GETTING THE HOT STRUCTURES

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ABSTRACT

The recent advances in levitation methods for materials processing now enable structural, thermo-physical property, and phase transition studies to be made on high temperature solids and liquids without container contamination. These studies have led to new insights into the liquid state and have revealed how local order in the liquid can dictate phase formation. In this article, levitation techniques are briefly discussed, focusing most on electrostatic levitation. Recent synchrotron studies of electrostatically-levitated undercooled Ti-Zr-Ni liquids are presented, which demonstrate that developing icosahedral short-range order in the liquid causes the nucleation of a metastable icosahedral quasicrystal instead of the stable tetrahedral Laves phase. In addition to providing the first experimental proof of a half-century-old hypothesis linking the order of the liquid with the nucleation barrier, these data raise new questions about the general applicability of the thermodynamic model assumed in the classical theory of nucleation. The combination of electrostatic levitation and synchrotron high-energy diffraction also allows rapid and accurate determinations of phase diagrams for high temperature materials. This is demonstrated using Ti-Fe-Si-O as a case study. This new technique, then, is of practical as well as basic importance.

INTRODUCTION

The local structural order in liquids and the similarity to the order in crystal phases that form from the liquid during freezing are fundamental questions. Since Fahrenheit’s studies of the crystallization of water, for example, it has been recognized that under the right conditions liquids can be maintained in a metastable state below the equilibrium melting temperatures for extended periods of time [1]. This ability to undercool (or supercool) the liquid demonstrates the existence of a barrier to the phase transition. The initial formation of small regions of the ordered phase, i.e. nucleation, involves a stochastic thermally-activated transition over this barrier that is typically analyzed within the classical theory of nucleation [2]. In this theory, the nucleation barrier arises from the high interfacial energy between the liquid and small clusters of the crystal phase, presumably due to a significant difference in the local atomic structures of the two phases. “Homogeneous nucleation” is the more fundamental of the two types of nucleation, occurring randomly in space and time. “Heterogeneous nucleation,” is more common, however, catalyzed at specific sites in the initial phase.

Until the middle of the last century, a failure to significantly undercool liquid metals was taken as evidence that the local atomic structures of the liquid and crystal phases were similar. In 1952, however, Turnbull showed that this was due to the tendency for heterogeneous nucleation in metallic liquids [3]; if the catalytic sites in the liquid were removed, liquid metals could also be undercooled, sometimes to as low as 2/3 of their melting temperature before crystallization (Figure 1). To explain this Frank postulated an icosahedral packing in the liquid, consisting of 20
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

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slightly distorted tetrahedra around a common center [4]. Although an icosahedral packing of hard spheres has the same coordination number as for the crystallographic close packings, such as fcc and hcp, translational periodicity is incompatible with the icosahedral point group symmetry. The formation of crystallographic phases, then, requires that the local icosahedral order be destroyed, giving rise to the observed nucleation barrier.

Figure 1. Dilatometric measurements of an emulsion of Hg as a function of temperature, demonstrating the large undercooling possible in many liquids (taken from reference [3]). The undercooling range, $\Delta T$, is indicated.

While Frank’s hypothesis has been supported by computer modeling studies [5-7] and undercooling [8, 9] and diffraction studies [9-11], only recently were we able to confirm it experimentally [12]. Using a new technique recently developed by us (BESL, for Beamline Electrostatic Levitation) the structures of electrostatically levitated deeply undercooled liquid droplets of a metallic Ti-Zr-Ni alloy were measured and correlated with the phase formation sequence during solidification. A growing icosahedral order in the liquid led to the preferential nucleation of a metastable icosahedral quasicrystal, demonstrating the relation between the local order in the liquid to the nucleation barrier. We have since discovered that icosahedral order is present even in some pure liquid metals, but it becomes distorted as the angular dependence of the inter-atomic potential becomes dominant [13].

Structural studies of phase transitions from equilibrium and metastable liquids/solids are also of practical value, allowing regions of the alloy phase diagram to be quickly and precisely mapped out. This is particularly important for the development of high temperature materials to support advanced propulsion technologies, where in many cases even the binary phase diagrams are unknown. X-ray and neutron diffraction studies, which could in principle allow the measurement of these data, are frequently hindered or prevented by the high reactivity of liquid metals with their containers. To demonstrate the ability with BESL to rapidly and accurately map out
interesting regions of the phase diagram of high temperature alloys, a case study is reported for Ti-Fe-Si-O alloys.

LEVITATION TECHNIQUES

Typically, liquids are undercooled until the onset of crystallization is detected by some macroscopic property change, such as the volume (dilatometry), heat evolution (calorimetry), and electrical resistivity. Most frequently the amount of undercooling, $\Delta T_u = T_m - T_u$, where $T_m$ is the liquidus temperature and $T_u$ is the undercooling temperature, is limited by heterogeneous nucleation on container walls, on the surfaces of the liquids, or on structural impurities within the liquid. A variety of methods have been developed to marginalize these impurities so that the homogenous nucleation behavior can be studied. These include the emulsion and substrate techniques, pioneered by Vonneguet [14] and Turnbull [3, 15-17], which compartmentalize the heterogeneous particles to a portion of the sample, and the more recent drop-tube and drop-tower methods [18-21], which allow samples to be studied in free-fall in the earth’s gravitational field, eliminating the need for a container.

There is a growing interest in new containerless processing methods, where samples are levitated in vacuum or a variety of gas environments using acoustic [22], aerodynamic [23], electrostatic [24], or electromagnetic [25] levitation techniques. Depending on the method used, the undercooling behavior of bulk samples of metallic, semiconducting, or insulating materials can be studied. Importantly, some of the recent developments of these techniques allow measurements of the structure and thermo-physical properties of the liquid phase down to the point of nucleation and growth of the ordered phase.

In principle, insulating, semiconducting, or metallic materials can be studied with aerodynamic and acoustic levitation methods. The flowing gas used in aerodynamic levitation makes temperature and positioning control difficult and may lead to an enhanced heterogeneous nucleation rate, however. In acoustic levitation, the large forces needed for terrestrial gravity conditions can cause fragmentation of the samples when melted. A combination of aerodynamic and acoustic levitation has proven most successful [23], allowing the melting of any nonvolatile material. While these methods are used to study undercooling and liquid structures, thermo-physical properties of the liquid cannot be measured. Such data are important, however. In addition to enabling quantitative modeling of nucleation behavior, they can reveal processes occurring in the undercooled liquid phase that can significantly impact the nucleation of ordered phases.

Electromagnetic (EML) and electrostatic levitation (ESL) are the most versatile of the levitation methods, allowing measurements of the undercooling, liquid structures, and thermophysical properties. A schematic diagram of an electromagnetic levitation facility is shown in Figure 2. A high frequency EM field induces eddy currents within an electrically conducting sample, which create a magnetic field that opposes the external field, leading to levitation. The eddy currents also heat the sample. Because of this coupling between levitation and heating, in cases where samples have a high density and low melting temperature, a cooling gas must be introduced to lower the temperature below the melting temperature. This increases the possibility of oxidation and heterogeneous nucleation, however, and makes thermo-physical property measurements
difficult, if not impossible. Positioning and heating can be decoupled in a low gravity environment, as demonstrated by an EML facility, TEMPUS, on the space shuttle (MSL-1). An excellent review of EML techniques is found in reference [25].

In ESL, samples are levitated by Coulomb forces acting on a charged sample using an electrostatic field [24, 26, 27]. The ESL method has several advantages; sample heating is completely decoupled from sample levitation, undercooling studies are made in an ultra-high vacuum, and samples are not limited by their electrical conductivity, allowing a wide range of samples to be processed. Because there is no minimum in the electrostatic potential, sample position can be maintained only with active computer feedback. A schematic illustration of electrostatic levitation is shown on the left side of Figure 3. Three sets of electrodes are used to position the samples during processing. Two dual-axis position sensitive detectors are used to locate the sample and to provide input for a PID control-loop computer. The sample position is maintained by adjusting the voltages applied to the electrodes to maintain the sample location (see reference [27] for further details of the positioning control). Samples are initially charged by induction, and the charge is maintained by the photoelectric effect, using a UV source. The samples are heated using one or more lasers, often a diode and/or a CO₂ laser. A superheated liquid Zr droplet levitated in the high vacuum ESL facility located at NASA, Marshall Space Flight Center is shown on the right side of Figure 3.
Recently, the ESL was modified to allow structural studies to be made on levitated samples at the beamline 6ID-D of the MU-CAT facility at the Advanced Photon Source (APS) located at Argonne National Laboratory, Argonne, Illinois. Nearly spherical samples obtained by arc melting (2.0 - 2.7 mm diameters, 20 – 100 mg mass) were levitated inside the 11" diameter ESL chamber under high vacuum (10^-7 - 10^-8 torr), as has been described elsewhere [12]. In this facility, the samples can be heated/cooled at a controlled rate, or held at any temperature between 300 and 2500 K by using laser heating. In addition, because of the absence of heterogeneous nucleation sites, the molten liquid can be retained in a metastable undercooled state far below the liquidus temperatures (typically 0.2 T_l for simple crystalline solids) for structural studies [12]. The sample temperature is measured using optical pyrometers (Mikron Infrared, Inc.) operating in 1.45 and 1.8 µm wavelength range. The chamber is mounted on a Eulerean cradle that is placed on a movable table with adjustable height so that the center of the sample can be adjusted to coincide with the center of the incident beam. The levitated samples are irradiated, with X-rays from the synchrotron source entering through a 2.5" diameter and 0.015" thick Be (99% pure, PF-60, BrushWellman Engineered Materials, Fremont, California) window. The diffracted beam exits through a wider window (4" diameter), mounted diametrically opposite to the entrance window, and is measured by an X-ray detector, situated outside the chamber. The available q-range (4 to 140 nm^-1, q = 4πSinθ/λ, where θ is the scattering angle for the X-ray beam of wave-length λ) is restricted by the beam stop on the low q-side, and by the electrode geometry and the exit window diameter on the high q-side. Since the diffraction data are collected in the transmission mode, they reflect the bulk structure. High energy X-rays (125 KeV, 0.099 Å) were used, available on beamline 6ID-D of the APS. Multiple samples (up to 12) were loaded in a movable carousel inside the chamber, allowing measurements on subsequent samples without breaking the high vacuum environment. Unlike many of the other levitation techniques
discussed (e.g. terrestrial-based EML, aerodynamic, acoustic), the high vacuum environment of ESL allows even the most oxygen-sensitive materials to be studied by this technique. The only factor limiting the samples that can be studied is the vapor pressure of the sample; if it is greater than 10 mtorr, levitation cannot be maintained for a sufficiently long time.

Figure 4 shows a schematic diagram of the BESL experimental arrangement. The novelty and versatility of this technique has been significantly enhanced by the choice of X-ray detectors. The MAR345 image plate (Fuji Photo Film Co. Ltd.) and the GE-Angio 41 cm detector (model 2304879, manufactured by PKI Inc. for GE Inc., Milwaukee, Wisconsin) have been used successfully, thus far. The cones of diffracted intensity emerging from the exit window of BESL were recorded with these detectors. The typical exposure times required to achieve reasonable counts were one second or higher for the MAR345, and 30 milli-seconds or higher for the GE-Angio detector. The complete diffraction data (intensity vs. $\theta$ or $q$), and therefore, the full structural information for a given material can thus be obtained in a fraction of a second. Data can be taken either while the sample is held at constant temperature or as a function of temperature during continuous heating/cooling at controlled rates. Because of the faster data acquisition rate, the GE-Angio detector is especially suitable for the latter experiments. This is particularly useful for the study of structures of short-lived metastable phases (e.g. supercooled liquids and metastable solids), continuous evolution of different solid and liquid phases as a function of temperature, and dynamical studies of structural transformations when the time scales are not too short (<30 ms) or too long (>hours).

These detectors contain active phosphors ($\text{Eu}^{+2}$ doped $\text{BaFBr}$ for MAR345 and $\text{CsI}$ for GE-Angio). For the MAR345, the natural point defects, called color centers or F centers trap electrons when an incident photon releases an electron by ionization. It remains in a metastable state at the defect site long enough (usually hours) to be released, detected, and counted (readout process) later by a laser. The electron count is, therefore, directly proportional to the flux of the incident beam. In the case of the GE-Angio detector, the photon released by the phosphor is detected by diodes positioned below the thin-phosphor layer.

![Image Plate](image.jpg)

Figure 4. A schematic diagram of the key components in BESL (adapted from reference [28]).
Thermo-physical properties such as solidus and liquidus temperatures, fusion enthalpy and specific heat of the solids, liquids, and undercooled metastable liquids [29, 30] can also be measured in BESL. The solidus temperature ($T_s$) can be clearly identified from the melting plateau during heating. However, because the thermal signature of the liquidus is often less distinct, this method is less suitable for determining the liquidus temperatures ($T_l$). The temperature at which all crystalline peaks disappear in the diffraction data is a more accurate measure of $T_l$. Compared to conventional methods, this is fairly easy and straightforward for BESL, since structural data can be collected continuously during heating. Therefore, except for high vapor pressure materials, complete structural and thermodynamic studies of almost any high temperature material can be carried out in a matter of minutes using BESL, as will be demonstrated in the next few sections.

ICOSAHEDRAL ORDER IN UNDERCOOLED LIQUIDS

Holzer and Kelton [31] first demonstrated that the interfacial free energy between an icosahedral quasicrystal phase (i-phase) and a metallic glass of the same composition was extremely small, indicating that the local atomic structures of the two phases were similar. Holland-Moritz [32] and others [9] have found a similar result in levitated undercooled metallic liquids that form quasicrystals (Table I). Liquids in which the i-phase is the nucleating phase show the least undercooling, consistent with a low barrier due to local icosahedral order in the liquid. The crystal approximant phases ($\lambda$-phase, $\mu$-phase and C14 Laves phase) show larger undercooling, reflecting greater differences between their icosahedral and tetrahedral structures and the local liquid structure. Simple crystal phases, such as $\beta$(Ti/Zr) and $\beta$(AlCuCo) show the greatest undercooling due to the incompatibility of the local structures in the crystal and liquid.

Table I. Reduced Undercooling ($\Delta T_r = \Delta T/T_l$) and Interfacial Free Energy for Quasicrystals and Crystal Approximants in Al-Transition Metal Alloys*.

<table>
<thead>
<tr>
<th>Quasicrystal</th>
<th>Crystal Approximant</th>
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<tbody>
<tr>
<td>Alloy Phase</td>
<td>$\Delta T_r$</td>
</tr>
<tr>
<td>Al$<em>{58}$Cu$</em>{34}$Fe$_8$ i-phase 0.09 0.09 ± 0.01</td>
<td>Al$_{13}$Fe$_4$ $\lambda$-phase 0.12 0.16 ± 0.01</td>
</tr>
<tr>
<td>Al$<em>{30}$Cu$</em>{34}$Fe$_6$ i-phase 0.09 0.09 ± 0.01</td>
<td>Al$<em>{10}$Cu$</em>{15}$Fe$_{25.5}$ $\lambda$-phase 0.14 0.15 ± 0.01</td>
</tr>
<tr>
<td>Al$<em>{17}$Pd$</em>{31}$Mn$_{17}$ i-phase 0.11 0.10 ± 0.01</td>
<td>Al$_2$Fe$_2$ $\mu$-phase 0.14 0.18 ± 0.01</td>
</tr>
<tr>
<td>Ti$<em>{37}$Zr$</em>{32}$Ni$_{25}$ i-phase 0.09 0.06 ± 0.01</td>
<td>Ti$<em>{17}$Zr$</em>{38}$Ni$_{25}$ C-14 Laves 0.14 0.10 ± 0.01</td>
</tr>
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*Data for Al-based alloys from reference [32]; data for Ti-Zr-Ni from reference [9]

These studies support, but do not prove, the notion that an increased degree of polytetrahedral order lowers the interfacial free energy between the crystallizing phase and the undercooled liquid, increasing the nucleation rate. A proof requires a radically decreased barrier for the nucleation of an i-phase in a liquid with demonstrated icosahedral short range order. This was recently obtained in a Ti-Zr-Ni alloy [12]. In-situ X-ray diffraction studies made using BESL in a Ti$_{37}$Zr$_{32}$Ni$_{25}$ liquid clearly showed that the i-phase was the primary nucleating phase from the undercooled liquid [Figure 5(b)]. However, the cooling data showed [Figure 5(a)] that within one to two seconds, a second recalescence event was observed; X-ray diffraction data showed that this was the transformation of the metastable i-phase to a C14 Laves phase, which is stable at elevated temperatures [Figure 5(b)].
Figure 5. (a) Cooling curves for electrostatically levitated 2.5 mm droplet of Ti$_{39.5}$Zr$_{39.5}$Ni$_{21}$ showing recalescence (indicated by arrows) as a function of temperature; (b) X-ray diffraction pattern as a function of momentum transfer, $q (=4\pi \sin \theta /\lambda)$, for the undercooled liquid of Ti-Zr-Ni alloy at 1029 K, during the 1st recalescence to the i-phase, and during the 2nd recalescence to the C14 phase (taken from reference [12]).

As is clear from Table I, the C14 Laves phase is also an easy phase to nucleate, as expected from its polytetrahedral local structure. That a metastable i-phase forms before the C14 phase, which has a greater driving free energy for formation, indicates that the nucleation barrier is smaller for the i-phase, reflected in the smaller value derived for the interfacial free energy. As shown in Figure 6, a shoulder on the high $q$ (momentum transfer) side of the second peak in $S(q)$ becomes more prominent with undercooling [12]. The peak intensity and location match those expected for icosahedral order, indicating that the lower nucleation barrier for the i-phase is due to developing icosahedral short range order – providing a direct experimental proof of Frank’s hypothesis in this alloy.

The diameter of the critical nucleus for the quasicrystal, calculated using the classical theory of nucleation, is approximately 3.8 nm at the recalescence temperature, close to the coherence length of the icosahedral short range order, 2.1 nm, estimated from the width of the first peak in $S(q)$. The icosahedral order is then acting as a template for the easy nucleation of the icosahedral quasicrystal, blurring the distinction between homogeneous and heterogeneous nucleation in this case. While making nucleation of the quasicrystal easier, the growing icosahedral order with undercooling causes an increasing nucleation barrier for the crystal phases. This is opposed to the normally expected decrease in the nucleation barrier due to a growing driving free energy, and can be an important factor in phase selection during solidification. More recent studies of pure transition metals using BESL have shown that with the increasing angular dependence of the atomic potential, the icosahedral short range order becomes distorted, likely becoming more tetrahedral in character [13]. This does not invalidate Frank’s original hypothesis, however. Since the local order in the liquid remains significantly different from that of the nucleating crystal phase, a sizable nucleation barrier still exists.
Figure 6. $S(q)$ for a Ti$_{39.5}$Zr$_{39.5}$Ni$_{21}$ liquid as a function of temperature. The shoulder on the high-q side of the second peak (indicated by the arrow) becomes more prominent as the temperature is lowered below the liquidus temperature (1083 K), indicating more developed icosahedral short-range order (taken from reference [12]).

**BESL FOR PHASE DIAGRAM STUDIES OF HIGH TEMPERATURE MATERIALS**

As pointed out earlier, high reactivity with the container materials and the environment are major obstacles in the study of high temperature materials. Although ESL processing eliminates those problems and allows reliable studies of thermodynamic properties, it does not provide any structural information. Conventional methods, including X-ray and electron microscopy, must be used for samples after ESL-processing to determine the phase formation sequence. In contrast, BESL provides an opportunity for *in-situ* structural studies of stable and metastable phases, including liquids, of a large variety of materials at any temperature of practical interest. As an illustration, we show here the phase formation sequence of a Ti-Fe-Si-O alloy studied by BESL from above $T_l$ down to room temperature, in a few minutes of experimental time. Large numbers of samples of different compositions, therefore, can be studied by BESL in a few days to determine the phase diagram of complicated ternary and quaternary alloys, particularly at high temperature. Low temperature solid-state transitions will require longer times due to the sluggish kinetics. This is in stark contrast to conventional methods (e.g. long-term high temperature annealing, quenching, X-ray and transmission electron microscopy studies, differential scanning calorimetry/thermal analysis, *etc*.), which would have taken years to complete. In addition, the BESL method is free from experimental artifacts introduced by impurities from reaction with container materials and the environment.

Based on conventional phase diagram studies [33] a number of interesting phases, including the $\alpha$-1/1 crystal approximant phase [34, 35], form in quaternary Ti-Fe-Si-O alloy system. The $\alpha$-1/1 phase is stable only over a narrow composition range in Ti$_{93-x}$Fe$_x$Si$_6$O$_y$ alloys ($22 \leq x \leq 26$, and $7 \leq y$), as shown in a section of the phase diagram, constructed from earlier studies (Figure 7). Microstructural studies of solids over this composition range could not clarify whether the $\alpha$-1/1 approximant phase nucleated directly from the liquid, or formed by a peritectic reaction. When
the liquid was allowed to cool in the ESL from above $T_l$, two recalescence events marking the nucleation and growth of two solids, were observed.

![Figure 7. A binary cut of the tentative phase diagram of Ti-Fe-Si-O alloys for fixed Si (6 at.%) and O (7-9 at.%).](image)

To identify these phases, *in-situ* X-ray diffraction experiments were made with BESL, using the GE-Angio detector. The levitated sample was superheated approximately 180 K above $T_l$ and the droplet was allowed to cool by turning off the laser power; the containerless environment and high vacuum ensured free radiative cooling. The temperature was measured every 60 ms and X-ray diffraction data were collected at 1 frame/s during cooling, as shown in Figure 8. The solid that nucleated after the first recalescence at 1584 K, changed little except for growing in intensity until the second recalescence occurred at 1460 K. The first nucleating solid was identified as a hexagonal phase ($a = 3.02 \text{ Å}, c = 4.89 \text{ Å}$), similar to the oxygen stabilized $\alpha$-Ti phase.

At the second recalescence temperature of 1460 K, another solid, identified as a bcc 1/1 crystal approximant phase ($13.19 \text{ Å}$) nucleated. A close examination of the diffraction pattern between $2 – 6 \text{ Å}^{-1}$ shows clear changes over this temperature range. The $\alpha$-Ti and some liquid phase still remained after the second recalescence. On further cooling, the 1/1 approximant phase started growing at the expense of the $\alpha$-Ti, consuming the remainder of the liquid. Finally, below approximately 1300 K, the entire sample solidified to the 1/1 approximant phase. This clearly shows that the 1/1 approximant phase forms by a peritectic reaction of the $\alpha$-Ti with the liquid. Interestingly, the as-cast alloy showed only the 1/1 approximant phase with a small amount of TiFe. Therefore, without *in-situ* studies, it would have been extremely difficult to identify the intermediate solid ($\alpha$-Ti) and the formation mechanism of the 1/1 approximant phase. The whole experiment lasted for only about 40 s, demonstrating the speed and power of this newly developed technique.
SUMMARY

A new technique for structural and thermo-physical properties, and phase transformation studies of high temperature liquids and solids was presented. Termed BESL, it combines the advantages of containerless processing in high vacuum by electrostatic levitation, with those of high-energy synchrotron X-ray diffraction techniques. The application of this technique to the study of metallic liquids has led to the first demonstration of a half-century old hypothesis, linking the nucleation barrier with growing short-range order in undercooled liquids and has produced new structural data on metallic liquids. The coupling between local ordering in the liquid and nucleation and growth will have a profound impact on phase selection during solidification in some cases. Further, the one-dimensional nature of the classical theory of nucleation makes it inappropriate for a quantitative understanding of such multiply-coupled nucleation processes. Density functional theories likely offer a better approach. Using Ti-Fe-Si-O alloys as a case study, the potential of BESL for rapid and accurate phase diagram studies of high temperature intermetallics was demonstrated, making the new technique of both practical and basic importance.
ACKNOWLEDGEMENTS

Support by NASA under contract NCC8-1682 and the NSF under grant DMR 03-07410 is gratefully acknowledged. We thank our collaborators G. W. Lee at Washington University, T. J. Rathz and J. R. Rogers at MSFC, Huntsville, Alabama, R. W. Hyers at the University of Massachusetts, Amherst, and D. S. Robinson at MU-CAT, Argonne, Illinois for their valuable contributions.

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