocouples which talk to each other by electronic feedback. Each platinum sample holder is in thermal contact with its own heat reservoir (a heater). The electronic feedback from the holders' thermocouples regulates the sample holder heater's power dissipation. This control loop allows the temperature of the sample holder to remain the same as that of the reference holder, for a given heating rate. This process is the defining element of the DSC, and is known as the "null-balance" principle.



Figure A.1: Schematic diagram of Perkin-Elmer DSC-2C [7]. (1) sample holder, (2) reference holder, (3) resistance thermometer, (4) heater, (5) argon inlet, (6) argon outlet, (7) aluminum body (heat sink), (8) thermometers for sample and reference, (9) heater power supplies, (10) sample confined in Al pan, and (11) reference sample.  $\Delta E$  is the enthalpy of sample phase transformation.

The reference platinum holder contains an empty Al pan and Al cover, while the sample platinum holder has an Al pan containing 5-15 mg of sample, sealed with an Al cover. The physical principle on which the DSC is based is the differing thermal responses in the two platinum holders. Whether the device is being run in isochronal

(constant heating rate) or isothermal (constant temperature) mode, during a unit of time both heat reservoirs send an equivalent amount of heat into both holders, and this process is the primary control loop. At constant sample pressure, the thermodynamic relation

$$dQ = C_p dT \tag{A.4}$$

(where dQ and dT are incremental heat flow and temperature) implies the temperatures of the two holders will change by differing amounts for the same input heat flow. This is of course due to the fact that the sample holder contains the sample as well, hence altering the net specific heat of that holder in comparison to the reference holder. The thermocouples register this temperature difference and act to minimize it by altering the heat flow to the sample holder. This is the feedback process, or secondary control loop, and it produces a non-zero unit power offset (being the difference in power dissipation between the two heaters) in DSC plots, defined as the baseline. Response time of the secondary loop has been guaranteed by Perkin-Elmer as to be sufficiently short so that both holders are effectively maintained at the same temperature at any instant in time. The vertical axis of a DSC plot is the unit power (mcal/s/mg) difference, input to the sample holder (by difference it is meant subtracting with respect to the unit power input to the reference holder); the horizontal axis represents (in the isochronal mode) the temperature of the reference holder (and thus the temperature the sample holder is brought to by thermocouple feedback), while in isothermal mode the axis represents time. Now, when the sample reaches a phase transition temperature, the reaction is either exothermic (in our case crystallization) or endothermic (glass transition). In such an instance there is a heat flow excess or deficit in the sample holder, and the secondary control loop will appropriately reduce or increase the sample heater's power, and this results in a peak deflection from the baseline; there may or may not be a change in heat capacity contribution. In most instances there is a negligible change in  $C_p$ , noted by the fact that after reaction, the DSC scan returns to almost the same baseline (see Fig.A.2). In such a case the area under any such "exothermic" or "endothermic" peaks observed in DSC plots is

proportional to the enthalpy (because of constant pressure, volume) of the reaction (i.e. the energy term in the Gibbs free energy difference between initial and final states for this given phase transformation). In the case that sample specific heat has appreciably changed during and after the reaction, a non-negligible offset occurs in baseline comparison before and after the reaction and in this case integrated peak area is not exactly proportional to the enthalpy of reaction, there is a specific heat correction to account for. In the course of our studies we did not detect any noticeable baseline shift (see Fig.A.2). Hence for our work no knowledge of heat capacity is required, and studies have established that while variations in thermal resistance might affect peak shape, it does not alter peak area (but in a DTA it does affect peak area).



Figure A.2: DSC scan where heat capacity negligibly changes after exothermic reaction  $(Al_{84.5}Y_{8.5}Ni_7)$ .

## A.2.2 Broadening of X-ray Diffraction Bragg Peaks

The Fourier transform of the electronic density of an *infinite* sized crystal lattice (is defined the Form factor) will be proportional to an infinite sum, over the lattice's

reciprocal space values  $\vec{K}$ , of delta functions. However, for a finite-sized crystal grain the intensity expression is [60]

$$I(\vec{K}) = I_{\epsilon} |F(\vec{K})|^2 C(N_1) C(N_2) C(N_3)$$
(A.5)

where

$$C(N_i) \equiv \frac{\sin^2(\frac{N_i}{2}\vec{K} \cdot \vec{a_i})}{\sin^2(\frac{1}{2}\vec{K} \cdot \vec{a_i})}.$$
(A.6)

 $\vec{a_i}$  (i = 1, 2, 3) are unit vectors spanning the crystal lattice,  $N_i$  the number of unit cells in the crystal grain along direction  $\vec{a_i}$ ,  $\vec{K} = \vec{k} - \vec{k_o}$  is the difference between incident  $\vec{k_o}$  and scattered  $\vec{k}$  wavevector, F is the form factor, and  $I_e = I_o \frac{e^4}{2m^2c^4R^2}(1 + \cos^2(2\theta))$ , where  $I_o$  is incident intensity, e and m are electron charge and mass, c is the speed of light, R is the sample-detector distance, and  $\theta = \sin^{-1}(\frac{M}{4\pi})$ . Debye expanded this expression in the neighborhood of a Bragg vector, acquiring the Gaussian approximation for peak broadening due to a finite-sized crystal system

$$I = I_e |F|^2 N^6 e^{-(Na/2)^2 (\Delta K)^2}$$
(A.7)

in the simple case where  $|\vec{a_1}| = |\vec{a_1}| \equiv |\vec{a_1}| \equiv a$  and  $N_1 = N_2 = N_3 \equiv N$ , and  $\Delta K$  is the deviation from the Bragg vector, i.e. deviation from the diffraction peak maxima.

That being said, it should be kept in mind that the Gaussian expansion is an *approximation*, and in fact more rigorous mathematical considerations suggest peak broadening due to finite crystal-size should rather produce a *Lorentzian* broadening. The gist of this argument can be put forth by making use of the convolution theorem, which states the Fourier transform F(k) of  $f(x) = g(x) \cdot h(x)$  is equal to the convolution of the Fourier transforms of g(x) and h(x),

$$F(k) = \int_{-\infty}^{\infty} G(y)H(k-y)dy.$$
 (A.8)

A finite-sized crystal system, or more importantly crystal grains, may be modeled by multiplying the scattering density for an infinite-sized system (let's call this the ideal density) by a *shape function*, defined as zero wherever the crystal grain is not present and one where it is [61]. This means the form factor is the convolution of the shape

function's Fourier transform and the ideal form factor (a sum over Bragg vectors of reciprocal-space delta functions). The shape function is effectively a complicated sort of step function, and the Fourier transform of a one-dimensional step-function (a valid approximation in a local region on the crystal grain surface) goes as  $1/k_i$ , where the *i* subscript indicates the *k*-space variable to be along the direction orthogonal to local grain surface defined by the step function. Once convolved with the Fourier transform of the scattering density, the form factor has a  $1/(k_i - K)$  dependence (K is the magnitude of the scattering vector  $\vec{K}$ ) peak broadening dependence. A mathematical accurate, and far more complicated treatment of the problem indicates a Lorentzian broadening in intensity (where  $I \propto |F|^2$ ).

The point of the last two paragraphs has been to illustrate that peak broadening due to finite crystal systems (what is called the *size effect*) can have a functional form that can pass as approximately Gaussian, and doing a Lorentzian fit will not necessarily give grossly different conclusions about crystal grain size.

The other important source to Bragg peak broadening is instrumental broadening. The effect is described by the superposition principle: X-rays emerging from different physical points on the X-ray source result (this is the most important instrumental correction) in a *multiplicity* of diffraction cones on the sample surface, thus the scattered radiation registered by the detector for a given scattering angle  $2\theta$  (wavevector q) in fact is a weighted linear combination of the multiple diffraction cones [62]

$$I_{detector}(q) = \int_{-\infty}^{\infty} g(y) I_{sample}(q-y) dy$$
(A.9)

where g(y), the weighting function, is due to the finite sized source. This correction is in fact a convolution, and there are a total of five other convolution corrections [63] whose cumulative effect can be represented as one net convolution correction. The other five convolution corrections are (2) variance in flatness of sample surface, (3) axial divergence in incident beam, (4) arbitrary sample penetration by beam prior to single scattering event, (5) receiving slit width (this is the second most important correction), and (6) correction due to subtle instrument mechanical imperfections or difficulty in synchronizing numerous alignment process variables. While corrections (2), (3) and (4) have asymmetrical effects on profile correction, they are not as important as (1) and (5); (1), (5) and for the most part (6) are *sample independent*. Thus once their correction can be determined, it can be applied to all experimentally acquired data.

## A.2.3 Goodness-of-Fit

Any of the experimental profiles which were fitted to a theoretical function were evaluated using a chi-square goodness of fit test. Such fits were done on both Xray diffraction and DSC data. This technique of fitting is known as the Maximum Likelihood Estimator. The subtlety of fitting data to a function which is characterized by parameters is that one cannot ask the question: what is the probability that a particular set of values for the fitting parameters are correct? This is because there is not a statistical universe of models to draw parameters from; there is only one physically correct model, and rather a statistical universe of data sets are drawn from it every time we make a measurement and get a data profile. The meaningful question to ask would be: given a particular set of parameters, what is the probability that the associated data profile could have occurred? This means the probability of the data for the given parameters may be considered the likelihood of the parameters, given the data. It is the maximization of this likelihood which gives the best fit [64]. Each measured data point, labeled  $y_i$  (i = 1, 2, ..., N data points)(corresponding to being associated with variable  $x_i$ ) has a measurement error independently random with a Gaussian distribution around the "true" model  $y(x_i)$ , with standard deviation  $\sigma_i$ . Then the probability of the data set is a product of the independent probabilities for each data point:

$$P_{data} \propto \prod_{i=1}^{N} \exp\left[-\frac{1}{2} \left(\frac{y_i - y(x_i)}{\sigma_i}\right)^2\right] \Delta y \tag{A.10}$$

where  $\Delta y$  is a small constant interval around  $y_i$ , where  $y_i$  and its probability distribution are continuous. Maximizing this quantity is equivalent to minimizing the negative of its logarithm, which is

$$\left[\sum_{i=1}^{N} \frac{[y_i - y(x_i)]^2}{2\sigma_i^2}\right] - N\ln(\Delta y).$$
(A.11)

Since N and  $\Delta y$  are constants, this corresponds to minimizing the quantity  $\chi^2$ , defined as

$$\chi^{2} = \sum_{i=1}^{N} \left(\frac{y_{i} - y(x_{i})}{\sigma_{i}}\right)^{2}.$$
 (A.12)

A chi-squared computer fitting program, established by Professor Mark Sutton at the McGill University Physics Department, was used to acquire a minimum  $\chi^2$  fit to experimental data. Since  $\chi^2$  obeys the chi-square distribution, it's minimum value is analytically predetermined as being equal to the number of degrees of freedom of the system, defined as the difference between the number of data points and the number of fitting parameters [64] [65]. The above-mentioned fitting program renormalizes it's chi-square value by its degree of freedom, hence the criteria for a good fit ends up simply requiring a value close to 1 with the fitting program. In fitting complicated functions to experimental data, the chi-square fitting program was used. The program operates in an iterative fashion, at each step altering initially suggested parameters (entered by us) by arbitrary amounts, hence moving off in some direction of parameter space.  $\chi^2$  is then calculated, and compared against the previous step's  $\chi^2$  value, and a now somewhat informed step is in made in parameter space. As will be mentioned in Appendix 3, metastable fitting scenarios have been encountered where the fitting program believes it has acquired a best fit, but in fact it is trapped in a locally stable region of parameter space which in fact is not the absolute minima. This underscores the grave importance of the initially suggested fitting parameter values: they must be informed guesses, not arbitrary suggestions. In cases where a simple linear fit was required, linear regression [65] was performed on the data sets, giving fit values for the straight line slope and intercept.

# A.3 Appendix 3: Error Analysis

# A.3.1 Nominal Alloy Composition



Figure A.3: Nominal composition Al85 Y7Ni8 and Al85 Y8Ni7.

As first mentioned in the Sample Preparation section, electron microprobe analysis indicated a systematic deviation in nominally prepared compositions. Y/Al content decreases/increases by approximately 0.5%, while Ni content remains close to nominal value. As such, preparing  $Al_{85}Y_8Ni_7$  and  $Al_{85}Y_7Ni_8$  nominal compositions gave microprobe determined compositions of  $Al_{85.5}Y_{7.5}Ni_7$  and  $Al_{85.5}Y_{6.5}Ni_8$ . DSC scans of such compositions are shown in Fig.A.3. These compositions have the characteristic broad first stage exothermic peak, but also manage to resolve the buried glass transition observed in  $Al_{85.5}Y_7Ni_{7.5}$  at high heating rates. In order to study two compositions close to this critical composition region, but which have strikingly different DSC scans (glass transition + sharp exothermic peak (nucleation and growth) versus broad primary peak (pure growth)), nominal compositions of  $Al_{84.5}Y_{8.5}Ni_7$  and  $Al_{85.5}Y_7Ni_{7.5}$  were prepared and studied.



Figure A.4: (a) DSC scan of zinc at different heating rates gives thermal lag. (b) X-ray diffraction of Al standard, artifact peaks are due to  $Cu-K\beta_1$ , W-L $\alpha_1$  radiation.

# A.3.2 Standards for DSC and X-ray Diffraction

## A.3.3 DSC: Isochronal Error Analysis

Crystallization and glass transition onset temperatures were measured using DSC- 2C computer software, however the exothermic peak areas, corresponding to enthalpy of crystallization, were measured both by DSC-2C software and by fitting the peaks with pseudo-Voigt functions (then measuring the area under these fitted peaks). The reason for this is that the individual stage exothermic peaks were never quite independent of each other, i.e. there was non-negligible overlap between neighboring exothermic peaks, and doing a simple area integration of the data under a specified temperature range is prone to error. To develop some understanding of the error range, pseudo-Voigt peaks were fitted to the data in an attempt to exactly fit the experimental DSC profile. However, reaction processes produce asymmetrical peaks. Pseudo-Voigt functions are symmetrical; therefore in order to model asymmetry, smaller pseudo-Voigt peaks were added either to the high or low temperature sides of the fitted pseudo-Voigt peaks. A suggestion for any future such fitting would be to independently fit the shape of a given exothermic peak on either side of it's crystallization temperature (i.e. the peak maximum). The enthalpy measurements presented in this thesis are in

fact weighted averages of the two measurement techniques: first stage enthalpy for  $Al_{85}Y_5Ni_{10}$  (see Fig.4.4) is closely approximated by DSC-2C software integration, second stage enthalpy for  $Al_{85}Y_{10}Ni_5$  is far better approximated by pseudo-Voigt fitting (see Fig.4.27.a).

For partial crystallization studies, the crystallization stage was reached at a heating rate of 40 K/min, whereupon the sample was rapidly cooled at 320 K/min. The question arises as to whether such a rapid cooling rate quenches a high temperature crystalline phase. Cooling at 10 K/min and doing x-ray diffraction proved this was not the case.

As mentioned in Experimental Techniques, DSC scans are subject to a thermal lag, due to thermal resistance between the Al sample pan and heating crucible. This lag manifests as a constant temperature offset in DSC scans, distinctly different for different heating rates. In order to present accurate crystallization  $T_x$  or glass transition onset temperatures  $T_g$ , and more importantly, for accurately calculating activation energies, all such temperatures computed from the raw data were corrected by this thermal lag. The thermal lag was determined by heating a zinc standard at the heating rates of interest, upto and past the measured melting point of zinc (see Fig.A.4.a). Since melting is a process of crystal destabilization, there is no concept of nucleation and growth, hence no temperature dependent activation energy. This means zinc should melt at the same temperature independent of heating rate. Any temperature offset in measured melting point will then be purely a thermal lag effect. Table A.1 lists the computed thermal lag corrections in temperature at different heating rates, which were then added to all  $T_x$  and  $T_g$ .

Uncertainty in measuring  $T_x$  or  $T_g$  stems from having a non-negligible background which varies with temperature. As stated in Experimental Techniques, all such background was eliminated by subtracting a background scan immediately after heating the glass. An upper limit on measurement uncertainty, due to a temperature evolving background, is  $\pm 1.0$  K.

Heating Rate	$\Delta T_{lag}$ correction
(K/min)	(add to data) $(K)$
10	2.44
20	1.45
40	-0.55
80	-4.06
160	-10.32

Table A.1: Thermal lag correction  $\Delta T_{lag}$  which was added to all temperature measurements taken from the DSC.

## A.3.4 DSC: Isothermal Error Analysis

The determination of Avrami exponents was very sensitive to error, due to the unfortunate overlap of multiply nucleating phases. Since the partial time integrals of nucleation and growth peaks are proportional to the fraction crystallized x(t) (which has the Avrami exponent as a parameter), the time derivative of such an expression would give a direct relationship between the functional form of a nucleation and growth peak and the Avrami exponent. Fitting linear combinations of such functions to data where nucleation and growth peaks overlap would then give a precise determination of the Avrami exponents of all the individual nucleation and growth process. The function to be fit f(t) to an individual raw data nucleation and growth peak will have the form

$$f(t) = A \frac{dx(t)}{dt} = A \frac{n(t-t_0)^{n-1}}{\bar{\tau}^n} e^{\left(\frac{t-t_0}{\bar{\tau}}\right)^n}$$
(A.13)

where n (Avrami exponent),  $\bar{\tau}$  (characteristic time constant),  $t_0$  (time offset) and A (total area integral of nucleation and growth peak) are the fitting parameters affecting the functional form of nucleation and growth. In theory this is a sound undertaking, however fitting the raw data to such functions has shown that good fits may be acquired for starkly different fitting parameter values.

As discussed in the Experimental Techniques section, all functional fits to experimental data were evaluated by the Chi-Square Goodness-of-Fit test. This can be

visualized as an m-dimensional phase space, where a sub-space of dimension m-1represents parameter space (i.e. each fitting parameter has values spanning one dimension, from minus to plus infinity), and the *m*-th dimension represent  $\chi^2$  values. For example, for two fitting parameters we would have a 3-dimensional phase space. The function plotted in this phase space (call it the goodness-of- fit function) is the  $\chi^2$ value for all fitting parameter values. Minimization of  $\chi^2$  then corresponds to locating the absolute minimum in the topology of this goodness-of-fit function. In order to approach fitting minima, an iterative approach is employed where parameter values are arbitrarily changed,  $\chi^2$  is computed and compared against the previous  $\chi^2$  value. A path of decreasing  $\chi^2$  is followed in phase space, until the minima is reached. Here lies a critical danger: if initial parameter values are chosen near a local minimum, the iterative fitting process may trap the goodness-of-fit in this local minimum. Individual local minima can most likely be identified by differing  $\chi^2$  values. This presents a closed-loop problem: in order to reach the absolute minimum, we need to guess at starting fit parameters which are sufficiently close to it, with respect to other local minima, but we have no a priori knowledge of what "sufficient" means. Parameters like  $\tau$  (the time at which 63% of phase has crystallized) and A (enthalpy of the phase) are difficult to determine in an isothermal scan like Fig.4.34.a. Best guesses were put forth for both quantities, and  $t_0$ , before beginning the iterative fitting process. Hence any Avrami exponents determined by such a fitting process should be considered to not necessarily represent absolute best fit values, and  $\chi^2$  should be looked at carefully. As an experimental rule of thumb, fits with  $\bar{\chi}^2$  values of 2 – 4 are considered "good" fits.

A suggestion for future work is to first attempt Gaussian function fits to the overlapping nucleation and growth peaks; this will give an ideal guess at starting parameter values for  $\tau$ , A and  $t_0$ . From these starting values, best fits should be acquired with good precision, provided we are fitting with the correct number of overlapping peaks (artefact peaks, due to superposition of two peaks, are possible and should be watched for).

Since fitting raw isothermal data is prone to indeterminate error in fitted Avrami exponents, the technique was used only in cases where the overlapping peaks had sufficient resolution to acquire good starting guesses for fitting parameters (this was only possible with isothermal scans of second stage  $Al_{85}Y_5Ni_{10}$  and first stage  $Al_{85}Y_{10}Ni_5$ ). Unfortunately, almost all the isothermal peaks have multiple nucleation events, hence the process of doing Avrami plots from their partial time integrals will not give accurate Avrami exponents. However, they do provide a lower bound limit for the Avrami exponent of the first nucleating event, provided that only crystallized fraction of roughly less than or equal to 0.5 is considered in the Avrami plot. Any error on the actual process of integration was tested by doing Avrami plots on isothermal scans done at different annealing temperatures, and whose integration limits were chosen independent of each other. Results indicate an uncertainty in exponents determined by Avrami plots of as much as  $\pm 0.5$ .

Isothermal anneals were performed in a systematic fashion: since different heating rates shift  $T_x$ , the annealing temperature was approached at a constant heating rate, one at which an isochronal scan had already been done. This established with certainty which crystallization stage was being studied by isothermal annealing. Since isothermal scans unfortunately gave multiple nucleation peak overlap, we did not bother to compute activation energies from variation of  $\tau$  with annealing temperature, nor plot time-temperature-transformation (TTT) diagrams, since they would carry no physical meaning. Kissinger activation energies presented in this work represent to some extent activation of the first or dominant phase amongst these multiply nucleating phases.

## A.3.5 X-ray Diffraction Error Analysis

X-ray diffraction was done with a Cu tube source, however extra peaks were observed in the diffraction scan of an Al standard (see Fig.A.4.b). This was determined to be from Cu- $K\beta_1$  and W- $L\alpha_1$  wavelengths, where the anode in the source is made of tungsten. For this reason, not all small peaks have been accounted for in identifying crystallized phases' Bragg peaks, since some of these small peaks may represent Bragg peaks due to these other two wavelengths.

While the problem with acquiring absolute  $\chi^2$  minima fits applies to fits of Xray diffraction data as well, we have more confidence in these fits since starting fit parameter values can be very accurately guessed for pseudo-Voigt functions (the fitting parameters have very obvious effects on the functional form of the plots). Indeed, it was for this very reason that pseudo-Voigt functions were used for fitting, as opposed to the theoretically accurate but practically cumbersome Voigt functions. A discussion about the relevance of using either of these functions can be found in [53]. For several crystallization stages the Al Bragg peaks were exclusively fitted, and their corresponding  $\chi^2$  are unusually high. This may be due to the fit getting trapped in local  $\chi^2$  minima, but the more likely cause is the far fewer data points which are being used to fit, combined with the fact that the Bragg peaks are not ideally symmetric. Uncertainty in such Al-peaks on fits of the Al lattice parameter was determined by fitting the Al standard diffraction plot: the error is ±0.004 Å. This error bar should be considered in interpreting any information from Al lattice parameter fits of the partially crystallized glasses.



Figure A.5: (a) X-ray diffraction of glass slide and double-sided sticky tape. (b) X-ray diffraction of (i) melt-spun  $Al_{85}Y_5Ni_{10}$  on glass slide and double sided sticky tape, (ii) melt-spun  $Al_{85}Y_5Ni_{10}$  mounted in an Al frame; their difference (i)-(ii) is the incoherent contribution from the glass slide and double-sided sticky tape. Note the sample's absorption effect on background in the  $2\theta = 20^{\circ}$  area.

X-ray diffraction of all samples was done by sticking pieces of the ribbons onto a double-sided sticky tape on a glass slide. This introduces a background shown in Fig.A.5.a, however this background could not be accurately subtracted from the diffraction raw data. This is because, despite the background correction discussed in Experimental Techniques, the ribbon pieces laid down on the sticky tape were not perfectly tiled next to one another, allowing for sticky tape to be seen through the cracks, and the x-ray window at 10° <  $2\theta$  < 20° is larger than the region over which the ribbons were laid on the glass slide. This contributes to a relatively high intensity amorphous peak at 20° < 2 $\theta$  < 30°, as shown in Fig.A.5.b. A difference plot of ribbons mounted in an Al frame versus a glass slide is compared against lone background diffraction in Fig.A.5.b. Attempts to correct this effect were made by subtracting a scan-angle dependent fraction (one minus the ratio of the tiled sample area to the X-ray window area) of background intensity, and a remaining fraction background intensity which is damped by absorption. This produced no noticeably different results, hence we did not implement this correction. This attempt at extra correction still remains an underestimate since there is also background correction coming through the aforementioned imperfect tiling of ribbon pieces. However, this artefact will have notable effect only on fitted peak integral breadths  $\beta$  and pseudo-Voigt fraction  $\eta$ . We are only concerned with  $\beta$  for the Al peaks, which are sufficiently far from the artefact region (in  $2\theta$  dimension) and narrow enough that chances of their being influenced does not seem to be the case (results are in good agreement with TEM imaging).

Since partially crystallized glasses were laid down in ribbon form on glass slides, a question arises as to whether texturing (directional growth of crystal phases in ribbon) may influence the intensity of the Bragg peaks. Indeed, texturing has been known to occur in melt-spun ribbons. However, it does not appear to be the case here. Several partially crystallized ribbons were ground up and scanned, giving identical diffraction plots. Rocking curves were performed on selected Bragg peaks (variation of detector  $\theta$  angle while maintaining fixed source-sample angle), and showed no



Figure A.6: X-ray diffraction rocking curves of (a) $Al_{85}Y_5Ni_{10}$  (fourth stage crystallization.) at  $2\theta = 22.8^\circ$ , (b) $Al_{85}Y_{10}Ni_5$  (first stage crystallization.) at  $2\theta = 38.1^\circ$ .

sudden discontinuities, hence verifying truly random orientation of crystallites (see Figs.A.6.a,b).

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