Doctoral Thesis

High-temperature, ultrahigh-gravity centrifugal processing of metallic melts

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High-temperature, ultrahigh-gravity centrifugal processing of metallic melts

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Dedication

For my parents and Ashley
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Summary

The 1st metallic glass discovery in 1960 was the result of rapidly quenching a deep eutectic composition (Au$_{81.4}$Si$_{18.6}$) with a cooling rate of approximately $10^7$ K/s. Metallic glass research has since then expanded to ternary, quaternary and more complex systems with the primary goal of increasing glass-forming ability. Much of this alloy development was done using empirical rules for glass formation and by trial and error, which requires a large time investment. In this thesis, an ultrahigh acceleration processing method is explored for direct and efficient identification of eutectic compositions in multicomponent alloys which, because of their high ratio between glass transition and liquidus temperature, are predicted to be good glass-forming compositions.

In order to produce the samples for ultrahigh acceleration processing and to improve the alloy development capability of the institute, a variety of metallic glass alloying and quenching equipment was constructed. This equipment includes (1) a drop tube for production of metallic glass spheres; (2) a piston-injection molding system for complex or thin specimens; (3) a silver-boat made exclusively for Mg-based alloy processing; (4) an electromagnetic levitation alloying-casting system for containerless processing; and (5) a melt extraction system for production of metallic glass wires. The design, construction and specific application of each equipment is described in the first part of this thesis.

High-temperature ultrahigh acceleration processing was then used on various alloys produced with the above equipment. Samples are melted in a crucible within a sealed capsule to avoid oxidation, and then slowly cooled during continuous applied acceleration of 60,000 g. The effect of this extreme acceleration is explored in binary, ternary and multicomponent alloys. Atomic-level stratification is shown to generate more phases than predicted by the Gibbs phase rule under normal gravity. This results from the fact that the chemical potential of the various phases is strongly modified by the high acceleration. A thermodynamic model for predicting the evolved phase volumes in binary alloys is presented and validated experimentally using the historically important Au–Si binary eutectic composition. Because of the atomic-level stratification, both primary phases and the eutectic phase appear simultaneously in one sample, i.e. the equilibrium phase diagram is spread out over a range of compositions at 60,000 g.
Centrifugal processing of the ternary Au–Si–Ge eutectic (Au$_{79.4}$Si$_{14.1}$Ge$_{6.5}$) is also presented. Again, this processing generates more phases than predicted by the Gibbs phase rule. Interestingly, the processing moves the ternary eutectic ($T_l=362^\circ\text{C}$) towards the global eutectic composition, which is the Au–Ge binary eutectic ($T_l=361^\circ\text{C}$).

Finally, the thesis describes the centrifugal processing of multicomponent alloys, i.e. two La-based alloys and one Mg-based alloy. For the La-based alloys it is shown that eutectic compositions with high glass-forming ability are isolated during cooling of compositionally off-eutectic melts. The identified ternary composition, La$_{64}$Al$_{13}$Cu$_{23}$, was cast amorphously to 3 mm in diameter, comparable to what has been reported in literature. The quaternary composition, La$_{65}$Al$_{13}$Ni$_{10}$Cu$_{12}$, was even cast amorphously to 10 mm in diameter, showing the highest glass-forming ability for this system. For the Mg-based alloy it is shown that starting from a “designed” multicomponent Mg–Zn–Ca–Al–Si composition, alloy components (in this case Si and Ca) can be excluded from the melt that do not thermodynamically lower the liquidus temperature. Within the last section of the sample to solidify (Mg–Zn–Al), three different glass-forming compositions evolved, which moved progressively towards the eutectic calculated by Pandat. These results show that instead of extensive traditional alloy development, it is sufficient to study one centrifugally-processed sample to discover the composition with the deepest eutectic, which often produces good glass-forming ability.
Zusammenfassung


Um Proben für die Verarbeitung unter ultrahohen Beschleunigungen zu produzieren und die Herstellungsmöglichkeiten von Legierungen im Labor zu verbessern, wurden eine Vielzahl von Legierungs- sowie Abschreckeinrichtungen konstruiert. Diese beinhalten (1) eine Fallröhre für die Herstellung von Kugeln aus metallischem Glas; (2) ein kolbengetriebenes Druckgußsystem für komplexe oder dünne Proben; (3) ein Silberboot für die Verarbeitung von Mg-Legierungen; (4) ein elektromagnetisches Schwebeschmelzsystem mit Gußoption für kokillenlose Fertigung; (5) eine Schmelzspinnapparatur für die Herstellung von Drähten aus metallischem Glas. Die Entwicklung und Konstruktion sowie spezifische Anwendungsmöglichkeiten der Einrichtungen werden im ersten Teil der Arbeit beschrieben.

Verschiedene mit den oben beschriebenen Geräten hergestellte Legierungen werden daraufhin unter sehr hohen Beschleunigungen (60'000 g) aus der Flüssigphase langsam abgekühlt, wobei die Proben dazu zur Vermeidung von Oxidation in einen Tiegel eingepaßt werden, welcher sich während dem Prozeß in einer geschlossenen Kapsel befindet. Die Auswirkungen dieser hohen Beschleunigung werden in binären, ternären und mehrkomponentigen Legierungen untersucht. Es wird gezeigt, daß die auf atomarer Ebene wirkende gravitationsbedingte Separation mehr Phasen erzeugen kann als von der Gibbs’schen Phasenregel unter normaler Schwerkraft vorhergesagt wird. Dies beruht auf der starken Veränderung der chemischen Potentiale der
verschiedenen Phasen unter hoher Beschleunigung. Ein thermodynamisches Modell für die Vorhersage der sich entwickelnden Phasenvolumina in binären Legierungen wird vorgestellt und anhand der historisch bedeutsamen eutektischen Zusammensetzung von binärem Au–Si experimentell bestätigt. Aufgrund der Separation auf atomarer Ebene erscheinen beide Primärphasen sowie die eutektische Phase gleichzeitig in einer Probe. Dies bedeutet, daß das Gleichgewichtsphasendiagramm bei 60'000 g über einen Bereich von Zusammensetzungen ausgedehnt wird.


Ferner beschreibt diese Arbeit das Zentrifugieren zweier La- sowie einer Mg-Legierung mit mehr als 4 Komponenten. Im Falle der nicht-eutektischen La-Legierungen wird gezeigt, daß das Abkühlen zu einer räumlichen Abgrenzung der eutektischen Zusammensetzungen führt, wobei diese Eutektika gute Glasbildungseigenschaften aufweisen. Die ermittelte ternäre Zusammensetzung La64Al13Cu23 konnte mit 3 Millimetern Durchmesser glasartig hergestellt werden, was vergleichbar mit Literaturwerten ist. Die quaternäre Zusammensetzung, La65Al13Ni10Cu12, wurde sogar mit einem Durchmesser von 10 mm amorph hergestellt und weist damit die beste Glasbildungseigenschaft dieses Systems auf. In Bezug auf die Mg-Legierung wird gezeigt, daß, ausgehend von einer entworfenen Mg–Zn–Ca–Al–Si-Legierung, gewisse Elemente von der Schmelze ausgeschlossen werden können (in diesem Fall Si und Ca), welche die Liquidustemperatur nicht verringern. Im zuletzt erstarrenden Probenbereich (bestehend aus Mg, Zn und Al) entwickeln sich drei verschiedene glasbildende Zusammensetzungen, die sich schrittweise zu dem mit Pandat berechneten Eutektikum hin bewegen. Diese Ergebnisse zeigen, daß es anstelle von aufwändiger traditioneller Legierungsentwicklung ausreicht, eine zentrifugierte Probe zu analysieren, um das tiefstschmelzende Eutektikum zu finden, welches oftmals eine gute Glasbildungseigenschaft aufweist.
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VI
1 Introduction

In the history of metallic alloys metallic glasses are relatively new, due mainly to the kinetic and thermodynamic constraints in their formation. In order to retain a completely amorphous structure from the melt (1) appropriate quenching techniques must be applied, and (2) careful alloy selection must be made so as to increase the maximum possible casting thickness. Sections 1.1 through 1.6 give an overview of metallic glass development focusing (1) on practical production methods and (2) on theoretical thermodynamic considerations of glass-forming ability. This introduction is followed by Sections 1.7 and 1.8, which state the aims of the thesis project and present an outline.
1.1 Glasses and glass formation

Glasses are usually defined as amorphous materials formed upon cooling from the melt which exhibit a glass transition temperature in differential scanning calorimetry (DSC). A glass is also defined as a vitrified liquid, or in other words a liquid which solidifies via configurational freezing instead of the classical crystal nucleation and growth processes. All glasses exist as a “frozen liquid” or an amorphous solid, where the word amorphous literally means “without form” and encompasses a wider spectrum of materials than just glasses. However, in this thesis the terms glass and amorphous will be used interchangeably.

Glass-forming systems have been found in all of the major bonding classes, including covalent, ionic, van der Waals, hydrogen bonding, and metallic [1]. Metallic glasses (MGs) are the most recently discovered, owing to the extremely high cooling rates (on the order of $10^5$ to $10^6$ K/s) needed to form them. This is due to the non-directional nature of metallic bonds and the fact that metals are comprised of individual spherical atoms, as opposed to non-spherical compounds such as SiO$_2$ and other oxide glasses. With metals, individual atoms can rearrange quickly into lower energy configurations or crystalline phases, thus requiring higher cooling rates to avoid crystallization.

A glass, by definition, is a metastable phase. So, forming a glass involves balancing thermodynamic and kinetic parameters. As a metallic melt cools below its melting temperature, the solid state is energetically favored over the liquid. This is the thermodynamic driving force behind nucleation and growth. To form a glass, nucleation and growth must be avoided. There are two ways to approach this problem: Thermodynamically, an alloy composition may be designed or discovered which is thermodynamically resistant to nucleation, and thus the critical cooling rate (CCR) is decreased and the critical casting thickness (CCT) is increased. This aspect is discussed in Section 1.4. Kinetically, the sample material may be “brute-force”-quenched fast enough so that only a few nuclei are frozen in. Rapid quenching restricts one dimension of samples so that heat can be rapidly extracted. In this case thin metallic glass ribbons can be obtained.
1.2 History of metallic glasses

Pol Duwez and co-workers from the California Institute of Technology (CalTech) were the first to successfully quench a binary Au–Si eutectic composition fast enough to form a metallic glass upon cooling from the melt (1960) [2,3]. This was followed by Chen and Turnbull in the late 1960s working with Pd-based alloys [4,5]. With further optimization Chen was the first to develop a metallic glass composition with a CCT greater than 1 mm [6]. This is opposed to “traditional metallic glasses” where one sample dimension is very thin (~50 μm) due to the required high CCR. Turnbull and collaborators also developed a fluxing technique, which reduced heterogeneous nucleation at the sample surface, resulting in a much lower CCR [7,8]. A significant development made by Inoue in the late 1980s was the production of La-based three- and four-component “bulk metallic glass” (BMG) alloys with CCT of several millimeters [9,10]. Finally, again at CalTech, Johnson and co-workers developed a five-component Zr-based series of alloys, “Vitreloy”, in the early 1990s [11,12]. More on the development of metallic glasses can be found in Refs. [13,14,15,16,17]. A summary of these historical developments is presented in Table 1.1, which clearly illustrates the trends of increased alloy complexity and decreasing CCR or increasing CCT.

Table 1.1: Metallic glass alloy development illustrating increasing alloy complexity and decreasing CCR.

<table>
<thead>
<tr>
<th>Year</th>
<th>Alloy</th>
<th>Researcher</th>
<th>Critical cooling rate (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960</td>
<td>Au–Si</td>
<td>Pol Duwez</td>
<td>10^5–10^6</td>
</tr>
<tr>
<td>1960s</td>
<td>Pd–Si, Pd–Cu–Si</td>
<td>Turnbull and Chen</td>
<td>10^5</td>
</tr>
<tr>
<td>1970s</td>
<td>Pd–Cu–Si</td>
<td>Chen</td>
<td>10^5</td>
</tr>
<tr>
<td>1980s</td>
<td>La–Al–Ni, La–Al–Cu, La–Al–Cu–Ni, Mg–Y–Cu, Mg–Y–Ni</td>
<td>Inoue</td>
<td>10^5</td>
</tr>
<tr>
<td></td>
<td>Zr–Cu–Ni–Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1982</td>
<td>Pd–Ni–P (Fluxing Method)</td>
<td>Greer and Turnbull</td>
<td>10</td>
</tr>
<tr>
<td>1990s</td>
<td>Zr–Ti–Cu–Ni–Be</td>
<td>Peker and Johnson</td>
<td>1</td>
</tr>
</tbody>
</table>

1.3 Apparatus to produce metallic glass

As alloy development progressed and lower critical cooling rates were required, the production equipment evolved from focusing on maximum possible cooling rates to larger and larger sample dimensions. Presented here is a brief
historical overview of the main quenching methods employed in the last 40 years of metallic glass alloy development.

Duwez used a gun quenching technique for quenching the Au–Si system, where cooling rates of $10^6$ to $10^8$ Kelvin per second were achieved. A schematic of the gun quenching setup is shown in Fig. 1.1(a) [2], where the prepared samples were thin enough for transmission electron microscopy (TEM) studies. The gun quenching system consists of an induction coil melting a small amount of material and a high-pressure inert-gas shockwave that splits the melt into smaller droplets and propels them against a cooling copper strip.

![Figure 1.1](image1.png)

Figure 1.1: (a) Gun quenching system used for producing Au–Si binary alloys; (b) splat quenching system currently used for Fe- and Al-based metallic glass development (images “taken after” [2]); (c) melt spinning technique used for commercial Fe-based MGs and for Mg-based metallic glass development; (d) casting box concept for laboratory production of BMGs (e.g., Zr-, Cu-, Pd-, and Au-based) (“taken after” [18]).
With the advent of ternary MGs, the piston-anvil technique or, more commonly, “splat-quenching” was developed to produce larger specimens. This technique, pictured in Fig. 1.1(b), reaches cooling rates of up to $10^6$ Kelvin per second. Modern splat quenchers utilize an electromagnetic levitation coil, which without a container holds and melts the sample until the current is switched off and the melt falls, triggering the two copper plates to impact together. A flat specimen of between 20 - 80 $\mu$m thickness and ~2 cm in diameter is thus produced. This technique is still used today for basic alloy development where a large number of different compositions are probed, as it introduces very little contamination and requires little material.

The next logical step in increasing sample size is to move from splats to ribbons. As shown in Fig. 1.1(c), in melt spinning or planar flow casting, the sample is inductively melted in a non-reactive crucible (quartz, graphite, or boron nitride) and then forced via inert-gas pressure onto a rotating copper wheel. A long thin ribbon is produced, and by varying casting pressure and wheel speed samples of 10 to 200 $\mu$m thickness can be produced. This technique has been commercialized and metallic glass ribbons several centimeters wide and several meters long are possible.

As still better glass-formers were found, specifically by the Johnson and Inoue groups, bulk samples became possible via traditional casting into copper molds. Copper has been used throughout due to its excellent heat conduction and relatively cheap cost compared to silver. The general schematic for a casting box is depicted in Fig. 1.1(d), illustrating (1) the induction coil to heat the sample; (2) the quartz tube to hold the sample; and (3) a copper mold to quickly cool the sample. Copper molds are not usually water-cooled, but instead made oversized so that the thermal mass of the mold is sufficient to cool the sample. Water cooling of the molds complicates the production of such equipment, as BMGs are usually processed under high vacuum conditions ($\sim 10^{-5}$ mbar).

### 1.4 Classical nucleation theory and rules of glass formation

Rapid quenching of a metallic melt works for traditional metallic glasses; however, it is ultimately limited by the thermal conductivity of the liquid. For a given composition the homogeneous nucleation rate and the thermal conductivity of the
liquid are set such that the CCT due to crystallization of the sample center is fixed, independent of the heat extraction rate at the sample surface. As the thermal conductivity is not significantly varied by composition, the only way to increase the CCT is to decrease the homogeneous nucleation rate. This is done by designing an alloy system that by the nature of its composition suppresses crystallization or stabilizes the liquid phase. To illustrate the theoretical background of this concept a brief overview of classical nucleation leading to the Turnbull criterion is presented below.

### 1.4.1 Classical nucleation theory

As a liquid melt is cooled past the melting point, the Gibbs free energy curves for the crystalline and liquid phases cross and the crystalline phase is thermodynamically favored. With continued decreasing temperature the difference between the two lines increases, thereby increasing the driving force for the liquid to crystallize. The relationship between the free energy difference and undercooling is given by Equation (1.1) [19]

$$
\Delta G_v = -\left\{ \Delta H_m^f \Delta T_r + T_m \int T_r \frac{\Delta C_p dT_r}{T_r}dT_r \right\} \frac{1}{V_m}.
\tag{1.1}
$$

Here $\Delta G_v$ is the free energy difference per unit volume, $\Delta H_m^f$ is the molar heat of fusion, $\Delta C_p$ is the molar difference in heat capacity between the liquid and the crystal, $V_m$ is the molar volume of the crystal, $T_r = T / T_m$ is the reduced temperature, and $\Delta T_r = (T_m - T)/T_m$ is the reduced undercooling, while $T_m$ and $T$ are defined as the melting temperature and the actual sample temperature on an absolute scale.

With the creation of a pre-nucleus or cluster, a solid-to-liquid interface is formed and creates a discontinuous boundary with an associated energy term per surface area. The thermodynamic driving force, Equation (1.1) above, must overcome this interface energy for the created nucleus to be stable. The balance of these two energies is written in Equation (1.2) [20],

$$
\Delta G = 4\pi r^2 \sigma + \frac{4\pi}{3} r^3 \Delta G_v,
\tag{1.2}
$$
where $\sigma$ is the interface energy (greater than zero and in energy/area) and $\Delta G_\nu$ is the free energy from Equation (1.1) (energy/volume). The critical radius at which a cluster will become a stable nucleus can be found by setting the derivative of Equation (1.2) equal to zero. The critical radius, $r^*$, and the maximum value for $\Delta G$, $\Delta G^*$, are

$$r^* = -\frac{2\sigma}{\Delta G_\nu}, \text{ and } \Delta G^* = \left(\frac{16\pi}{3}\right)\left(\frac{\sigma^3}{\Delta G_\nu^2}\right). \quad (1.3), (1.4)$$

The two energy terms along with the sum are shown graphically in Figure 1.2 [20]. Assuming a spherical cluster, the interface energy goes positively with the surface area and therefore $r^2$, while the driving force goes negatively with the volume and therefore $r^3$. The summation, line $\Delta G$, shows the radius, $r^*$, where a cluster becomes a stable nucleus or below which it dissolves. If a stable nucleus forms, $r > r^*$, the growth process increases the radius and the free energy decreases along the line $\Delta G$.

Figure 1.2: Sum of competing interface and volume energy as a function of radius $r$, where $r^*$ divides stable nuclei from clusters which dissolve.

It should be noted that deep in the undercooled region, that is between $T_m$ and $T_g$, the growth rate can be very high and growth is impossible to stop even with very high quenching rates. Hence, limiting the nucleation process must be exploited to form glasses with very low CCRs. The homogeneous nucleation rate is described classically by
\[ I_v = K \exp \left[ -\frac{(q + \Delta G^*)}{k_B T} \right], \quad (1.5) \]

where \( I_v \) is the homogeneous nucleation rate (nuclei/volume time), \( K \) is a constant to be determined, \( q \) is the free energy of activation for diffusion across the phase boundary, \( \Delta G^* \) is the maximum value given by Equation (1.4), and \( k_B \) is the Boltzmann constant.

### 1.4.2 Turnbull criterion

Based on the classical equations, Turnbull related the reduced glass transition temperature \( (T_{rg} = T_g/T_m) \) to the homogeneous nucleation rate. Assuming that (1) if one stable nucleus was formed the entire material would crystallize; (2) the atomic jump time was proportional to the viscosity; and (3) there is no difference between the heat capacity of the liquid and the crystal \( (\Delta C_p = 0) \), the Turnbull approximation for the free energy difference can be derived, as shown in Equation (1.6):

\[ \Delta G_v = \Delta H_m^f \Delta T \left( \frac{1}{V_m} = \Delta S_m^f (T_m - T) \right) \frac{1}{V_m}, \quad (1.6) \]

where \( \Delta H_m^f \) is the molar heat of fusion, \( \Delta S_m^f \) is the molar entropy of fusion, and \( V_m \) is the molar volume of the crystal. Turnbull introduced two terms to account for the interfacial tension and the entropy of fusion:

\[ \alpha = \frac{(NV_m^2)^{\frac{1}{2}} \sigma}{\Delta H_m^f}, \quad \text{and} \quad \beta = \frac{\Delta H_m^f}{RT} = \frac{\Delta S_m^f}{R}. \quad (1.7), (1.8) \]

In these equations \( N \) is Avogadro’s number and \( R \) is the universal gas constant. Using \( \alpha \) and \( \beta \) in Equation (1.6), the homogenous nucleation rate for a spherical nucleus results in

\[ I_v = \frac{k_n}{\eta} \exp \left( -\frac{16\pi}{3} \frac{\alpha^3 \beta}{\Delta T_c^2 T_c} \right), \quad (1.9) \]

where \( k_n \) is a constant to be determined by the model used and \( \eta \) is the viscosity.

Using a Vogel-Fulcher type expression [21] to describe viscosity change with temperature in the undercooled region, the graph shown in Fig. 1.3 can be developed. It shows that with increasing \( T_{rg} \), the maximum homogenous nucleation rate drops dramatically. The curves get progressively narrower, indicating a smaller range of
temperature in which the nucleation can occur. Varying $T_{rg}$ from 0 to 2/3, the maximum nucleation rate can be seen to drop by approximately 24 orders of magnitude. Based on this analysis, Turnbull concluded that $T_{rg}$ is a critical parameter for glass formation.

Figure 1.3: Maximum homogeneous nucleation rate vs. reduced temperature ($T_r = T/T_m$).

1.4.3 Turnbull criterion for metallic glass alloy development

From the Turnbull criterion it is clear that $T_{rg}$ must be maximized in order to increase the CCT or glass forming ability (GFA). This can be done by increasing $T_g$ or decreasing $T_m$. $T_g$ has been found to scale with the bulk modulus of the main alloy component [22]; however, $T_g$ changes little within a given alloy system or with small compositional changes. $T_m$ on the other hand changes significantly with small composition changes within a given alloy system, e.g. a binary eutectic. This indicates that the most likely place to find good glass-forming compositions is near a deep eutectic. This is true for many binary and ternary metallic glasses; in fact the first MG was the Au–Si binary eutectic composition.

1.4.4 Empirical rules for glass formation

In the course of metallic glass alloy development, several empirical trends have been observed and alloy component selection rules proposed to guide future alloy development. These rules are not strictly required for glass formation, but correlate well with good GFA. They are: (1) at least three components; (2) large
atomic size difference (usually greater than 12%); (3) large difference in electron valence configuration; and (4) negative heat of mixing between the main components [23,24]. It is interesting to note that these rules roughly oppose the Hume-Rothery rules for solid solution [25]. Rules 1 and 2 are assumed to destabilize crystallization by making unit cells larger, thus requiring increased diffusion length or time to form a crystal. This concept has been expanded upon by the “role of confusion” [26] or “frustration” [14]. As the number of components increases from three to four and five elements, the system becomes more and more confused or frustrated by chemical disorder.

1.5 Historical alloy development methods

Even with the alloy selection rules of section 1.4.4, alloy development of BMGs has been mainly by trial and error. Usually a system is selected and a grid of samples is made with even compositional spacing so as to cover the entire composition range; the La–Al–Cu system, for example, has been roughly covered by 60 samples [27]. All samples are tested for GFA and, if a glass is found, a finer grid of samples is made to map out the glass-forming region and maximum GFA exactly. This is a labor-intensive and time-consuming method of probing multicomponent space. More recently a method of tracing the liquidus lines via DSC to the lowest point, the eutectic, was proposed by Li [28], which optimized the La–Al–Cu system in only 30 samples.

1.6 Centrifugal processing

In this thesis a new alloy development method is presented using ultrahigh acceleration to identify the eutectic composition in just one sample. A metallic melt is subjected to 60,000 g (g = gravitation acceleration) applied acceleration and slowly cooled to room temperature [29,30]. This generates two effects: (1) sample composition becomes spatially dependent due to the density difference; and (2) primary crystals quickly sediment, changing the remaining liquid towards the eutectic, which solidifies last. A brief overview of classical sedimentation theory and relevant thermodynamics, used to describe these two effects, is given here.
1.6.1 Sedimentation theory

Sedimentation of macroscopic particles is well described in chemistry, biology, and the polymer and medical fields. The distribution in time and space of a macroscopic concentration, \( c(\vec{r}, t) \), of particles in a liquid is modeled by the diffusion equation,

\[
\frac{\partial c(\vec{r}, t)}{\partial t} = D \nabla^2 c(\vec{r}, t)
\]  

(1.10)

where \( D \neq D(\vec{r}) \) is the effective diffusion constant for the particles and \( \nabla^2 \) is the Laplace operator. Considering only the radial dependence \( r \) in cylindrical coordinates, Equation (1.10) becomes

\[
\frac{\partial c(r, t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r D \frac{\partial c}{\partial r} \right).
\]  

(1.11)

Using this rotating frame with frequency \( \omega \) around an axis from Equation (1.11), the total effective diffusion is governed by the Lamm Equation \[ 31 \],

\[
\frac{\partial c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r D \frac{\partial c}{\partial r} - s \sigma^2 r^2 c \right).
\]  

(1.12)

The sedimentation coefficient \( s \) is related to the materials properties and is taken by the Svedberg Equation \[ 32 \],

\[
s = D m_p \frac{1 - (\rho_i / \rho_p)}{k_B T} 
\]  

(1.13)

where \( D \) is the particle diffusivity, \( m \) is the mass of the particle, and \( \rho_i \) and \( \rho_p \) are the densities of the liquid and particle. The Stokes-Einstein Equation (1.14) can then be used for \( D \):

\[
D = \frac{k_B T}{(3\pi \eta \phi)}.
\]  

(1.14)

where \( \eta \) is the viscosity and \( \phi \) is the particle diameter.

The steady state (\( \partial c / \partial t = 0 \)) time-dependent transient solution to the Lamm equation leads to the Archibald solution \[ 33 \]. For a liquid confined to a cylinder of length \( L \) and with an average concentration of \( c_0 \), the Lamm equation can be rewritten in dimensionless form. Introducing the dimensionless time \( \tau = tD / L^2 \), length \( z = r / L \), concentration \( C(z, \tau) = c(r, t) / c_0 \), and rotation frequency \( \Omega = \omega t \), the dimensionless Lamm Equation is obtained, which has the form
\[
\frac{\partial C}{\partial \tau} = \frac{1}{z} \frac{\partial}{\partial z} \left( z \frac{\partial C}{\partial z} - \Omega^2 z C \right).
\]  (1.15)

The solution of this differential equation determines the spatial and temporal evolution of the particle distribution. The characteristic rotational frequency, Equation (1.16), for which acceleration-induced particle sedimentation becomes important, is

\[
\omega = \sqrt{\frac{D}{sL^2}} = \sqrt{\frac{k_b T}{L^2 M_p (1 - \rho_l / \rho_p)}}.  
\]  (1.16)

This equation also applies if the corresponding particle is a single atom in a liquid melt. In this case, \(M_p\) is replaced by the atomic mass \(M\), and \(\rho_p\) becomes \(M / \nu_a\) with \(\nu_a\) the partial molar volume per atom in the liquid solution. Thus, Equation (1.16) also predicts that atomic-level concentration gradients can develop in a homogeneous liquid above a certain rotation frequency \(\omega_c\). The consequences of this important conclusion are discussed in more detail in section 1.6.2.

The characteristic time \(\tau_c\) for complete sedimentation of a spherical particle of diameter \(\phi\) in a liquid confined in a cylindrical container of length \(L\) can be found by setting the drift velocity \(L / \tau_c\) equal to the average inertial acceleration \(\omega^2 \langle R \rangle\) times the sedimentation coefficient, \(s\). \(\tau_c = L / (\omega^2 \langle R \rangle s)\), where \(\langle R \rangle\) is the root mean square of the distance from the center of the centrifuge to the two sample ends, \(R_1\) and \(R_2\).

Substituting in Equations (1.13) and (1.14) gives

\[
\tau_c = \frac{18 \eta L}{s L^2 \langle R \rangle \phi^2 (\rho_p - \rho_l)}.
\]  (1.17)

This result means that the separation time \(\tau_c\) apart from geometrical and material parameters, is only dependent on the rotational frequency \(\omega\). In bulk metallic glasses, the equilibrium melt viscosity is very high, on the order of a few Pa-s. For a density difference of 2 g/cm\(^3\), \(L = 4\) cm, and \(\langle R \rangle = 8\) cm, particles of 10 \(\mu\)m sediment completely within 18 seconds at \(\omega = 2500\) Hz. However, for particles of 1 \(\mu\)m this time increases to 30 minutes. This appears to be the lower limit of separation possible at 2500 Hz, which corresponds to an acceleration of more than 50,000 \(g\). Figure 1.4 represents graphically Equation (1.17) for the above parameters, showing the minimum separated particle size of 1 \(\mu\)m in 30 minutes. For this reason all centrifugally-processed samples are spun for 2 hours as liquids to ensure complete purification.
Figure 1.4: Theoretically derived sedimentation time for a BMG, where a 1-μm-diameter particle separates in approximately 30 minutes (from Ref. [34]).

1.6.2 **Thermodynamics under ultrahigh gravity**

During ultrahigh acceleration, equilibrium thermodynamics are modified, as described in the following. For the calculations, the gravitational acceleration is assumed to be constant across the sample, which is valid for \( R \gg L \) and reasonable for our experimental setup. The origin of these thermodynamic effects is the fact that the individual atomic species may separate already in the melt purely based on density. For a simple binary system this can be expressed with a pressure gradient imposed on each phase \( \nu \) in a sample, given by

\[
\frac{\partial p^\nu}{\partial h} = \rho^\nu a , \tag{1.18}
\]

where \( h \) is the distance measured from the sample top, \( \rho^\nu \) is the average density of phase \( \nu \), and \( a \) is the acceleration expressed in multiples of gravitation acceleration \( g \).

Following this logic, the chemical potential for a component \( x \) in a phase \( \nu \) also changes under ultrahigh gravity. Not only is it dependent on the partial molar Gibbs energy of the component \( x \) in the phase \( \nu \), \( g_x^\nu(c_x,T,p) \), but also on the gravitational potential, as shown in Equation (1.19):

\[
\mu_x^\nu = g_x^\nu(c_x,T,p) - M_x^\nu a h . \tag{1.19}
\]

This gravitational component is encompassed in the last term, where \( M_x^\nu \) is the atomic...
mass of component $x$ in the phase $\nu$. At accelerations of $10^4$ to $10^5$ g, the $M_{ah}$ term becomes quite important. For example, in the Au–Si system it is on the order of 2 kJ/mol given $a = 10^5$ g and $h = 5$ cm, as compared to the heat of fusion for gold which is on the order of 10 kJ/mol.

### 1.6.3 One-component systems

In Figure 1.5, we consider a one-component system (e.g. Si) that can exist as liquid phase $\lambda$ or a solid phase $\alpha$, depending on temperature and pressure. Although of little practical application, this one-component example is given for completeness and the equations are simplified due to the fact that there are no chemical effects to consider. The pressure at the $\lambda$–$\alpha$ interface is $\rho^\lambda ah_i$, where $h_i$ is the position of the interface measured from the top of the sample. The actual location of the liquid/solid interface is determined by the Clapeyron equation,

$$\frac{dT_m}{dp} = \frac{\Delta V_f}{\Delta S_f}$$  \hspace{1cm} (1.20)

where $\Delta V_f$ and $\Delta S_f$ are the change of molar volume and entropy upon fusion, respectively. From Equation (1.20), the change of the melting temperature over the sample can be described by

$$T_m(h) = T_{m0} + \frac{\Delta V_f}{\Delta S_f} \rho^\alpha ah,$$  \hspace{1cm} (1.21)

where $T_{m0}$ is the melting point at zero pressure. Thus, the melting transition is spread out over a range of temperatures along the height of the sample.
Figure 1.5: Sample of length \( L \) in a constant gravitational field. Two phases \( \lambda \) (liquid) and \( \alpha \) (solid) are shown. The height \( h \) is measured from the “Top” of the sample, which is located at a distance \( R_1 \) from the center of the centrifuge, and \( h_i \) is the position of the liquid/solid interface.

### 1.6.4 Two-component systems

Next, a two-component alloy \( A_x B_c \) is analyzed, where \( c \) is the local alloy composition \((0 < x < 1)\). For the case of a simple eutectic alloy possessing two primary crystalline phases “A” and “B” with structures \( \alpha \) and \( \beta \), and a liquid phase \( \lambda \), Equation (1.19) describes the (gravity-dependent) chemical potential with \( x = A \) or \( B \) and \( \nu = \alpha, \beta, \) or \( \lambda \). In steady-state equilibrium, the chemical potential is constant for both components in each phase. At constant temperature, the differential of the total chemical potential has the form

\[
d\mu^\nu_x = \frac{\partial g^\nu_x}{\partial p^\nu_x} \frac{\partial p^\nu_x}{\partial h} dh + \frac{\partial g^\nu_x}{\partial c^\nu_x} \frac{\partial c^\nu_x}{\partial h} dh - M^\nu_x adh = 0. \tag{1.22}
\]

Using Equations (1.18) and

\[
\frac{\partial g^\nu_x}{\partial h} = \left(1 - c^\nu_x\right) \frac{\partial^2 g^\nu_x}{\partial c^\nu_x^2}, \tag{1.23}
\]

the concentration variation of component \( x \) in a given phase \( \nu \) over the sample height \( h \) becomes

\[
\frac{\partial c^\nu_x}{\partial h} = \frac{(\rho^\nu_x - \rho^\nu_x)\nu_x a}{\left(1 - c^\nu_x\right) \frac{\partial^2 g^\nu_x}{\partial c^\nu_x^2}}, \tag{1.24}
\]
where \( g^\nu \) is the (total) molar Gibbs energy of the phase \( \nu \), \( \nu x^\nu = \partial g^\nu_x / \partial \rho^\nu \) is the partial molar volume, and \( \rho^\nu_x \) is the partial molar density of the component \( x \) in the phase \( \nu \).

The very general Equation (1.24) expresses the induced concentration gradient in terms of molar Gibbs energy of a binary solid solution of any liquid phase or solid phase in a uniform gravitational acceleration. This equation is generally not recognized in literature. To make finding an exact solution easier the following assumptions are made: (1) a simple binary system; (2) zero heat of mixing; (3) ideal solution behavior; and (4) \( \sum_{h=0}^{h_f} Cdh = \bar{C} \) (the sum of the compositions over the sample is equal to the composition prior to centrifugation). From these assumptions a solution for the composition of component \( x \) in a given phase \( \nu \) with position \( h \) can be obtained:

\[
c_x^\nu = \frac{A \bar{c}_x^\nu h_f}{\exp(Ah)} \frac{\exp(Ah)}{\exp(Ah_f) - 1}, \quad (1.25)
\]

where

\[
a = \left( \frac{\rho^\nu_x - \rho^\nu} {k_b T} \right)^\nu_x a.
\]

(1.26)

Variables from Equations (1.25) and (1.26) include \( x = A \) or \( B \) atoms, \( \nu = \alpha, \beta, \) or \( \lambda \) phases, \( M^\nu_x \) is the atomic mass of \( x \) atoms in phase \( \nu \), \( a \) is the acceleration, \( g^\nu_x \) is the partial molar Gibbs energy of \( x \) atoms in phase \( \nu \) in absence of gravitational field, \( \rho^\nu_x \) is the partial molar density, \( \rho^\nu \) is the average molar density, \( \nu x^\nu \) is the partial molar volume of \( x \) in phase \( \nu \), and \( h_f \) is the total sample height.
1.7 Aims of the thesis

The goal of this thesis is a two-fold approach to metallic glass formation encompassing both the practical alloy production and alloy development aspects. First, rapid quenching equipment was designed and constructed to facilitate the production of BMGs. Second, an ultrahigh acceleration processing technique was used to explore the spatial dependence of thermodynamics in binary alloy systems, and determine glass-forming compositions in multicomponent alloys in a less time-consuming way.

1.7.1 Construction of metallic glass processing equipment

Various pieces of BMG processing equipment were designed and constructed, to which the first part of this thesis is devoted. These systems were used to produce the samples required for the second part of this thesis and continue to be used in the Laboratory of Metal Physics and Technology (LMPT). The equipment includes (a) modification of a casting box, produced by the author for a Master’s thesis, to also function as a drop tube casting system (Section 2.2), (b) an injection molding system for casting complex shapes (Section 2.3), (c) a silver-boat specifically for Mg-based BMG production (Section 2.4), (d) an electromagnetic levitation suction-assisted casting system for containerless processing of Mg- and Ca-based BMGs (Section 2.5), and (e) a melt extraction or wire spinning system for producing Mg-based wires (Section 2.6).

1.7.2 Centrifugal processing: Spatial dependence in binary and ternary alloys

A high-temperature ultrahigh acceleration centrifuge [34] was used to apply 60,000 g acceleration to binary and ternary metallic melts. This acceleration introduces atomic-level stratification based solely on the difference in atomic density. The amount of separation can be predicted thermodynamically and measured by the amount of primary phases that evolve when the sample is cooled under ultrahigh gravity. For the selected Au–Si eutectic composition, both primary phases (Au and Si) and the eutectic are observed, which is not possible under normal acceleration (1g).
The measured phase volumes correlate well with the thermodynamically predicted values.

The ternary Au–Si–Ge eutectic composition was also processed, again resulting in atomic-level stratification and multiple primary phases, i.e., the eutectic and three primary phases (Au, Si, and a Si–Ge solid solution) evolved. This thesis describes in detail why upon ultrahigh gravity centrifugal processing more phases evolve than predicted by the Gibbs phase rule under normal gravity.

1.7.3 Centrifugal processing: Metallic glass development in multicomponent alloys

A variety of multicomponent alloys were processed to determine their eutectic compositions with the aim of increasing the GFA as predicted by the Turnbull criterion. Upon cooling, primary phases separate to the sample ends due to the density difference, changing the composition towards the eutectic, which solidifies last. These primary phases are easily identified after processing and sediment in the order of formation. Results for two La-based and one Mg-based sample are presented in detail showing that the GFA of off-eutectic glass-forming alloys can be increased by identifying the eutectic or very near eutectic compositions, and that atomic species that do not help lower the liquids temperature can be eliminated, resulting in a eutectic with fewer components than the starting alloy. This thesis shows that centrifugal processing is a very effective method for developing metallic glass-forming alloys in a less time-consuming way.

1.8 Outline of the thesis

The results of this thesis are presented in the following order. Chapter 2 presents an overview of the five pieces of processing equipment constructed for BMG production. Chapter 3 describes thermodynamics under ultrahigh acceleration, resulting in extra phase formation and eutectic isolation. Chapters 4 and 5 apply this eutectic isolation ability to glass formation, presenting three different examples of finding a eutectic composition in one sample each with the result of increasing GFA. Chapter 6 concludes with a short summary and outlook.
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2 Construction of metallic glass processing equipment

This chapter describes metallic glass processing equipment that was constructed within the framework of this thesis along with the equipment’s specific applications. The chapter is concluded by a brief discussion of the unique high-temperature centrifugal system required to process molten metallic samples at 60,000 g.
2.1 Processing of BMGs

Production of monolithic BMGs is almost always critically linked to the purity of the constituent elements and the processing atmosphere with regard to oxygen contamination. For this reason, high-purity elements (>99.99%) are used and an exact processing procedure is followed. The following purification procedure is used for most of the processing methods discussed here: (1) all surfaces and samples are cleaned with acetone and ethanol; (2) rough vacuum to 10^{-2} mbar (rotary vane pump) is used; (3) purging is carried out with high purity argon (Ar) gas (99.999%) to 800 mbar; (4) steps 1 and 2 are repeated twice; (5) high vacuum to < 5 × 10^{-5} mbar (diffusion or turbo pump); and (6) a final purging with ultra-high purity Ar gas (99.99999%) is performed prior to processing. A Ti or Zr slug, separate from the sample, is melted for 10 - 15 seconds to remove latent oxygen present in the ultra-high purity Ar gas, thus creating a “Ti- or Zr-gettered” atmosphere.

Quite a few laboratory scale heating methods exist, each with advantages and disadvantages in terms of maximum temperature, temperature control, temperature gradient and applicable materials. An overview of various synthesis methods is presented in Table 2.1, which lists the limitations and advantages of each system.

Table 2.1: Summary of common BMG processing techniques highlighting materials to be processed in each and their possible disadvantages.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Maximum temperature</th>
<th>Temperature measure / control</th>
<th>Alloy systems</th>
<th>Disadvantages / Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistive furnace</td>
<td>1200 °C (Limited by heating element and quartz tube)</td>
<td>Good (Thermocouple-controlled)</td>
<td>Au, Pd, Mg</td>
<td>Low max temperature, heating rate, quartz tube</td>
</tr>
<tr>
<td>Arc melting</td>
<td>3000 °C</td>
<td>None</td>
<td>Zr, Fe, Ti, Co, La, Ce</td>
<td>High temperature gradient, little control of temperature, no low-vapor pressure materials</td>
</tr>
<tr>
<td>Silver-boat</td>
<td>2000 °C</td>
<td>Pyrometer (Feedback control to generator)</td>
<td>Zr, Ti, Cu, Co, Mg, Ca</td>
<td>High temperature gradient</td>
</tr>
<tr>
<td>Levitation</td>
<td>3000 °C</td>
<td>Pyrometer (No control possible)</td>
<td>Ca, Mg, Zr</td>
<td>One-piece samples necessary (prealloying)</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>1200 °C (Limited by quartz tube)</td>
<td>Pyrometer (Feedback control)</td>
<td>Zr</td>
<td>Quartz tube reactions</td>
</tr>
<tr>
<td>Injection casting</td>
<td>1200 or 3000 °C</td>
<td>Pyrometer (Feedback control with quartz crucible only)</td>
<td>Zr, Mg, Ca</td>
<td>Quartz tube or BN reactions</td>
</tr>
</tbody>
</table>
At the start of this project the LMPT BMG processing lab consisted of (1) a small arc-melting system; (2) a splat-quenching combination melt-spinning machine; (3) a “silver-boat”; and (4) an Ar-gas-pressure casting box. The small arc-melting system, purchased from Edmund-Buehler, melts samples at up to 3000°C on a water-cooled copper hearth via a low-voltage high-current arc in an inert Ar atmosphere. The combined splat-quenching and melt-spinning machine, also purchased from Edmund-Buehler, inductively melts a sample which is either splatted between a pair of copper plates with a thickness of 20-100 μm or injected onto a rotating copper wheel, resulting in long ribbons of 50-300 μm thickness. The silver-boat is an inductively heated water-cooled copper hearth system for alloying. The Ar-gas-pressure casting box system is also induction-heated, and samples are injected into a Cu mold. If only Zr-based BMGs were required, this equipment would serve well to produce small amounts of material in simple casting geometries. However, as more alloy systems, larger volumes, and more complicated sample shapes were required more equipment was needed.

In order to facilitate sample production of the wide variety of samples needed both by the lab in general and for the second part of this thesis, five pieces of processing equipment were designed and constructed. These included (1) a drop tube for production of metallic glass spheres; (2) a piston-injection molding system; (3) a silver-boat exclusively for Mg processing; (4) an electromagnetic levitation alloying-casting system; and (5) a melt extraction or amorphous wire spinning system. Each of these pieces of equipment were designed and constructed in-house with technical support from the LMPT and the ETHZ Department of Materials workshop.

2.2 Drop tube

A 2.5 meter drop tube was constructed to test the possibility of producing metallic glass spheres. Possible applications range from high-performance ball bearings to ballpoint pens. This system is presented first, as it was a modification of a casting box built for the author’s Master’s thesis. The existing Ar-gas-pressure injection molding system is shown in Fig. 2.1(a) and in the inset of Fig. 2.1(b). The inset illustrates the main components, including the induction heating coil, a necked quartz tube containing the sample, and a copper mold. The induction coil melts the
sample inside the quartz tube under vacuum and the Ar pressure forces the melt into the copper mold. The drop tube system was created by removing the copper mold and replacing the bottom vacuum chamber plate with 2.5 meters of vacuum chamber as shown in Fig. 2.1(b) and (c). The same procedure for melting was followed except that a helium atmosphere of 800 mbar was used to cool the droplets during the 2.5 meter fall. Using just a simple circular opening in the quartz tube, spheres of 0.2 to 1.2 mm could be solidified. This procedure of making metallic glass spheres is being evaluated for industrialization by a spin-off company (Advanced Metal Technology AG) from the ETH Zurich.

Figure 2.1: (a) Ar-pressure injection vacuum chamber; (b) constructed drop tube, (inset) inside vacuum chamber showing induction coil, quartz tube and Cu mold; (c) side view of drop tube showing generator connected to the rear side.
2.3 Injection molding system

The original Ar-pressure casting box, as briefly described above, was designed to cast 1-5 cm³ of Zr-based metallic glasses. The coil size, crucible size, crucible material (quartz), and mold size were all designed around the specific properties of Zr-based alloys. Other materials can be processed, however, with the following limitations: (1) low vapor pressure; (2) a melting point lower than the softening point of quartz glass (~1100ºC); and (3) no reactions with quartz glass. Also inherent in the gas-pressure injection molding design is the possibility of producing hollow samples, which is exaggerated for low surface tension materials, e.g. magnesium (Mg), and calcium (Ca). To overcome some of these complications and to produce more complicated sample geometries the injection molding system (IMS) was built.

The conceptual design of the IMS, as shown in Fig. 2.2, is very similar to that of the Ar-pressure box, but is inverted so that the molten sample is pressed by a piston from the bottom instead of by gas pressure from the top. This eliminates two of the problems of the original casting box design. First, the quartz tubes had to be exactly formed to match sample viscosity/surface tension to prevent the sample from dripping before melting fully; this is not necessary with the new design. Second, the possibility that gas pressure will produce hollow samples is reduced because the piston geometry fills the mold evenly. Also, due to the simple geometry of the crucible, it is feasible to use boron nitride or graphite crucibles as they can be reused. Further, a variety of crucible materials allows the crucible to be matched to a sample composition so that higher melting materials can be processed and specific reactions can be avoided. To cast Zr-, Al-, Ni-, Pd- and rare-earth-element-based alloys the quartz/graphite crucible assembly (shown in Fig. 2.3) is used, while cubic boron nitride (CBN)/graphite crucible assemblies are used for Mg- and Ca-based alloys. During melting the sample sits inside the crucible on top of the piston. When the pre-set temperature, measured by a pyrometer, is reached the pneumatic system is triggered and quickly pushes the melt into the mold.
The machine consists of five major parts: (1) the high-frequency induction coil to heat the specimens; (2) the pneumatic piston and control system; (3) the interchangeable crucible system and crucibles; (4) an external support frame to hold the vacuum chamber and support the injection force; and (5) a high vacuum chamber to contain the mold and crucible assembly, while allowing inductive heating and linear motion pass-through. A 3D model and a full set of technical drawings were made and the machine was built in-house with the final assembly shown in Fig. 2.3.
With the IMS system complete, the Mg-based samples for the second half of this thesis project were cast. Rods of 3 mm diameter and lengths up to 100 mm could be produced, demonstrating the high aspect ratios possible with this system. The IMS has meanwhile also been used for various Ph.D. projects in the LMPT group, including microforming of metallic glasses and bulk metallic glass matrix composites.

Compared to the Ar-pressure system, the IMS offers more control over the casting process because the temperature and injection speed can be controlled. The piston geometry also provides a uniform pressure while driving the molten alloy into the mold, creating fully dense samples as shown in Fig. 2.4(a) as compared to hollow samples from the Ar gas system as shown in Fig. 2.4(b).
2.4 Silver-boat

As used in the drop tube and IMS, induction heating is also used for the silver-boat. The name silver-boat results from the first boats built, which were made of silver for the good thermal conductivity. However, today Cu is used, for economic reasons. The generators used for induction heating vary greatly depending on sample size and required power: small samples, for example, require a high frequency. Using a high-frequency generator has advantages because (1) induction coils are simple to construct and modify; (2) the heating power/rate is easily adjustable; and (3) the induced electrical currents generate stirring in the melt and thus homogenizes it.

The already existing silver-boat was designed for very large volumes of material, and accordingly the induction coil was matched to a large sample size, rendering processing of small amounts of material impossible. The second silver-boat was, therefore, designed to facilitate production of small amounts of material more suitable for alloy development. Silver-boats are simple constructions [see Fig. 2.5(a)], consisting of an induction coil, a vacuum chamber with quartz tube and inert-gas inlet, and a water-cooled copper tube (inside the glass tube) with indents on the surface. Fig. 2.5(b) depicts the silver-boat in operation, melting a Zr-based alloy. The multiple indents, seen in Fig. 2.5(b), allow melting of various amounts of material, multiple samples, and the Ti getter. This silver-boat system was used to produce various alloys for the second half of this Ph.D. project. It also allows for the production of BMG composites using foreign-particle reinforcement [1]. In this case, the foreign particles are added to the metallic glass melt and homogenized by the inductive stirring.
A downside of this type of system is the water-cooled Cu hearth on which the sample is melted. The silver-boat was designed so that contamination from hot crucibles (graphite, quartz and ceramics) could be avoided, but has the flaw that heat is lost to the Cu hearth and that thermal gradients exist in the sample. This leads to limitations on the maximum temperature possible and microstructural inhomogeneities. This problem is even more pronounced in low surface tension metals, as shown in Fig. 2.6. Upon melting, high surface tension metals ball up causing an increase in sample cross-sectional area which improves heating from the coil and also decreases the contact area with the boat, minimizing the thermal transfer to the boat. Low surface tension metals do the opposite, with the result that alloying is very difficult. Because both the arc-melting system, with too-high temperatures, and the silver-boat, due to its inability to heat enough, are not ideal systems for processing Ca and Mg, another system was required and is presented in the next section.
2.5 Electromagnetic levitation system

Various systems using induction heating already been discussed; however, the real versatility of this technique becomes apparent when electromagnetic (EM) levitation is used, because it makes possible containerless processing. This drastically reduces contamination compared to traditional hot crucibles and produces a more homogeneous sample temperature compared to the water-cooled copper hearth configuration. The heating aspect is still via induction; however, the coil is shaped like a cone so as to produce a varying magnetic field, which can be designed (because of the resulting Lorentz force) to support the sample’s weight.

The physics behind EM levitation are described extensively in literature; see Refs. [2,3,4]. The essential equations and parameters are briefly summarized here. The Equations (2.1)-(2.3) express the lifting force with $K_z$ (in Newtons) for an assumed spherical sample lying on the coil axis:

\[
K_z = \frac{3}{2} \mu I^2 a^3 G(x) \sum_n \frac{b_n^2}{[b_n^2 + (z - z_n)^2]^{3/2}} \sum_n \frac{b_n^2(z - z_n)}{[b_n^2 + (z - z_n)^2]^{3/2}}
\]  

(2.1)

with

\[
G(x) = 1 - \frac{3}{4x} \left( \frac{\sinh 2x - \sin 2x}{\sinh^2 x + \sin^2 x} \right).
\]

(2.2)

with

\[
x = \frac{a}{\delta} = a(\mu I \gamma)^{1/2}.
\]

(2.3)
Here, $\mu$ is the permeability, $I$ the current, $f$ the frequency, $\gamma$ the electrical conductivity, $\delta$ is the skin depth ($\delta = 1/\sqrt{(2\pi \mu \gamma f)}$), and $a, b, z$ are the geometries of sample and coil expressed in meters [see Fig. 2.7(a)].

The force $K_z$ is a function of the sample and coil geometry, the applied current in the coil, and the parameter $G(x)$ [3]. When designing a levitation system all three of these variables must be taken into account based on the required samples. First, it is important to match the coil size to the approximate sample size desired. Too large a coil and the sample will not levitate, too small and the sample will not fall cleanly out of the coil. For maximum levitation, the opening angle of the bottom wraps, i.e. the cone angle, should be $\sim 60^\circ$ and the top bucking wrap should have approximately the same diameter as the desired sample volume. Second, the more current applied to the coil the more levitation it provides, which is useful for dense elements and compensates for decreasing electrical conductivity with increasing temperature. Third, Equation (2.2) is a correction factor which takes into account non-linear effects in case the skin thickness becomes more than 1/10th the radius of the sample. This can be avoided by increasing the frequency.

The main components of the EM levitation system are (1) a conical coil with a reverse or “bucking” turn on top; (2) a vacuum chamber with appropriate gas connections; (3) a manipulator arm to support the sample prior to levitation; (4) a suction casting system to improve mold filling; and (5) a copper mold in which the material is cast. The system in our lab [Fig. 2.7(b)] was constructed to process samples of 1-2 cm$^3$, and Ca-, Mg-, Al-, Ti-, and Zr-based samples have successfully been levitated. In practice, samples must have enough cohesion to remain in one piece during levitation. This is typically brought about by pre-alloying samples in the arc (Zr-based) or mechanically pressing pure elements into a pellet (Ca- and Mg-based). At the beginning of the experiment samples are supported by a movable arm [see Fig. 2.7(b)], which is removed as soon as the coil is energized and the material levitates. The onset time of melting during levitation depends strongly on the specific weight of the material and the applied power needed to support levitation. For Zr- or Ti-based alloys, melting occurs within five seconds, while for Ca- and Al-based metals up to 60 seconds are needed. Once the molten sample is homogenized (enhanced by the induced stirring), the coil is switched off and the melt drops onto a copper mold where a suction system assists in filling the mold.
2.6 Melt extraction system

In collaboration with another Ph.D. project [5], a melt extraction (ME) system was constructed to produce metallic glass wires. In this context, metallic glasses can show high strength in combination with ductile behavior, as improved plastic strain is observed with small sample dimensions [6]. Similar to the previous construction projects, a 3D model was drawn up for the ME system [see Fig. 2.8(a)] and built in-house. The completed machine can be seen in Fig. 2.8(b), with production of an amorphous wire in Fig. 2.8(c). Thus far Zr- and Mg-based amorphous wires have been successfully produced using this apparatus; the advantageous mechanical properties of the metallic glass wires are currently being tested.
2.7 **High-temperature ultrahigh acceleration centrifuge**

Although not a BMG processing or quenching system, the centrifuge is included here as its construction is quite a complicated materials problem in itself, it is used for BMG alloy development, and it introduces well the experimental procedure for the following sections. The experiments were performed in collaboration with the company Test Devices in Hudson, MA, USA [7], which usually performs low cycle fatigue and burst testing for jet turbine manufacturers. For our experiments, a rotor made of IN 100 (a Ni-based gamma-gamma prime superalloy) was constructed, which contains eight cavities for the samples. Samples were housed inside molybdenum crucibles and vacuum-sealed inside Inconel (an austenitic Ni-based superalloy) capsules, which fitted with an accuracy of ± 0.1 mm into the rotor cavities. To achieve a relatively constant acceleration $a$ at the sample position, a rotor with a diameter of 25 cm was constructed. The technical drawing for the rotor is shown in Fig. 2.9. The rotor containing the samples was connected to an
air-powered drive turbine and encased inside a circular furnace. For security purposes, the whole spinning setup was housed inside a containment unit consisting of multiple layers of steel, lead, and concrete. A diagram showing the drive turbine, rotor and furnace is depicted in Fig. 2.10. The rotor temperature was monitored by four thermocouples directly attached to the rotor, within a centimeter of the samples. With this configuration the temperature of the samples could be measured with an accuracy of $\pm 2$ K.

Figure 2.9: Schematic produced by Test Devices, Inc. for the top half of the centrifugal rotor with the 8 cavities for samples shown.
Figure 2.10: Schematic produced by Test Devices, Inc. showing (from top to bottom) including (1) the air-turbine drive device; (2) the top safety cover; (3) the high-temperature furnace; and (4) the high-acceleration rotor.

2.8 References

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3 Thermodynamic considerations at ultrahigh gravitational acceleration

A thermodynamic model is presented for predicting atomic-level stratification and the evolved volume fractions of primary phases formed upon cooling a binary metallic melt under ultrahigh acceleration. The binary Au–Si eutectic (Au$_{81.4}$Si$_{18.6}$) processed under 60,000 g exhibits both primary phases and the eutectic, thus apparently violating the Gibbs phase rule under normal gravity. The volume fractions of both primary phases are correctly predicted by the model. Centrifugal processing of the ternary Au–Si–Ge eutectic (Au$_{79.4}$Si$_{14.1}$Ge$_{6.5}$) is also presented. Here, the model does not accurately describe the volume fractions of the primary phases, since the starting (ternary) eutectic composition changes towards the (binary) Au–Ge eutectic, which has a lower liquidus temperature. The latter can be used to find eutectic compositions in complex multicomponent alloys, which is of great importance for bulk metallic glass alloy development.

3.1 Introduction

Large inertial forces applied to a liquid or a liquid/solid mixture during solidification or melting produces a number of physical effects including sedimentation, liquid “clarification”, separation, and stratification. These phenomena are well known from the biological and medical fields, and in the enrichment of U\textsuperscript{235} for nuclear power. However, processing of metallic liquids under high inertial forces remains largely unexplored in metallurgy and materials science. This is partly due to the experimental difficulties that result when processing a metallic liquid at temperatures of several hundred degrees centigrade and accelerations of several $10^5$ g ($g = \text{gravitation acceleration}$). Therefore, it has yet to be fully recognized that high accelerations (>10\textsuperscript{5} g) modify the chemical potential of the involved species and thus the corresponding phase equilibria, which are determined by temperature, pressure and concentration.

It is shown in a centrifugal experiment that the concentration of each atomic species becomes spatially dependent, i.e. the sample has no longer a single composition but shows a composition gradient prior to solidification. This observation bears three fundamental physical consequences. First, under ultrahigh acceleration more phases than predicted by the Gibbs phase rule ($f = N - P + 2$, where $f = \text{the degrees of freedom}$, $N = \text{number of components}$, $P = \text{number of phases}$) can exist. This may, in the case of a simple binary system, lead to the recording of the complete phase diagram by processing only one sample. Second, the volume fractions of the primary phases may be predicted by theoretical considerations accounting for the induced atomic-level stratification. Third, if the starting alloy composition is not the global eutectic, the system may change towards the composition with the lowest liquidus temperature. Exploiting this effect, the lowest possible eutectic composition in complex multicomponent alloys may also be found in only one sample. The latter has great potential for the development of new bulk metallic glass (BMG) alloys as eutectics are thermodynamically predicted to have good glass-forming ability (GFA) [1].

The theory of stratification and sedimentation in liquids at the macroscopic level is well established, and is based on the density difference between solid particles in a fluid, as described by Lamm [2]. Here we apply these equations at the atomic level to encompass the influence of large inertial accelerations on phase equilibria.
We start our discussion with thermodynamics under ultrahigh acceleration and demonstrate the resulting modifications on phase equilibria in a binary system. For a binary system with two phases of different densities, the thermodynamic effects arise from a pressure gradient \( \frac{\partial p^\nu}{\partial h} \) impressed on each phase \( \nu \) over an incremental change in height \( h \)

\[
\frac{\partial p^\nu}{\partial h} = \rho^\nu a , \quad \text{(3.1)}
\]

where \( \rho^\nu \) is the average density of phase \( \nu \), and \( a \) represents the inertial acceleration, expressed in multiples of gravitational acceleration \( g \). The variable \( h \) is the position measured from the top of a specimen in the direction of acceleration.

The key result is that the total chemical potential becomes acceleration-dependent. The chemical potential (per mole) for component \( X \) in phase \( \nu \) changes so that it is not only dependent on the partial molar Gibbs energy, \( g^\nu_x(c_x,T,p) \), but also on the gravitational potential, i.e.,

\[
\mu^\nu_x = g^\nu_x(c^\nu_x,T,p) - M^\nu_x ah , \quad \text{(3.2)}
\]

where \( M^\nu_x \) is the atomic mass and \( c^\nu_x \) is the concentration of component \( x \) in phase \( \nu \).

At or above accelerations of \( 10^4 \) to \( 10^5 \) \( g \), \( M^\nu_x ah \) contributes significantly; e.g., in the Au–Si binary system, \( M^\nu_x ah \) is on the order of 2 kJ/mol for \( a = 10^5 \) \( g \) and \( h = 5 \) cm, as compared to the heat of fusion for gold of approximately 10 kJ/mol.

Let us in the following assume a simple eutectic alloy \( A_{1-c}B_c \), where \( c \) is the local alloy composition \( (0 < c < 1) \), with a liquid phase \( \lambda \) and two primary crystalline phases “A” and “B” with structures \( \alpha \) and \( \beta \), respectively. Under steady-state equilibrium conditions the chemical potential is constant for both A and B atoms in each phase. At constant temperature, the variation of the concentration of a given phase in a field of uniform acceleration \( a \) can be derived. Using Equation (3.1) and the derivative \( \partial g / \partial c \) yields

\[
\frac{\partial c^\nu_x}{\partial h} = \frac{(\rho^\nu_x - \rho^\nu) v^\nu_x a}{(1-c^\nu_x) \frac{\partial^2 g^\nu_x}{(\partial c^\nu_x)^2}} , \quad \text{(3.3)}
\]

where \( g^\nu \) is the (total) molar Gibbs energy in phase \( \nu \), \( v^\nu_x \) is the partial molar volume of \( X \) atoms in phase \( \nu \), and \( \rho^\nu_x \) (and \( \rho^\nu \)) are the partial (and average) molar density of the
liquid solution subjected to the inertial acceleration \( a \). Equation (3.3) is a general solution, which expresses the induced concentration gradient in terms of the molar Gibbs energy of a binary solid solution of any liquid or solid phase. To our knowledge, this equation has not yet been recognized in literature.

In the following, the derived equation is tested for validation of atomic stratification in the melt. To do so, the binary eutectic \( \text{Au}_{81.4}\text{Si}_{18.6} \) and the ternary eutectic \( \text{Au}_{79.4}\text{Si}_{14.1}\text{Ge}_{6.5} \) have been investigated. The \( \text{Au}–\text{Si} \) system was selected since it contains a simple binary eutectic at a composition of 18.6 at.% Si and 360°C. Moreover, the densities of Au and Si are significantly different (19.0 and 2.3 g/cm\(^3\), respectively), so that a particularly high concentration gradient in the liquid is expected from Equation (3.3). Also with regard to metallic glasses, which has become an exciting research field itself [3,4], \( \text{Au}–\text{Si} \) was the first metallic glass, discovered by Duwez and co-workers in 1960 [5].

3.2 Experimental procedure

The centrifugal experimental setup at Test Devices, Inc. (Hudson, MA) consists of a disc-shaped rotor, which holds eight samples per run, a safety spin pit, a furnace for melting the samples, and an air turbine able to reach 60,000 g or an angular frequency of 2600 Hz. Samples were contained in molybdenum crucibles during melting and vacuum-sealed in Inconel capsules to protect against oxidation. After heating to 500°C the samples were cooled down to room temperature at 4°C per minute during continuous centrifugation at 60,000 g. Longitudinally sectioned samples were investigated by optical and scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) to deduce chemical information. Further experimental details are found in a previous publication [6] and in chapter 2.

3.3 Results and discussion

The optical image, shown in Fig. 3.1(a), depicts the whole \( \text{Au}–\text{Si} \) sample after processing while Figs. 3.1(b-d) show (b) the primary Si phase, (c) the eutectic, and (d) the primary Au phase. Primary phase volume fractions of 0.52 % for Si and 1.78 % for Au were measured, with the remaining 97.7 % solidifying as the eutectic. This
result clearly demonstrates that both primary phases and the eutectic can be produced under ultrahigh acceleration in one sample. It is important to point out that at normal acceleration this result is not possible, as the maximum number of phases is limited to $N = 3$ by the Gibbs phase rule at constant pressure (i.e. a maximum of two phases can solidify): at 1 g acceleration, only primary Au or primary Si would form along with the eutectic, or simply the eutectic alone would form, depending on the starting composition. At ultrahigh acceleration, in contrast, atomic stratification can occur in the melt prior to solidification, leading to Si-enrichment at the top of the sample and Au-enrichment at the bottom. Thus, upon cooling of the melt, both liquidus lines on either side of the eutectic are intersected so that both primary phases form, as seen in Fig. 3.1.

Figure 3.1: (a) Au–Si sample separated into two primary phases and the eutectic; (b) the primary Si phase; (c) the eutectic; and (d) the primary Au phase.

To explain the results of Fig. 3.1 more quantitatively, the general Equation (3.3) is modified to calculate the induced concentration gradient in a simple binary alloy system. The following assumptions are made for further calculation: ideal solution behavior in a simple binary system, zero heat of mixing, and the sum of the...
concentration over the whole sample at any time is equal to the starting eutectic concentration. The selected Au–Si system satisfies these three assumptions very well. Integrating Equation (3.3) over the total sample height $h_f$ the concentration of component $x$ in phase $\nu$ as a function of height $h$ then yields

$$c^\nu_x = \frac{\widetilde{A}c^\nu_x h_f}{\exp(\widetilde{A} h_f) - 1} \exp(\widetilde{A} h),$$  \hspace{1cm} (3.4)

with $\widetilde{A}$ defined as

$$\widetilde{A} = \left( \rho^\nu_x - \rho^\nu_v \right) \nu^\nu_x a \frac{k_B T}{c^\nu_v}. \hspace{1cm} (3.5)$$

The use of the experimental and materials parameters for the current Au–Si alloy leads to a calculated concentration gradient as shown in Fig. 3.2. The average Au and Si (eutectic) concentrations are plotted as dashed lines to compare the effect of the induced atomic stratification in the liquid phase. The Au concentration is shifted towards the sample bottom (i.e. to the outside of the centrifuge), as expected from its larger density. The opposite behavior can be seen for Si, which is enriched at the top of the sample. The maximum percentage increase is 1.2 at.% for Au (bottom) and 1.4 at.% for Si (top). Integrating the shaded grey areas, the effective percentage of the total sample length, which is enriched by the maximum amount for each element, is calculated to be 25.4 % for Au and 24.9 % for Si.

![Figure 3.2](image.png)

Figure 3.2: Calculated atomic-level stratification (concentration gradient) due to ultrahigh gravitational acceleration, calculated according to Equation (3.4) for a binary Au–Si alloy processed at 60’000 g and 500°C.
Using the lever-arm rule along with the equilibrium Au–Si phase diagram, the volume fraction of primary Au for a sample of composition Au$_{82.6}$Si$_{17.4}$ (1.2 at.% richer in Au than the eutectic) is calculated to be 6.45 vol.% (1.2/18.6). The same is done for the volume fraction of primary Si for a sample of composition Au$_{80}$Si$_{20}$ (1.4 at.% richer in Si than the eutectic) which results in 1.8 vol.% (1.4/81.4). These volume fractions need to be multiplied by the effective percentage of the total sample length to find the predicted primary volume fractions, which results in 1.64 vol.% for Au and 0.45 vol.% for Si. These theoretically predicted values compare very well with the experimental values of 1.78 vol.% Au and 0.52 vol.% Si (extracted from Fig. 3.1).

In the following we address the ternary case. Figure 3.3 shows the centrifugally processed Au–Si–Ge system, where three primary phases and a eutectic phase can be distinguished. This reveals again the apparent violation of the Gibbs phase rule under ultrahigh gravity, as the sample concentration is no longer a point in the phase diagram but spreads into a line. Figure 3.3(b), taken at the top of the sample, shows primary Si (dark black) and the solid solution Si$_{78}$Ge$_{22}$ (grey particle); Fig. 3.3(c) shows the eutectic phase and Fig. 3.3(d), taken at the bottom of the sample, shows primary Au with a eutectic in between. The volume fractions were determined to be 0.05 vol.% Si, 1.79 vol.% Si$_{78}$Ge$_{22}$, 96.24 vol.% eutectic, and 1.92 vol.% Au.

Figure 3.3: (a) Au–Si–Ge sample, 3 cm in length, separated into three primary phases and the eutectic; (b) the primary Si phase and the Si-Ge solid solution; (c) the eutectic; and (d) the primary Au phase.
Although Equation (3.4) predicts atomic-level stratification and thus the occurrence of more phases than predicted by the Gibbs phase rule, it cannot be used in the ternary case to predict the experimentally determined phase volumes as the final eutectic may be different from the starting eutectic. In fact, the starting ternary eutectic $\text{Au}_{79.4}\text{Si}_{14.1}\text{Ge}_{6.5}$, ($T_l = 362°C$) lies on the only liquidus line connecting the two binary eutectic compositions ($\text{Au}_{81.4}\text{Si}_{18.6}$ at 363°C and $\text{Au}_{72}\text{Ge}_{28}$ at 361°C). Apparently, this is a local eutectic, but not the global eutectic. Consequently, the liquid composition moves along the liquidus line towards the (global) Au–Ge binary eutectic. Such behavior was not possible in the binary example since, there the sample started already at the global eutectic composition.

Thus, in the ternary case, the observed primary phases form not only because of atomic-level stratification but also because of the change in liquid composition towards the deepest eutectic. The above theoretical considerations do not account for the latter case. However, the ability to identify the lowest lying eutectic composition in multicomponent alloys is of highest value for BMG alloy development. [6, 7, 8, 9].

3.4 Conclusions

In summary, a model is presented which describes atomic-level stratification in metallic liquids under ultrahigh gravitational acceleration. This atomic-level stratification, as shown experimentally for binary Au–Si, leads to both primary phases and the eutectic existing in one sample. The presented model accurately predicts the evolved primary phase fractions from only experimental and materials parameters. In the ternary case, multiple primary phases evolve, but a change of liquid composition towards the deepest eutectic can also be observed. The latter is of great importance for the development of bulk metallic glasses, i.e. multicomponent metallic systems with deep eutectic compositions.

3.5 Acknowledgments

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3.6 References

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Two eutectic multicomponent La-based alloys with high glass-forming ability were identified by ultrahigh acceleration centrifugal processing during cooling of compositionally off-eutectic melts. The identified ternary composition, La$_{64}$Al$_{13}$Cu$_{23}$, was cast amorphously to 3 mm in diameter, comparable to previous studies. The quaternary composition, La$_{65}$Al$_{13}$Ni$_{10}$Cu$_{12}$, was cast to 10 mm in diameter, showing the highest glass-forming ability for this system. These results show that instead of extensive traditional alloy development, it is sufficient to study one centrifugally processed sample to discover the composition with the deepest eutectic, which (as predicted by Turnbull) produces good glass-forming ability.

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4.1 Introduction

Since the first discovery of bulk metallic glasses (BMGs) in the 1960s [1], their glass forming ability (GFA) has mainly been improved through intensive alloy development work [2]. During this period theoretical and empirical descriptions of GFA have been put forth as guides for further development. Turnbull first linked the GFA with the ratio between the glass transition ($T_g$) and the liquidus temperature ($T_l$) [3]. According to this criterion, a high GFA is achieved if the reduced glass transition temperature ($T_{rg} = T_g / T_l$) approaches $2/3$. As the glass transition temperature does not vary significantly for a given main alloy component [4], the liquidus temperature must be reduced to maximize $T_{rg}$. This has focused alloy development on the discovery of eutectic compositions in order to minimize $T_l$.

It was further recognized that for good GFA the deep eutectic compositions require several characteristics, such as a negative heat of mixing, significant atomic size mismatch (more than 12%), and a composition of multiple elements [5]. This premise was expanded upon by the “confusion principle” [6] or the role of “complexity and frustration” [7]. These concepts state that the more diverse the included atomic species, the less likely the system will be to find a crystal structure that can accommodate all the elements, i.e. the crystal structure will be frustrated or confused by chemical disorder. Therefore, the suggestion is that alloy development should be directed towards finding complex multicomponent eutectic compositions.

The problem with probing multicomponent space for eutectics becomes immediately clear when the number of sample compositions to be prepared and analyzed is considered: 100 samples for binary, over 4800 for ternary, over 150,000 for quaternary, and several millions for quinary systems, assuming a 1 at.% difference for each sample. Even following the guidelines of Inoue [5] and alternative approaches [8,9], such an alloy development endeavor is very labor-intensive and requires a large investment in raw materials to identify a eutectic composition.

In order toshortcut this time-consuming alloy development process, we present a new method for finding eutectic compositions. By processing the metallic melt under ultrahigh gravity, separation of primary crystallizing phases occurs upon cooling from the melt, changing the remaining liquid composition towards the eutectic, which solidifies last and can be clearly identified. Once identified, these multicomponent eutectic compositions are remade and tested for GFA. Preliminary
studies successfully showed that eutectic compositions form when a multicomponent melt is cooled under ultrahigh gravity \cite{10,11,12}. Here we go one step further and show that the eutectic compositions found do in fact exhibit good GFA when reproduced in the lab. This is demonstrated with results obtained for ternary (La$_{55}$Al$_{25}$Cu$_{20}$) and quaternary (La$_{55}$Al$_{25}$Ni$_{10}$Cu$_{10}$) La-based alloys, originally developed by Inoue \cite{13,14}. These starting compositions were chosen for good GFA but are of off-eutectic composition.

### 4.2 Experimental procedure

The three- and four-component La-based starting alloys were prepared by arc melting of the individual elemental components (La: 99.8\% from Treibacher Industrie AG; Al: 99.999\%, Ni: 99.97\%, and Cu: 99.999\% from CERAC, Inc.) on a water-cooled copper hearth in a Ti-gettered ultra-high purity Ar atmosphere at a gauge pressure of 0.2 bar. Complete homogenization of the samples was ensured by flipping between each of four meltings, followed by suction casting into a copper mold of 3 mm diameter and 30 mm length. For centrifugal processing, the samples were placed into molybdenum crucibles, shown in Fig. 4.1(a), of inner diameter 3 mm and 3 mm wall thickness so as to contain the sample when melted. To suppress oxidation during melting, the crucibles were hermetically sealed by electron beam welding in a vacuum of $10^{-4}$ mbar inside an Inconel (austenitic Ni-based superalloy) capsule, also shown in Fig. 4.1(a). The capsules fit directly into an IN100 (gamma-gamma prime Ni-based superalloy) rotor which, when spun at an angular frequency of 2600 Hz, produces an applied acceleration of 60,000 $g$ at the center of the samples. Centrifugal processing was performed in collaboration with the company Test Devices, Inc. in Hudson, MA, using the experimental setup shown in Fig. 4.1(b). During the experiment, the samples were heated to 680$^\circ$C, spun for two hours and finally cooled down to room temperature at 4$^\circ$C per minute. In-depth details of the centrifugal experimental setup can be found in a previous publication \cite{12} and in chapter 2.
Once removed from the Inconel capsules, the samples were sectioned lengthwise along the applied gravitational axis with a diamond saw, and metallographically prepared for optical and scanning electron microscopy (SEM). SEM investigations were performed with a CamScan (Series 4) microscope with an attached Norman Instruments energy-dispersive X-ray (EDX) spectrometer for elemental composition analysis and mapping. All compositions listed here are in atomic percent and are assumed to have an accuracy of ±1 at.%, after calibration to a known reference. Samples were imaged using backscattered electron (BSE) detection mode. BSE images were assembled into montages showing the elemental contrast between the separated phases. The composition for each separated phase was determined by EDX with a minimum of 5 measurements each.

The eutectic microstructure compositions measured by EDX for each sample were then remade in the lab following the arc alloying method described above. Splats of approximately 35 μm thickness were produced in a splat quenching system.
(Edmund Bühler GmbH) as fully amorphous references. Cylindrical, or rod-shaped, samples of three, five, seven, and ten millimeters diameter were produced by casting in an arc-melting system to test the maximum critical casting thickness.

Differential scanning calorimetry (DSC) was performed using a SEIKO DSC200 at a scan rate of 0.333 K/s under continuous argon flow. X-ray diffraction (XRD) was carried out on longitudinally-sectioned samples using a Philips X’Pert PRO MPD XRD with Cu Kα source, operated at 40 kV and 45 mA, in the θ-2θ configuration. The stated critical casting thicknesses, as determined by DSC and XRD, are for the specified starting elemental purities, alloying method, and casting process only.

4.3 Experimental results: Centrifugal processing

4.3.1 Ternary La-based alloys

Fig. 4.2(a) is a montage which shows the whole ternary La-based sample (La₅₅Al₂₅Cu₂₀) after centrifugation, where the ‘top’ and ‘bottom’ are labeled with respect to the applied acceleration direction. The molybdenum crucible, which was left to ensure the mechanical stability of the sample, is visible at the far right of Fig. 4.2(a). The lower set of micrographs [(b)-(d)] presents an enlarged, sectional view of the sample. The BSE SEM micrograph shown in Fig. 4.2(b) provides chemical and microstructural contrast information. Fig. 4.2(c) and (d) show EDX maps, in which the elements Al and Cu are highlighted according to their abundance.
Figure 4.2: (a) La$_{55}$Al$_{25}$Cu$_{20}$ (starting composition) sample separated into two primary phases and eutectic La$_{64}$Al$_{13}$Cu$_{23}$; (b) BSE SEM image; (c-d) EDX maps showing (c) Al-rich phase La$_{56}$Al$_{35}$Cu$_9$ and (d) Cu-rich La$_{40}$Al$_{20}$Cu$_{40}$.

The ternary La-based alloy separated into two primary phases and one eutectic microstructure. The phase compositions determined by EDX are [from top to bottom in Fig. 4.2(a)]: a plate-like Al-rich phase, La$_{56}$Al$_{35}$Cu$_9$ [see Al EDX map, 4.2(c)]; eutectic La$_{64}$Al$_{13}$Cu$_{23}$ (darkest phase in the BSE image, Fig. 4.2(b) or 4.3); and a Cu-rich angular phase, La$_{40}$Al$_{20}$Cu$_{40}$ [see Cu EDX map, Fig. 4.2(d)]. Also note that the phases have separated according to (calculated) density with a positive gradient from top to bottom. Fig. 4.3 shows the eutectic structure in higher magnification, surrounded by the Al-rich phase.
Figure 4.3: Magnified region of the eutectic microstructure that occupies the central section of the three-component La-based alloy.

4.3.2 Quaternary La-based alloys

The quaternary La-based alloy, La$_{55}$Al$_{25}$Ni$_{10}$Cu$_{10}$, presented in Fig. 4.4(a) shows a less pronounced stratification of phases in comparison to the ternary system. However, the three separate primary phases and one eutectic phase can be clearly identified in the BSE SEM image of Fig. 4.4(b). The three primary phases are an Al-rich phase, La$_{56}$Al$_{36}$Ni$_{17}$Cu$_{7}$ [see Al EDX map (c)]; a Cu-rich phase, La$_{40}$Al$_{70}$Ni$_{17}$Cu$_{23}$ [see Cu EDX map (d)]; and a Ni-rich phase, La$_{34}$Al$_{33}$Ni$_{23}$Cu$_{10}$ [see Ni EDX map (e)]. The Al- and Cu-rich phases have compositions similar to the two primary phases seen in the ternary alloy, with Ni partially substituting Cu. The eutectic, La$_{65}$Al$_{13}$Ni$_{10}$Cu$_{12}$, is shown at increased magnification in Fig. 4.5.
Figure 4.4: (a) Quaternary La$_{55}$Al$_{25}$Ni$_{10}$Cu$_{10}$ (starting composition) separated into three primary and one eutectic phase (La$_{65}$Al$_{13}$Ni$_{10}$Cu$_{12}$); (b) BSE SEM image; (c-e) EDX maps showing (c) Al-rich La$_{56}$Al$_{36}$Ni$_{10}$Cu$_{7}$, (d) Cu-rich La$_{40}$Al$_{20}$Ni$_{17}$Cu$_{23}$, and (e) Ni-rich La$_{34}$Al$_{33}$Ni$_{23}$Cu$_{10}$.

Figure 4.5: Magnified region of the eutectic structure in the four-component La-based alloy.

### 4.4 Experimental results: Alloy development

#### 4.4.1 Ternary La-based alloys

The DSC scans shown in Fig. 4.6(a) were obtained for a splat-cooled sample with 35 μm thickness, as well as for 3 mm and 5 mm cast samples, all reproduced from the three-component eutectic phase, La$_{64}$Al$_{13}$Cu$_{23}$. The splat and the 3 mm
sample clearly display a glass transition at 122°C followed by an undercooled liquid region of 58°C and three exothermic peaks at temperatures of 180, 200, and 250°C, respectively, indicating multiple crystallization events from an originally amorphous state. The 5 mm sample, in contrast, only shows a straight line. The XRD plots, shown in Fig. 4.6(b) for the same samples, show crystalline peaks for the 5-mm-thick sample, while both the splat and the 3-mm-thick samples only display two amorphous halos typical of an amorphous structure.

Figure 4.6: (a) DSC and (b) XRD scans of the centrifugal alloy La$_{64}$Al$_{13}$Cu$_{23}$ showing that the splat and the 3-mm-thick sample are amorphous while the 5-mm-thick sample is crystalline.

The melting intervals for the centrifugal alloy and two reproduced alloy compositions are compared in Fig. 4.7. The La$_{66}$Al$_{14}$Cu$_{20}$ is the eutectic composition originally published by Li [15], and is verified here to be eutectic with a critical casting thickness of 2 mm. The alloy La$_{62}$Al$_{14}$Cu$_{24}$ is a composition which was used in Ref. [16] for quaternary/quinary alloy development. Its critical casting thickness was measured here to be 3 mm. All the scans show the onset of melting ($T_{m1}$) close to 400°C with one main peak, immediately followed by a much smaller second peak and even a third peak 40°C higher for the La$_{62}$Al$_{14}$Cu$_{24}$ alloy. The centrifugal alloy (middle curve) can be seen to fall between the other two alloys in terms of both composition and melting interval ($T_{m2} - T_{m1}$), although it still shows increased GFA over the eutectic.
Figure 4.7: DSC scan illustrating the melting intervals of various ternary La-based alloys. The centrifugal alloy La₆₄Al₁₃Cu₂₃ (middle) has a melting interval \( (T_{m2} - T_{m1}) \) similar to Li’s eutectic composition (La₆₆Al₁₄Cu₂₀) \(^{[15]}\), while obtaining the same GFA as La₆₂Al₁₄Cu₂₄ \(^{[16]}\).

### 4.4.2 Quaternary La-based alloys

Fig. 4.8(a) shows DSC scans for samples of varying thickness made from the identified eutectic quaternary phase, La₆₅Al₁₃Ni₁₀Cu₁₂ (see Fig. 4.5). All scans show a glass transition at 124°C followed by an undercooled liquid region of 37°C and three crystallization steps. The crystallization behavior is consistent for all samples except that of 10 mm thickness, indicating that the 10 mm sample is only partially amorphous. Due to some degree of crystallization the remaining amorphous composition has changed, such that the exothermic peaks are different from that of the amorphous samples. The XRD scans in Fig. 4.8(b) confirm this conclusion, with samples up to 7 mm thickness exhibiting only amorphous halos, while the 10 mm sample exhibits some Bragg peaks, showing its partially crystalline structure.
Figure 4.8: (a) DSC and (b) XRD scans of the centrifugal alloy La$_{65}$Al$_{13}$Ni$_{10}$Cu$_{12}$, showing that the samples up to 7 mm thickness are amorphous, while the sample cast to 10 mm reveals some crystallinity.

To compare the GFA of the centrifugally determined compositions with two good glass-forming alloys originally published in a detailed work by Li (La$_{66}$Al$_{14}$Ni$_{10}$Cu$_{10}$ and La$_{62}$Al$_{14}$Ni$_{12}$Cu$_{12}$) [17], we reproduced these alloys in our experimental apparatus. Here we wanted first to rule out any measurement differences, and second to show differences between production methods and equipment. DSC scans of produced samples up to 7 mm casting thickness show a glass transition at 130°C followed by an undercooled liquid region of 43°C and three crystallization steps [see Fig. 4.9(a)]. The crystallization behavior for the 7-mm-thick sample deviates from the pattern present at lower casting thicknesses, which suggests that the 7 mm sample is only partially amorphous. The 10-mm-thick sample even displays no crystallization events, i.e. it has fully crystallized during casting. The XRD scans in Fig. 4.9(b) support this conclusion: below 7 mm casting thickness only amorphous halos are present, while at 7 mm and above crystalline peaks are clearly detectable.
Figure 4.9: (a) DSC and (b) XRD scans of Li’s maximum glass-forming alloy, La$_{62}$Al$_{14}$Ni$_{12}$Cu$_{12}$, showing that the samples from splat to 5 mm thickness are amorphous, while the 7-mm-thick sample is only partially amorphous and the 10 mm sample is completely crystalline.

The influence of varying sample production methods on critical casting thickness is evident when comparing the critical casting thickness of 7 mm found here for Li’s maximum GFA alloy, La$_{62}$Al$_{14}$Ni$_{12}$Cu$_{12}$, with that of 12 mm originally published in Ref. [17]. This difference can be attributed to many processing factors including starting element purities, inert atmosphere purity, alloying method, processed sample volume, and casting method. Since our centrifugally-determined alloy was produced under the same conditions as Li’s best glass-forming alloy, but shows a critical casting thickness of 10 mm, we may conclude that the centrifugally processed sample shows the highest GFA in the La-Al-Ni-Cu quaternary system.

The melting intervals for the centrifugal alloy and two alloy compositions originally produced by Li – the eutectic (La$_{66}$Al$_{14}$Ni$_{10}$Cu$_{10}$) and the maximum glass-former (La$_{62}$Al$_{14}$Ni$_{12}$Cu$_{12}$) [17] – are compared in Fig. 4.10. All the scans show the onset of melting ($T_{m1}$) close to 400°C with one main peak, and for La$_{62}$Al$_{14}$Ni$_{12}$Cu$_{12}$ a second peak 30°C higher is also seen. The centrifugally determined composition, La$_{65}$Al$_{13}$Ni$_{10}$Cu$_{12}$ (middle curve), which is intermediate in composition with respect to the other two alloys, displays a melting interval ($T_{m2} - T_{m1}$) similar to the eutectic composition, La$_{66}$Al$_{14}$Ni$_{10}$Cu$_{10}$, but shows better GFA than Li’s best glass-forming quaternary alloy.
Figure 4.10: DSC scans illustrating the melting intervals of various quaternary La-based alloys. The centrifugal alloy $\text{La}_{65}\text{Al}_{13}\text{Ni}_{10}\text{Cu}_{12}$ (middle) has a melting interval ($T_{m2} - T_{m1}$) similar to the eutectic composition, $\text{La}_{66}\text{Al}_{14}\text{Ni}_{10}\text{Cu}_{10}$, while obtaining a larger GFA than the maximum glass former, $\text{La}_{62}\text{Al}_{14}\text{Ni}_{12}\text{Cu}_{12}$.

4.5 Discussion

Two known La-based, glass-forming, off-eutectic alloys, $\text{La}_{55}\text{Al}_{25}\text{Cu}_{20}$ and $\text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_{10}$ [13,14], processed under ultrahigh centrifugal acceleration, allowed us to short-cut the alloy development process by identifying the deepest eutectic composition via production of only one sample. The separation of primary phases to both ends of the samples was successfully induced by the centrifugal process, and the eutectic/near-eutectic phase was left at the center of the sample. The composition in the ternary alloy changed from $\text{La}_{55}\text{Al}_{25}\text{Cu}_{20}$ to $\text{La}_{64}\text{Al}_{13}\text{Cu}_{23}$, which represents a 3% increase in Cu content, a decrease in Al to 13%, and an increase in La of almost 10%. The quaternary alloy changed composition from $\text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_{10}$ to $\text{La}_{65}\text{Al}_{13}\text{Ni}_{10}\text{Cu}_{12}$, resulting in compositional percentage changes similar to the three-component alloy for Cu, Al and La, while the Ni content stayed constant. Both samples represent a significant change in compositional space from the starting alloy to reach the final composition, which illustrates the efficiency of the ultrahigh acceleration centrifugal method for inducing compositional change in multi-component alloys.

Table 4.1 presents thermodynamic data for Li’s eutectic, $\text{La}_{62}\text{Al}_{14}\text{Cu}_{24}$, and the current centrifugal alloy. The referenced alloys [15-17] were reproduced so that a
direct comparison could be made and equipment/processing variables affecting GFA could be compared. The two starting off-eutectic compositions originally found by the Inoue group [13,14] were not remade, since both the three- and four-component centrifugal alloys have significantly lower \( T_l \). This first comparison with the starting alloys illustrates that the centrifuge, by separation of crystallizing primary phases, does result in a compositional shift towards a lower \( T_l \) composition.

The listed three-component La-based samples have similar \( T_m1 \) values, with melting intervals \( (T_m2 - T_m1) \) of 28, 67, and 45°C, and critical casting thicknesses of 2, 3, and 3 mm for La_{66}Al_{14}Cu_{20} (eutectic by Li), La_{62}Al_{14}Cu_{24}, and La_{64}Al_{13}Cu_{23} (centrifugal sample), respectively. The centrifugally processed composition is off the eutectic composition stated by Li towards the La_{62}Al_{14}Cu_{24} composition. It is interesting to note that the centrifugal alloy maintains the higher GFA of 3 mm but with a smaller melting interval and \( T_l \) than the La_{62}Al_{14}Cu_{24} alloy. This shows that improved GFA can be found closer to the actual eutectic. The smaller melting interval in the centrifugal sample is likely due to the absence of a high-temperature phase that is still present in the La_{62}Al_{14}Cu_{24} alloy. The GFA of the latter two alloys is approximately the same, as both alloys are fully amorphous at 3 mm and completely crystalline at 5 mm. While in Li’s work many different samples had to be produced to find the eutectic, the ultrahigh centrifugal processing method found a composition with a comparable \( T_l \) and increased GFA by processing just one sample. This confirms the effectiveness of the centrifugal processing method in discovering new BMGs.

### Table 4.1: Thermodynamic data on the ternary La-based alloys

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>( T_g ) (°C)</th>
<th>( T_x ) (°C)</th>
<th>( T_m1 ) (°C)</th>
<th>( T_m2 ) (°C)</th>
<th>( T_m2 - T_m1 ) (°C)</th>
<th>( T_l ) (°C)</th>
<th>Critical casting thickness [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) La_{66}Al_{14}Cu_{20}</td>
<td>114</td>
<td>172</td>
<td>403</td>
<td>431</td>
<td>28</td>
<td>384</td>
<td>2</td>
</tr>
<tr>
<td>(2) La_{62}Al_{14}Cu_{24}</td>
<td>121</td>
<td>179</td>
<td>404</td>
<td>471</td>
<td>67</td>
<td>448</td>
<td>3</td>
</tr>
<tr>
<td>(3) La_{64}Al_{13}Cu_{23}</td>
<td>112</td>
<td>170</td>
<td>396</td>
<td>441</td>
<td>45</td>
<td>418</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4.2 lists the results for the four-component La-based alloys. A trend similar to the three-component alloys is seen in terms of composition and melting
interval relative to the alloys in literature. The centrifugal sample, La₆₅Al₁₃Ni₁₀Cu₁₂, and Li’s eutectic alloy, La₆₆Al₁₄Ni₁₀Cu₁₀, can both be seen to have a small melting interval of only ~17°C, as shown in Fig. 4.10. In contrast, Li’s best glass-forming alloy, La₆₂Al₁₄Ni₁₂Cu₁₂, shows a melting interval of 63°C, which is again probably due to a small amount of high-temperature phase. However, in contrast to the three-component system, the GFA of the centrifugally processed alloy was even higher than that of Li’s alloy with maximum GFA. The alloy La₆₂Al₁₄Ni₁₂Cu₁₂ was amorphous when cast to 7 mm in our experimental setup, while the centrifugally processed sample, La₆₅Al₁₃Ni₁₀Cu₁₂, stayed amorphous to a casting thickness of 10 mm. This result again confirms the great effectiveness of the centrifugal processing method for discovering new BMGs without labor-intensive alloy development.

Table 4.2: Thermodynamic data on the quaternary La-based alloys: (1) Li’s eutectic composition; (2) Li’s maximum GFA composition; and (3) best glass-forming composition obtained after centrifugal processing.

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>( T_g ) (°C)</th>
<th>( T_x ) (°C)</th>
<th>( T_{m1} ) (°C)</th>
<th>( T_{m2} ) (°C)</th>
<th>( T_{m2} - T_{m1} ) (°C)</th>
<th>( T_l ) (°C)</th>
<th>Critical casting thickness [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) La₆₆Al₁₄Ni₁₀Cu₁₀</td>
<td>125</td>
<td>164</td>
<td>396</td>
<td>413</td>
<td>17</td>
<td>372</td>
<td>3</td>
</tr>
<tr>
<td>(2) La₆₂Al₁₄Ni₁₂Cu₁₂</td>
<td>130</td>
<td>173</td>
<td>401</td>
<td>462</td>
<td>63</td>
<td>432</td>
<td>7</td>
</tr>
<tr>
<td>(3) La₆₅Al₁₃Ni₁₀Cu₁₂</td>
<td>124</td>
<td>161</td>
<td>396</td>
<td>415</td>
<td>19</td>
<td>390</td>
<td>10</td>
</tr>
</tbody>
</table>

4.6 Conclusions

With the aim of finding deep eutectic compositions and thus alloys with increased GFA, two La-based off-eutectic glass-forming alloys (La₅₅Al₂₅Cu₂₀ and La₅₅Al₂₅Ni₁₀Cu₁₀) were centrifugally processed at 680°C and cooled at 4°C/min under 60,000 g acceleration. Solidifying primary phases separated to the sample ends, changing the remaining liquid composition toward the eutectic which solidified last. The identified ternary composition, La₆₄Al₁₃Cu₂₃, was cast 3 mm amorphous, as verified by DSC and XRD, which is comparable to the highest known GFA in the ternary La–Al–Cu system. The identified quaternary composition, La₆₅Al₁₃Ni₁₀Cu₁₂, was cast to 10 mm amorphous: the highest GFA in the quaternary La–Al–Ni–Cu system. These two bulk metallic glass-forming alloys are remarkable in that both compositions were identified using only one sample each, and the time-consuming
alloy development process was avoided. Our results verify that ultrahigh centrifugal acceleration processing can be used in a straightforward way to find eutectic or near-eutectic compositions in multicomponent alloy systems, and is thus a very useful method for discovering new bulk metallic glasses.

4.7 Acknowledgments

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4.8 References

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Ultrahigh centrifugal acceleration processing has been shown to separate primary crystallizing phases, leaving the eutectic to solidify last, and to identify improved glass-forming compositions in just one sample starting from a known off-eutectic glass-forming alloy. Here it is shown that starting from a “designed” multicomponent Mg–Zn–Ca–Al–Si composition, ultrahigh acceleration processing can exclude alloy components (in this case Si and Ca) from the melt that do not thermodynamically lower the liquidus temperature. In the last section of the sample to solidify (Mg–Zn–Al), three different compositions evolve, which move progressively towards the eutectic calculated by Pandat. All of these compositions show partial glass-forming ability when melt-spun, with one composition being fully amorphous.

5.1 Introduction

Ever since bulk metallic glasses (BMGs) were discovered in the 1960s [1], improving the glass-forming ability (GFA) of alloys has been accomplished through time-consuming alloy development [2]. Several descriptions of GFA have been put forth to guide alloy development; as an example, the Turnbull criterion correlates good GFA with a high ratio of a material’s glass transition temperature ($T_g$) to its liquidus temperature ($T_l$) [3]. As $T_g$ for a given alloy system varies little [4], $T_l$ is reduced to maximize the reduced glass transition temperature ($T_{rg} = T_g/T_l$). In alloy development terms, this means searching for low-lying eutectic compositions, which are characterized by negative heats of mixing, significant atomic size mismatch (more than 12%), and a composition of at least three elements [5]. This mixture of diverse atomic species stabilizes the liquid or limits the system’s ability to find an accommodating crystal structure for all the components. For this reason we focus our alloy development on discovering complex multicomponent eutectic compositions.

The history of Mg-based metallic glasses is seen to follow the above general guidelines, starting with two binary eutectics (Mg–Cu and Mg–Zn) [6,7]. From these two eutectics, a large family of ternary amorphous alloys was developed with the form Mg–TM–RE (with TM = transition metal and RE = rare earth). In this class of alloys, the Mg–Cu–Y system has been the most heavily investigated [8,9]. Other commonly used TM elements include Ni, Zn, Ag [10,11] or even Ca [12], and RE elements include Gd, La, Ce or Nd [13]. The Mg–TM–RE formula often leads to good GFA; however, when trying to develop a lightweight BMG, the low density of Mg is offset by the large densities of the TM and RE metals.

With the idea of developing a new lightweight Mg-based BMG alloy that is not prone to embrittlement [14] a five-component starting composition was designed from a recently developed Mg-based RE-free BMG system, Mg–Ca–Zn [15]. The composition $\text{Mg}_{54}\text{Zn}_{11.25}\text{Ca}_{9.75}\text{Al}_{22}\text{Si}_{3}$ is a 75-25 mix of the Mg-rich eutectic in the Mg–Zn–Ca system, Mg$_{72}$Zn$_{15}$Ca$_{13}$, and the Al–Si eutectic, Al$_{88}$Si$_{12}$. The Al–Si binary was selected due to the low density of Al and the small atomic size of Si.

To quickly identify the eutectic composition, ultrahigh gravitational acceleration processing was used. This method works by melting and then slowly cooling a metallic alloy under 60,000 $g$ applied acceleration. In this case, primary crystallizing phases separate to the sample ends, changing the remaining liquid
composition towards the eutectic, which solidifies last and can be clearly identified. In particular, this method shortcuts the time-consuming alloy development process of finding eutectic compositions in multicomponent alloys. Once the eutectic compositions are identified, they are remade and tested for GFA. Previous studies showed that eutectic compositions form when a multicomponent melt is cooled under ultrahigh gravitational acceleration \([16,17,18]\), and that known off-eutectic glass-forming alloys can be processed to find increased GFA \([19]\). Here we show, for a newly-designed Mg-based composition, the separation of primary crystallizing phases, which result in the exclusion of specific alloy components. We also show that atomic-level stratification can generate more phases than predicted by the Gibbs phase rule under normal gravity. Further, we demonstrate that eutectic or near-eutectic compositions with good glass-forming ability can be isolated from the original Mg–Zn–Ca–Al–Si alloy.

### 5.2 Experimental procedure

The Mg-based alloy, Mg\(_{54}\)Zn\(_{11.25}\)Ca\(_{9.75}\)Al\(_{22}\)Si\(_{3}\), was prepared by induction-melting the individual elements in a graphite crucible in a Ti-gettered ultrahigh purity argon atmosphere at 800 mbar. The elements used were Ca (99%) from Alfa Aesar, and Mg (99.99%), Zn (99.999%), Al (99.999%), and Si (99.999%) from CERAC, Inc. An injection molding system was used to cast the final sample shape (3 mm diameter by 40 mm length) in a copper mold. For centrifugal processing the sample was contained in a molybdenum crucible and sealed inside an Inconel (Ni-based superalloy) capsule under 10\(^{-4}\) mbar vacuum, both shown in Fig. 5.1(a).

The sample capsule was mounted in an IN100 (Ni-based superalloy) rotor [see Fig. 5.1(b)] and spun at an angular frequency of 2600 Hz resulting in 60,000 \(g\) applied acceleration. The company Test Devices, Inc. of Hudson, MA provided technical support for the centrifugal processing, whose setup is shown in Fig. 5.1(c). The sample was heated to 680°C, spun for two hours and finally cooled down to room temperature at a rate of 4°C per minute under continuous centrifugation. An in-depth explanation of the centrifugal experimental setup can be found in Ref. \([17]\) and chapter 2.

After centrifugal processing, the sample was sectioned axially (direction of applied acceleration) with a diamond blade and prepared for microscopic
investigations. A Camscan (Series 4) scanning electron microscope (SEM) in backscattered electron (BSE) detection mode was used for microstructural imaging, while a Norman Instruments energy-dispersive X-ray (EDX) spectrometer was used for compositional analysis and mapping. All compositions are stated in atomic percent and are assumed to have an accuracy of ±1 at.% after calibration to a known reference.

The compositions for the last three two-phase microstructures to separate from the melt were plotted on a Pandat [20] calculated ternary Mg–Zn–Al liquidus projection using the PanMagnesium database. These three compositions and the eutectic calculated by Pandat were remade in the lab following the alloying method described above and quenched via melt-spinning into ribbons. A graphite nozzle was used and the Cu wheel surface speed was set to 25 meters per second, resulting in meter-long ribbons of ~50-80 micron thickness with a smooth surface finish.

Differential scanning calorimetry (DSC) was performed with a SEIKO DSC200 at a scan rate of 0.333 K/s under continuous argon flow. All liquidus temperatures ($T_l$) stated were measured as the onset of crystallization during cooling. X-ray diffraction (XRD) was performed on the top side (free surface) of the melt-spun ribbons with a Co-$K_{\alpha}$ XRD source at 45 kV and 40 mA in the Debye-Scherrer geometry using a Stoe 120° detector.
5.3 Experimental results

5.3.1 Centrifugal analysis: Bottom and top sections

Figure 5.2(a) shows an optical micrograph montage of the whole Mg-based sample, Mg$_{54}$Zn$_{11.25}$Ca$_{9.75}$Al$_{22}$Si$_3$, after centrifugation, where the applied acceleration direction is shown with an arrow. The molybdenum crucible, which to ensure mechanical stability was not removed, is visible at the borders of the micrograph. The BSE micrographs, shown in Fig. 5.2(b)-(d), present enlarged views of three distinctly separated sections of the sample. Note that the phase contrast is reversed between optical and BSE images. The “bottom” section occupying the lower 38% of the sample separated first, Fig. 5.2(b), and four distinct phases evolved. This section ends abruptly at a crack in the sample, which occurred during diamond saw cutting of the
sample, as material from the bottom section can be seen on both sides of the crack. The “top” section, which separated secondly from the melt, occupies the upper 59% of the sample. As can be seen in Fig. 5.2(c) it also contains four phases. The final “middle” section, which makes up only 3% of the sample volume, did not fully separate but appears as islands within the top section of the sample. This middle section exhibits a variety of two-phase and eutectic-like microstructures, as shown in Fig. 5.2(d).

Figure. 5.2: (a) Optical montage of Mg$_{54}$Zn$_{11.25}$Ca$_{9.75}$Al$_{22}$Si$_3$ sample (starting composition) with three distinct regions. (b-d) Backscattered SEM images: (b) bottom section (solidified first); (c) top section (solidified second); and (d) middle section (solidified last).

The BSE micrographs from Fig. 5.2 are presented in Fig. 5.3 along with EDX maps for Mg, Zn, Ca, Al, and Si, where brighter areas indicate an increased content of the respective element. The order of separation is apparent from left to right, as the EDX maps clearly show that the bottom section contains all five elements, the top section no Si, and the middle section no Si and Ca. Also apparent in the EDX maps are the main components of each phase, with Table 5.1 listing the measured phase compositions.

The bottom section contains four distinct phases: (A) a Mg-rich phase, presumably hcp Mg, with soluble amounts of Zn and Al (darkest in BSE); (B) a Zn-rich phase that falls within the AlMgZn-$\tau$ phase region assuming some Ca solubility
(lightest phase in BSE); (C) an Al-rich phase, presumably Al$_2$Ca with additional soluble components; and (D) a Ca- and Si-rich phase previously identified as MgCaSi$_2$\cite{21}. While the phases C and D are difficult to distinguish in BSE, the enriched components (Al and Si) can be clearly seen in the corresponding EDX maps of Fig. 5.3 (left column).

In changing from the bottom to the top section, Si is eliminated, but four phases still evolve of which three are the phases A, B, and C from the bottom section. The fourth phase (E), labeled in the Al-EDX map of the top section, is differentiated from B, the lightest phase seen in the eutectic microstructure, by the large difference in composition (more Mg and less Zn, Al; see Table 5.1), but is still within the AlMgZn-\(\tau\) region. The evolution of these phases proceeds from the upper left to lower right of Fig. 5.2(c). In the upper left-hand corner all four phases (A-C and E) initially exist together. Then, phase C, not distinguishable in BSE but clearly seen in the Al EDX map (Fig. 5.3, center column), ceases to exist. Next the disappearance of E, the grey globular phase in BSE, is followed by a burst of phase A, the Mg-rich phase (darkest in BSE), which forms a dividing line (bottom left to upper right) between the globular phases and the two-phase microstructure in the lower right corner of Fig. 5.2(c). This two-phase microstructure, designated T1, consists of phases A and B and is also seen (in coarser form) on the lower left of Fig. 5.2(d) (middle section). The following section is devoted to a detailed description of the last solidified middle section in order to further elucidate the solidification process.
Figure. 5.3: BSE images and EDX maps for the bottom, top and middle sections (left, center, right) in order of separation. Left-hand column: all five components and four phases A-D exist. Center column: four components (no Si) and four phases A-C, E exist. Right-hand column: three components (no Si or Ca) and four two-phase microstructures exist; illustrated further in Fig. 5.4.
Table 5.1: Elemental compositions determined by EDX for all phases present in Mg₅₄Zn₁₁₂₅Ca₉₇₅Al₂₂Si₃ after centrifugal processing. Also listed are the compositions of the two-phase microstructures T1, M1, M2, and M3 as well as compositions for their constituent phases A, B and A, F. The constituent phases of the fine “eutectic” M2 could not be resolved exactly by EDX.

<table>
<thead>
<tr>
<th>Location</th>
<th>Mg at. %</th>
<th>Zn at. %</th>
<th>Al at. %</th>
<th>Ca at. %</th>
<th>Si at. %</th>
</tr>
</thead>
<tbody>
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<td><strong>Bottom</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>93</td>
<td>3</td>
<td>4</td>
<td></td>
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</tr>
<tr>
<td>B</td>
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<td>4.5</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>2</td>
<td>61.5</td>
<td>30.5</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>57</td>
<td>10</td>
<td>28</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>T1=A+B</td>
<td>70</td>
<td>15</td>
<td>13</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td><strong>Middle</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1=A+F</td>
<td>74</td>
<td>21</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>88</td>
<td>9.5</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>51</td>
<td>37</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2=A+F</td>
<td>67.5</td>
<td>27.5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M3=A+F</td>
<td>67</td>
<td>23</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>91</td>
<td>6</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>50.5</td>
<td>33</td>
<td>16.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.3.2 **Centrifugal analysis: Middle section details**

The middle section that separated last contains three microstructures comprised of the two phases A, F and the three remaining components, Mg, Zn, and Al (no Si and Ca). In the lower left-hand corner of Fig. 5.4 a small area of the top section microstructure T1 is seen. During the growth of this two-phase microstructure T1 the remaining liquid becomes enriched in Mg until the (Mg-poor) phase B can no longer form, which results in a burst of phase A. After this burst, the middle section solidifies first as two-phase microstructure M1, as M1 is the microstructure richest in Mg (see Table 5.1). With the decrease in the Mg content, either the eutectic-like structures M2 or M3 solidify from M1. The fact that two eutectic-like binary microstructures can solidify (and not the ternary eutectic) may be a consequence of solidification under ultrahigh gravity, as will be discussed in section 5.4. The high gravitational acceleration generates atomic-level stratification or spreading of the remaining liquid. This causes an extended section of the multicomponent phase diagram to be resolved by the centrifugal processing method. As such, either M3 or
M2 can solidify from M1. Since M2 is 5% richer in Zn and 5% poorer in Al than M3, the “heavier” eutectic-like microstructure M2 solidifies more towards the bottom of the centrifuge (see Fig. 5.4).

Figure. 5.4: BSE image of the middle section with microstructures T1, M1, M2, M3 and phase A labeled.

Pandat was used to calculate the ternary liquidus projection, which is shown in Fig. 5.5. The phase compositions determined by EDX are also plotted using the same identification as in Fig. 5.4 and Table 5.1. Note that composition T1 (denoted with a triangle) is only plotted approximately as it contains two percent Ca. The eutectic-like microstructures M1, M2, and M3 are represented as squares and the Pandat-calculated eutectic composition (PD) is marked with a star. The phases A and F which make up microstructures M1 and M3 are also shown. As expected according to the discussion above, the evolution of the experimentally determined eutectic-like microstructures does not follow the equilibrium liquidus intersections exactly. In fact, while T1 still lies on a liquidus intersection, M1 is outside of it and forms first before the solidification of M2 and M3. Interestingly, the Pandat calculated eutectic PD lies approximately on the tie-line of M2 and M3, with PD nearer to M2, which shows the finest microstructure. This gives evidence that centrifugal processing makes it possible to identify the deepest eutectic within a very close composition range.
5.3.3 Alloy development

The compositions of M1, M2, M3 and PD (i.e. Mg_{70}Zn_{25}Al_{5}) were remade via melt-spinning to test them for GFA. XRD scans of these four samples are shown in Fig. 5.6; M1 and PD exhibit typical amorphous halos, while M2 and M3 show prominent Bragg peaks, indicating crystalline phases. DSC scans of the four compositions (Fig. 5.7) confirm the XRD results, with M1 and PD showing large exothermic peaks proving the presence of a large fraction of amorphous phase. M3 shows slightly smaller exothermic peaks and M2 only shows one exothermic peak, corresponding to a smaller amorphous percentage and almost no amorphous content, respectively. This result correlates well with the M3 and M2 XRD scans (see Fig. 5.6) and observations of brittle versus ductile behavior. During preparation of samples for DSC and XRD, the alloys with composition M1 and PD showed “ductile” behavior, defined here as the ability to be cut without spontaneous fracture, while M3 only showed some ductility in thin regions of the ribbon and M2 was completely brittle.

The DSC results, which are summarized in Table 5.2, also confirm what is expected from the Pandat liquidus projection. M1, not located on a liquidus line, exhibits the largest melting interval $\Delta T_m$ of 77°C, defined as the melting offset ($T_{m2}$)
minus the onset \( T_{\text{mi}} \). PD, the calculated eutectic, shows the smallest melting interval of 21ºC, while M3 and M2, which also lie on liquidus lines, show intervals of 29ºC and 37ºC, respectively. The liquidus temperature \( T_l \), measured during cooling, is also listed for these four compositions, reconfirming (1) the solidification order of M1 → M2, M3, and (2) that PD is closest to the actual eutectic having the lowest \( T_l \) of 326ºC and showing single-step solidification upon cooling.

Figure 5.6: XRD scans for melt-spun ribbons with compositions of the three microstructures solidifying last and of the Pandat eutectic; M1 and PD show typical amorphous halos.

Figure 5.7: DSC scans for melt-spun ribbons with compositions of the three microstructures solidifying last and of the Pandat eutectic; M1 and PD show the largest crystallization enthalpies.
Table 5.2: Thermodynamic data for phases observed in the middle section; $T_{m1}$ is the onset of melting, $T_{m2}$ is the offset of melting, $\Delta T_m$ is the difference between $T_{m2}$ and $T_{m1}$, and $T_I$ is the onset of solidification during cooling.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta T_m$ (°C)</th>
<th>$T_I$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>338</td>
<td>415</td>
<td>77</td>
<td>389</td>
</tr>
<tr>
<td>M2</td>
<td>339</td>
<td>376</td>
<td>37</td>
<td>357</td>
</tr>
<tr>
<td>M3</td>
<td>337</td>
<td>366</td>
<td>29</td>
<td>347</td>
</tr>
<tr>
<td>PD Eutectic</td>
<td>338</td>
<td>359</td>
<td>21</td>
<td>326</td>
</tr>
</tbody>
</table>

5.4 Discussion

Starting with a mix of the Mg–Zn–Ca and the Al–Si eutectics, Mg$_{54}$Zn$_{11.25}$Ca$_{7.5}$Al$_{22}$Si$_3$, ultrahigh acceleration processing isolates the deepest eutectic, here the Mg–Zn–Al eutectic. This means Ca was completely replaced in the Mg–Zn–Ca ternary by Al, resulting in a lower liquidus temperature. This can be easily understood by considering the relevant eutectic temperatures: 577ºC for Al–Si, 400ºC for Mg–Zn–Ca and 326ºC for Mg–Zn–Al. This result also means that both Si and Ca were completely removed from the melt during solidification.

The evolution of phases which removed the Si and Ca components can also be understood by comparing the binary heats of mixing for all components. The first phase MgCaSi, which consumed all of the Si, contains two of the most negative heats of mixing pairs, Ca–Si and Mg–Si, listed in Table 5.3 [22]. The second phase Al$_2$Ca, which removed the Ca content, is the second most negative binary pair. This brief analysis correlates well with the actual phases to evolve in the centrifuge, and it can be concluded that in the Mg–Zn–Al system, Ca does not and Si may not help to reduce the liquidus temperature. The element Ca does not help because it will form the Al$_2$Ca intermetallic if both components are present, but Si cannot be conclusively excluded since it was removed by the MgCaSi phase; however, from Table 5.3 it is likely that Mg$_2$Si would form if no Ca was present.
Table 5.3: Binary heats of mixing of possible binary pairs in Mg–Zn–Ca–Al–Si, listed in order of most to least negative. [22]

<table>
<thead>
<tr>
<th>Binary System</th>
<th>Heat of Mixing (kJ/mol)</th>
<th>Binary Intermetallics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca–Si</td>
<td>-59.5</td>
<td>Ca$_2$Si, CaSi, CaSi$_2$</td>
</tr>
<tr>
<td>Al–Ca</td>
<td>-21.8</td>
<td>Al$_4$Ca, Al$_2$Ca, AlCa, Al$_3$Ca$_8$</td>
</tr>
<tr>
<td>Ca–Zn</td>
<td>-19</td>
<td>Ca$_3$Zn, Ca$_5$Zn$_3$, CaZn, CaZn$_2$, CaZn$<em>3$, CaZn$<em>5$, CaZn$</em>{11}$, CaZn$</em>{13}$</td>
</tr>
<tr>
<td>Mg–Si</td>
<td>-18.6</td>
<td>Mg$_3$Si</td>
</tr>
<tr>
<td>Mg–Ca</td>
<td>-8</td>
<td>CaMg$_2$</td>
</tr>
<tr>
<td>Mg–Zn</td>
<td>-5.8</td>
<td>Mg$<em>{12}$Zn$</em>{13}$, Mg$_2$Zn$_3$, C14, Mg$<em>2$Zn$</em>{11}$</td>
</tr>
<tr>
<td>Al–Mg</td>
<td>-3</td>
<td>Al$<em>{14}$Mg$</em>{89}$, Al$<em>{30}$Mg$</em>{23}$, Al$<em>{12}$Mg$</em>{17}$</td>
</tr>
<tr>
<td>Al–Si</td>
<td>-2.8</td>
<td>No intermetallics</td>
</tr>
<tr>
<td>Si–Zn</td>
<td>2</td>
<td>No intermetallics</td>
</tr>
<tr>
<td>Al–Zn</td>
<td>2.6</td>
<td>No intermetallics</td>
</tr>
</tbody>
</table>

Focusing on the middle section, the order of microstructure evolution, M1→M2, M3, was confirmed by DSC experiments and plotted on a Pandat-calculated Mg–Zn–Al ternary liquidus projection (Fig. 5.5). Following T1 to M1 to M2, M3 does not reproduce the progression of liquidus lines towards the eutectic. This results from atomic-level stratification or spreading of the remaining liquid composition. In fact, the chemical potential of each phase is modified by the term $M a h$ where $M$ is the atomic mass of the phase, $a = 60,000$ g, and $h$ is the position of the phase in the sample [17]. At 60,000 g this term is of the order of 1 kJ/mol. Thus the spatial dependence of the chemical potential implies that not only a local but a larger section of the multicomponent phase diagram can be resolved by the centrifugal processing method. Apart from the occurrence of several two-phase microstructures, this also explains why more phases solidify in the centrifuge than what is predicted by the Gibbs phase rule under normal gravity. As such, depending on the position in the centrifuge, either M3 (the “eutectic” richer in Al) or M2 (the “eutectic” richer in Zn) solidifies more or less at the same time (see Fig. 5.4). The absence of the lowest eutectic PD may be explained by the small temperature difference in this region of the phase diagram (resulting in a very low thermodynamic driving force of forming the eutectic), or it may in fact have formed but was not present in the current sample cross-section studied. Nevertheless, the results show the efficiency of the centrifugal processing method in identifying the deepest eutectic, since the eutectic-like
microstructures M2 and M3 (which are very close to the deepest eutectic PD) were found in the last 3% of the solidifying multicomponent liquid.

As a final comparison, the four compositions corresponding to the microstructures M1, M2, M3, and PD are plotted on a Mg–Al–Zn rapidly solidified structure diagram originally published by Inoue and Masumoto in Ref. [23] (Fig. 5.8). All four compositions fall within the amorphous region, with M2 and M3 lying closest to its edge. This means that M1 and PD should have better GFA, which is confirmed by the XRD and DSC results. PD was verified here to be the eutectic by identifying one-step melting in the DSC. Further, a variety of compositions around M1 were also made to check the range of the amorphous region, which is comparable to but somewhat smaller than that shown in Fig. 5.8. The fact that the amorphous compositions were found in the last section to solidify shows that ultrahigh centrifugal processing is a viable method for finding good glass-forming compositions. The method appears to be more effective and much less time-consuming than conventional BMG development procedures, which often involve the synthesis of hundreds of different alloy compositions.

Figure. 5.8: Mg–Al–Zn ternary phase diagram showing ranges of various crystalline and amorphous microstructures obtained via rapid solidification [23], together with compositions obtained through centrifugal processing and rapidly solidified in the lab.
5.5 Summary

With the goal of discovering lightweight Mg-based metallic glasses, a newly designed five-component starting alloy (Mg–Zn–Ca–Al–Si) was melted and slowly cooled under 60,000 g applied acceleration. The ultrahigh acceleration induced the separation of crystallizing phases to the sample ends, moving the liquid composition to lower and lower liquidus temperatures and ultimately leaving eutectic-like microstructures to solidify last. By lowering the liquidus temperature Si and Ca were sequentially eliminated from the remaining liquid, leaving the ternary Mg–Zn–Al system as last. Even though the ternary system only existed for the last 3 vol.% of the sample, three different two-phase or eutectic-like microstructures evolved. The compositions of these microstructures measured via EDX and plotted on a Pandat-calculated Mg–Zn–Al liquidus projection reveal an evolution towards the eutectic calculated by Pandat. The measured compositions for the two-phase microstructures along with the calculated Pandat eutectic composition were reproduced and melt-spun into ribbons to test for GFA. All four compositions showed some amorphous content, and M1 and PD were fully amorphous. This result shows that ultrahigh centrifugal processing of a designed starting composition can generate new alloys with improved GFA in a very effective “combinatorial” way.

5.6 Acknowledgements

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5.7 References

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6 Summary and outlook

This chapter presents a summary of the most important results of the thesis and gives an outlook for further alloy processing and construction of a second-generation centrifuge.
6.1 General summary

In this thesis, metallic glass formation has been addressed from both the practical alloy production and alloy development aspects. Metallic glass processing equipment for alloying and quenching of a variety of sample geometries has been constructed to produce alloys needed for this thesis and other projects at the LMPT. An ultrahigh acceleration centrifugal processing technique [1] has been applied to the metallic alloys produced, resulting in atomic-level stratification in the liquid prior to solidification, separation of primary crystallizing phases, and isolation of deep eutectic compositions. The results of atomic-level stratification fit well with a thermodynamic model presented in this thesis. Further, the ability of the centrifugal processing technique to isolate eutectic compositions has been applied to develop new bulk metallic glasses.

6.1.1 Metallic glass processing equipment

As metallic glasses are highly sensitive to contamination and quenching rate, specialized equipment is required for their successful production. Thus, five pieces of equipment were produced during this thesis: (1) a drop tube for metallic glass spheres; (2) a piston injection molding system; (3) a silver-boat designated for Mg-based alloy production; (4) an electromagnetic levitation system for containerless processing of Ca- and Mg-based materials; and (5) a melt extraction system for the production of Mg-based metallic glass wires. This equipment has been used to produce the alloys for centrifugal processing.

6.1.2 Centrifugal processing: Thermodynamics at ultrahigh gravity

To study thermodynamics at ultrahigh gravity, two eutectic Au-based alloys, Au$_{81.4}$Si$_{18.6}$ and Au$_{79.4}$Si$_{14.1}$Ge$_{6.5}$, were centrifugally processed at 60,000 g. In both alloys, atomic-level stratification occurred in the melt prior to solidification, which led to the extraordinary effect that more phases existed upon solidification than what is predicted by the Gibbs phase rule under normal gravity. The variation of the chemical potential at 60,000 g is approximately 2 kJ/mol. Apparently, at such high accelerations, the equilibrium phase diagram is spread out over a range of
concentrations, i.e. a single point in the equilibrium phase diagram becomes a line so that a simple binary equilibrium phase diagram (like Au–Si) can be reconstructed by the measurement of only one composition. In fact, for the Au–Si system, we observed the eutectic, as well as primary Au and primary Si upon solidification of the Au–Si melt.

The ternary Au–Si–Ge sample exhibited the same effect of atomic-level stratification in the melt, as evidenced by the solidification of three primary phases and the eutectic. In addition, the centrifugal processing moved the starting local eutectic towards the global eutectic composition with the lowest eutectic temperature. This result illustrates the possibility of isolating the deepest eutectic composition in a multicomponent alloy.

### 6.1.3 Centrifugal processing: Metallic glass alloy development

According to the Turnbull criterion, good glass formers show a high ratio of the glass transition to the liquidus temperature, i.e. bulk metallic glasses generally have deep eutectic compositions. Thus, to discover new bulk metallic glasses, various multicomponent alloys have been centrifugally processed in this thesis with the aim of identifying the deepest eutectic compositions in these alloys.

First, to demonstrate the feasibility of the technique, two (already-known) La-based off-eutectic glass-forming compositions were processed, La55Al25Cu20 and La55Al25Ni10Cu10 [2,3]. The processing resulted in two and three primary phases, respectively, and clearly visible eutectics. When reproduced in the lab, the measured eutectic compositions resulted in glass-forming ability comparable to the maximum known in the ternary system (3 mm) and significantly increased for the quaternary system (10 mm vs. 7 mm known so far). This is a very significant result in that multicomponent alloy development to date has been very labor-intensive with only some empirical rules for glass-formation existing. The centrifugal processing technique, which separates the primary phases as they crystallize and changes the remaining liquid towards the eutectic composition, is thus an important tool for metallic glass development.

A designed five-component Mg–Zn–Ca–Al–Si alloy was also processed in the centrifuge at 60,000 g. The processing excluded two alloy components (Si and Ca) and led to several Mg–Zn–Al eutectics, which all showed good glass-forming ability.
This shows that the centrifugal processing technique can map out a complete glass-forming region by processing only one sample.

6.2 General outlook

6.2.1 Centrifugal processing

As to the thermodynamic modeling of atomic-level stratification, a series of Au–Si samples with various lengths should be processed. This may give further evidence for our thermodynamic model at ultrahigh gravity [see Equations (3.3)-(3.5)]. In addition, to probe the effect of non-zero heat of mixing, a variety of Al-based binaries may be studied. Of course, further multicomponent alloys should also be processed in the centrifuge to discover new bulk metallic glasses.

6.2.2 Second-generation centrifuge

Currently, the design of an in-house centrifuge (‘second-generation centrifuge’) is in progress. Improvements of this centrifuge focus on crucible materials and sample-heating method. This centrifuge should also allow for processing at higher temperatures so that a wider spectrum of phase diagrams could be investigated.

When Al–Cu and Al–Si were processed in Mo crucibles, an intermetallic phase formed, as is shown in Fig. 6.1. In fact, many metals (e.g. V, Cr, W, Mn, Ti, Mo, Ta, and Nb) form an intermetallic phase with Al within 8 °C of the Al melting point. This shows the problem of using metallic crucibles: they must always be matched to a given alloy system so as to avoid reactions. Another possibility would be to coat the metallic crucibles with a ceramic (for example yttria-stabilized zirconia), so as to combine the high fracture toughness and strength of the metal with the low chemical reactivity of the ceramic.
Processing of the Al$_{84}$Cu$_{16}$ eutectic resulted in the Cu-rich intermetallic phase and the eutectic, but no Al-primary phase; processing of Al$_{61}$Ag$_{39}$ resulted in the Ag-rich intermetallic phase and the eutectic, but again no Al-primary phase. In both cases, the Al was consumed by either the Al$_{12}$Mo or Al$_3$Mo intermetallic.

The first-generation rotor was made of IN100, a disk alloy from the turbine industry, with an upper temperature limit of 875ºC. For processing of alloys with higher melting temperature, another rotor material or another method of heating is needed. A ceramic rotor is one possibility; however, implementing a ceramic material in a high tensile strength structural application is not generally recommended. Another possibility is to heat only the sample and not the whole rotor. If the sample is adequately thermally insulated from the rotor, the sample can be melted and the rotor can be made of a low-temperature (max ~ 300 ºC) high-strength alloy. However, in this configuration, heating options are inductive or resistive and pose problems: the induction system must be designed so as to heat the sample but not the rotor, while the resistive system must be powered by an electrical pass-through rotating at 20,000 rpm for several hours without interruption.

Apparently, research on centrifugal processing of metallic liquids remains interesting and further results (with regard to bulk metallic glass development and materials science in general) can be expected.

6.3 References

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7 Appendices
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