Growing intermetallic single crystals using in situ decanting

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Abstract
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Keywords
single crystal, crystal growth, solvent, high temperature, decanting

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Growing intermetallic single crystals using \textit{in situ} decanting

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High temperature metallic solution growth is one of the most successful and versatile methods for single crystal growth, and is particularly suited for exploratory synthesis. The method commonly utilizes a centrifuge at room temperature and is very successful for the synthesis of single crystal phases that can be decanted from the liquid below the melting point of the silica ampoule. In this paper, we demonstrate the extension of this method that enables single crystal growth and flux decanting inside the furnace at temperatures above 1200° C. This not only extends the number of available metallic solvents that can be used in exploratory crystal growth but also can be particularly well suited for crystals that have a rather narrow exposed solidification surface in the equilibrium alloy phase diagram.

\textbf{Keywords:} single crystal; crystal growth; solvent; high temperature; decanting

1. Introduction

Crystal growth from high temperature metallic solutions has been successfully employed in many scientific disciplines over the past several decades, including solid state physics, chemistry and materials science (for a recent review see, for example, [1]). Intermetallic solution (flux) lowers the melting point of the solute and is well suited for crystal growth of intermetallic phases that melt congruently as well as incongruently. In particular, it showed great success in synthesis of various compounds containing combinations of high melting point rare earth (transition metal) and low melting point metal or metalloid elements. The crystals however, had to be etched or mechanically removed from the solidified flux after going through the solidification line in the alloy phase diagram. This approach is limited by the availability of chemical etchants that would remove solidified flux and at the same time leave the grown crystals intact. Another potential issue is that chemical etching introduces significant roughness that could be a problem for certain physical properties measurements such as point contact Andreev spectroscopy due to possibility for multiple junctions. Moreover, flux solidification exposes the crystal

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to stress and enhances the possibility for the creation of secondary phases. Fisk and Remeika pioneered decanting of low melting fluxes outside the furnace, using the centrifuge at the room temperature [2]. Canfield and Fisk [3] perfected the method in detail, exploring the wide variety of fluxes and crucible materials in single crystal synthesis that would also include semiconducting intermetallic phases such as Ce$_3$Bi$_4$Pt$_3$. Finally, Canfield and Fisher [4] utilized arc welded Ta tubes for the creation of crystals containing highly reactive elements, elements with high vapour pressure at high temperatures and quaternary phases from flux eutectics. The examples include icosahedral R–Mn–Zn and RNi$_2$B$_2$C quasicrystals and borocarbide ($R$ = rare earth) crystals.

Centrifugal casting is used at scales from jewelry to ship building whereas centrifugal force has been used for a long time at high temperatures to improve molten metal flow. In this paper we will show how the crystal decanting temperatures can be pushed above the silica melting point in the high temperature flux–in situ decanting (HTF-ISD) method. This enables the use of novel fluxes and expands the potential materials space available for exploratory crystal growth. The method is tailored for crystal growth of materials containing high melting and low vapor pressure elements such as B and C. This work could be considered as an extension of the earlier papers published on this technique [2–4].

2. Experimental methods

Single crystals grown by the HTF-ISD method were made by mixing elemental ingredients into alumina or graphite crucibles. Excess Sb and Al were used as fluxes. FeSb$_2$ crystals were grown in alumina and graphite crucibles that were heated up to 900°C in 4 h, kept there for 2 h, cooled to 850°C in 1 h and then cooled to 650°C in 16 h. Al$_{1.67}$B$_{22}$ and YbB$_4$ crystals were grown in graphite and alumina crucibles, respectively, that were heated up to 1450°C in 2 h, soaked at the same temperature for 2 h and then cooled to 1280°C in 18 h (Al$_{1.67}$B$_{22}$) or 67 h (YbB$_4$). The crystals were decanted inside the furnace with rotation speed of 500 revolutions per minute (rpm) at 650°C (FeSb$_2$) or at 1280°C (Al$_{1.67}$B$_{22}$ and YbB$_4$). A constant flow of inert Ar gas was maintained in the furnace during the temperature treatment and decanting procedure.

X-ray diffraction (XRD) spectra were taken with Cu K$_\alpha$ radiation ($\lambda = 0.15418$ nm) using a Rigaku Miniflex X-ray machine. The lattice parameters were obtained by fitting the XRD spectra using RIETICA software [5]. A split design 1800°C furnace with Mo–Si$_2$ heating elements was commissioned at The Mellen Company. The furnace was designed with a custom rotating tube mechanism. The rotation of the tube (and therefore the sample) inside the furnace is performed via a speed adjustable DC motor that is connected by a timing belt to the rotation axis of the tube. The sample is inside a special mounting assembly (inside the tube), which is fixed in place (relative to the tube) by four hollow internal support rods of relatively small diameter. The furnace is remotely controlled by Mellen’s PC based ADAPT software.
3. Experimental results and discussion

Crystal growth from intermetallic fluxes in its common practice requires encapsulating the crucibles in silica tubes to prevent oxidation and (most often) using the silica wool for filtration. Consequently, decanting is possible for temperatures below the silica melting point (1200°C). However, removing crucibles out of the furnace for decanting above 1000°C leads to temperature gradients since the samples cool by the time the crystals are separated from the flux in the centrifuge at the room temperature. Thus, crystals cannot be grown near the end of the exposed liquid to solid surface of the alloy phase diagram. Some metal fluxes (such as Al) contribute to increased sensitivity of the silica ampoule due to chemical reactivity, thereby increasing the probability of silica rupture and oxidation of crystals during crystal decanting. In addition, high decanting temperatures increase the likelihood of silica breaking due to the increased softness of silica at temperatures near its melting point. Finally, silica wool commonly used for decanting of intermetallic liquid can in some cases react with the melt and contaminate the crystals. Therefore, in order to avoid the use of silica and silica wool in the crystal growth process we have designed crucibles (Figure 1) that use filters with machined holes for liquid decanting at high temperatures (fritted crucibles). The crucible design is modification of a BN crucible set commonly used in Ames Laboratory. Each crucible set consists of three

![Figure 1. Filter crucibles used in the HTF-ISD method. Top (a), angle (b) and side (c) view of alumina crucibles. The design is rather versatile since crucibles can be made with different size of holes in filter discs (a). When shaped to fit the silica tube, the same crucible design can be used for single crystal decanting from molten metallic fluxes outside the furnace or for crucibles made of different materials such as graphite (d).](image-url)
pieces: two identical cups and a filter disc. The filter disc attaches to both cups with threads made on the inner side of each individual cup and on the disc’s edge. Figure 1a shows alumina crucibles with 1 and 2 mm hole size, whereas Figure 1b and c show angle view of a cup and side view of an assembled crucible set, respectively. When assembled and ready for loading in the furnace, the bottom crucible in a set contains the work charge and the top crucible is empty and serves as a “catch” crucible for liquid decanting. Figure 1d shows an example of a graphite crucible set.

Fritted crucibles are often used in the normal high temperature flux method when the sample is decanted in the centrifuge outside the furnace. For example, Sn flux decanted at really low temperatures (around 270°C) does not pass through the silica wool in the catch crucible probably due to large surface tension at low temperature and rather small holes of the silica wool. In contrast, when the silica wool filter is replaced with the fritted crucibles, it is possible to decant Sn at low temperatures.

In the regular practice of metal flux decanting, the flux is decanted outside the furnace in a centrifuge. Therefore the crucible set rotates in the horizontal plane when fully accelerated or at some sharp angle between the horizontal plane and the vertical direction during acceleration. Consequently, gravity cannot cause the backflow of the molten flux in the work charge space since the “catch” crucible is always closer to the perimeter of rotation than the crucible with work charge (crystals). Room temperature laboratory centrifuges used to decant metal fluxes outside the furnace usually have the bottom of the charge crucible at 7 cm from the centre of rotation and are capable of achieving up to a 1000 rpm. In the case of the HTF-ISD method, however, the crucible rotates in the vertical plane. Therefore in the simplest analysis, in order to prevent the backflow of the liquid at the “12 o’clock” position, the centrifugal force has to be greater than the gravity when the viscosity of the flux is neglected: \( mg < m\omega^2 R \), where \( m \) is the mass of the charge, \( \omega \) is the angular velocity and \( R \) is the radius of the rotation. Therefore, the charge should be moved as close as possible to the perimeter of the rotation.

Let us first consider only gravity force. At the “12 o’clock” position all flux would fall down from the “catch” crucible if there would be no rotation. However, due to rotation, centrifugal force will push the liquid upwards if \( m\omega^2 R > mg \). Since the bottom of the crucible is at 4 cm from the center of rotation, the centrifugal force per unit mass is \( F_{CF} = n^2 (2\pi \text{ radians/60 s})^2 0.04 \text{ m}, \) where \( n \) is given in revolutions per minute (rpm). Therefore, \( F_{CF} = n^2 \times 0.0109 \times 0.04 \text{ m/s}^2 \). From this simple calculation it follows that 500 rpm is equivalent to 110 m/s\(^2\) \( \sim \) 11 g and 279 m/s\(^2\) \( \sim \) 28 g at 800 rpm. The above consideration neglects the influence of viscosity.

Let us now consider viscosity force at high temperatures. The resistance force of the liquid metal fluid to the flow during the decanting process at high temperature can be crudely approximated as \( F = \mu A (v/y) \), where \( \mu \) is the viscosity, \( A \) is the cross-section area through which the liquid flows and \( v/y \) is the velocity gradient of the flow. The cross-section diameter of the crucible is in cm range (0.023 m), and for filter it is in mm range (~0.001 m), whereas \( A \) is circular for both crucible and filter. The distance \( y \) is 1 cm (crucible height) for the crucible flow and 3 mm (for the filter flow). In this simplest approximation, the viscosity force is \( \mu (0.5 \times 10^{-3} \text{ m}^2) (v_c/0.01 \text{ m}) \) for the flow through the crucible before the filter. Here \( v_c \) is the fluid (flux) velocity in the crucible. When rotating at 500 rpm (11 g), decanting times are
(empirically) of the order of 1 second. We can estimate $v_c = at$, where $a$ is the acceleration ($\sim 10 \text{ g}$) and $t \sim 1 \text{ s}$ is the time; hence $v_c$ should be $\sim 100 \text{ m/s}$. The limit of viscosity force can be then estimated as $\sim \mu 10^2 \text{ Pa}\cdot\text{s}$. Since the values of $\mu$ are in the $10^{-3} \text{ Pa}\cdot\text{s}$ range \[6,7\], the viscosity force during the flow in the body of the crucible is $\sim 10^{-2} \text{ N}$. Common decanting masses are of the order of grams ($10^{-3} \text{ kg}$). Hence, in terms of $"g"$ values, the viscosity will contribute at most $10 \text{ m/s}^2$, i.e. $\sim 1 \text{ g}$ force resistance during the decanting. Due to the continuity equation, $v_c A_c = v_f A_f$, where $v_f$ is the fluid flux velocity through the filter, $A_c$ is the crucible cross-section area and $A_f$ is the sum cross-section area of the filter holes. For 1 mm hole crucibles (51 hole) $A_c \sim 0.5 \times 10^{-3} \text{ m}^2$, whereas $A_f \sim 0.5 \times 10^{-5} \text{ m}^2$; hence $v_f = v_c A_c / A_f = v_c 10^2$, therefore $v_f = 10^4 \text{ m/s}$. The viscosity force through the filter can be approximated as $\mu (0.5 \times 10^{-5} \text{ m}^2) (v_f / 0.003 \text{ m}) = \mu 17 \text{ m}^2/\text{s}$. For the values of $\mu$ in the $10^{-3} \text{ Pa}\cdot\text{s}$ range \[6,7\], the viscosity force during the flux flow through the filter can be estimated to be about $\sim 2 \times 10^{-2} \text{ N}$. Therefore in terms of $"g"$ values, the viscosity will add $\sim 17 \text{ m/s}^2$, or about $1.7 \text{ g}$ resistance. Similarly, for 2 mm hole crucibles (37 holes) we get $A_f \sim 1.16 \times 10^{-4} \text{ m}^2$, $v_f \sim v_c 4.3 \sim 4.3 \times 10^2 \text{ m/s}$. The corresponding viscosity force is $\mu (1.16 \times 10^{-4} \text{ m}^2)(v_f / 0.003 \text{ m}) = \mu 16 \text{ m}^2/\text{s} \sim 1.6 \times 10^{-2} \text{ N}$ and the resistance force is somewhat smaller and equivalent to about $1.6 \text{ g}$.

The above analysis suggests that larger cross-section area of filter holes favors decanting of heavier element fluxes and is probably very important for decanting at lower temperatures since the viscosity of liquid metals falls with the Arrhenius law as the temperature is increased \[6,7\].

Figure 2 shows HTF-ISD furnace at work at Brookhaven National Laboratory. Figure 2a shows the side of the rotary tube where the process gas exits (yellow line). The large black box on the side of the unit is the power supply and control signal connection area. This is where the thermocouple signal connection (thin gray cable) is made, as well as the power connection (thick gray cable). The power cable carries the 100 A at 208 V to the furnace. The two Y-shaped holders on both sides of the furnace serve as a support for the tube during sample loading and unloading. In Figure 2a they are shown in their lowered position, when the tube is ready for the
rotation. The power supply contains an independent over-temperature alarm as well as rotation speed and direction controllers (clockwise and counter-clockwise) as well as the rotation indicator in rpm, and the main furnace breaker. The opposite side of the furnace (Figure 2b) houses the rotation motor that connects with a timing belt (inside the vertical stainless steel enclosure) to the extension of the stainless steel disc plate. The process gas enters the furnace on this side. The other Y-shaped holder is visible as well as the small door with a black knob (next to the yellow gas line) that houses the lever used to release or tighten the timing belt when the furnace is in its loading or in operating mode respectively. At the end of the temperature treatment, the furnace tube is rotated with desired angular velocity and the liquid is decanted. Care should be taken to ensure chemical compatibility of materials and gases used with the silicon carbide tube and internal assembly parts of the furnace.

Figure 3. Inner retort assembly (a) enables rotation up to 1000 rpm. The end of the inner assembly (shown here with alumina support tubes) attaches to the pins on the inner side of the steel cover (b). Three pins are closed whereas the fourth one carries the process gas (inert Ar in this case). The gas fills the whole volume of the furnace tube via holes in the support tube that attaches to the gas pin. Inner assembly (shown with silicon carbide support rods and graphite plates) is shown in (c) and (d). The first three graphite plates are for heat shielding but the inner graphite/silicon carbide plate has a space for a filter crucible, denoted by the white arrow. Note that the opposite support tubes are connected with alumina pins in order to enhance stability during rotation. The ends of the furnace tubes are cooled by air fans on both sides (d).
Figure 3 shows some additional details of the HTF-ISD method sample loading and unloading. An inner retort assembly (Figure 3a) enables rotation up to 1000 rpm. Furnace bore inner diameter is 6.25” and the heated length of the furnace is 12”. The rotary tube is 36” long whereas its inner and outer diameters are 6” and 5.5”, respectively. The front and back stainless steel end-caps serve both as tube plugs and as means to hold the inner assembly stable and firm during the rotation. In addition to high temperature silicone O-rings, the end-caps contain four pins on the inner side (Figure 3b). Three pins are solid whereas the fourth serves as a process gas inlet (front end-cap) or outlet (rear end-cap). The support rods (made of high density alumina or silicon carbide) attach to the end-caps by four steel pins with O-rings in order to accommodate for thermal expansion at high temperatures. The support rod that attaches to the gas carrier pin contains holes that allow for the process gas to be fed directly to the work-charge area and displace air and flow freely in the furnace. This provides an inert atmosphere for intermetallic crystal growth. Figure 3c and d show the inner assembly with silicon carbide support rods, half way drawn outside the furnace and ready to accept a crucible. The place for the crucible is depicted by the white arrow. The position of the growth crucible during heating and cooldown (i.e. before decanting) is below the “catch” crucible, and the crucible set is at “12 o’clock” position. The first graphite heat shield set is shown in the main part of both figures and the silicon carbide/graphite disk that houses the crucible is behind. After the temperature cycle and rotation, the furnace tube is fixed so that the filter crucible is at

Figure 4. Crystals grown by HTF-ISD method by rotation inside the furnace at 650°C: FeSb$_2$ grown in alumina crucible set (a) and the corresponding “catch” crucible (b) showing excellent antimony flux decanting. FeSb$_2$ crystals grown in graphite crucible set (c, d).
the bottom of the support assembly in the vertical plane (six o’clock position), preventing any backflow of the liquid during subsequent cooling of the furnace to the room temperature.

Single crystals grown by cooling from 900°C and decanted inside the furnace at 650°C are shown in Figure 4. Figure 4a shows crystals grown using an alumina crucible set. The flux decanting is excellent, as shown in Figure 4b. This is similar to results obtained with a graphite crucible set, however the crystals made in the graphite crucible set are smaller on the average even though the growth parameters were similar. This points to the higher number of nucleation sites that are probably caused by the reactivity of Fe–Sb melt with the graphite crucible interior. Reactions with crucible walls usually contribute to higher impurity levels in as-grown crystals.

Single crystals grown by cooling from 1450°C and decanted at 1280°C inside the furnace are shown in Figure 5. YbB4 (Figure 5a) crystals grown in an alumina crucible set have irregular polyhedral shape and black metallic color. Figure 5b shows enlarged details of the alumina filter in YbB4 growth after decanting. Some filter holes contain solidified Al flux, most likely due to the remnant wetting of the filter when the furnace is allowed to cool or from the final splashes of the liquid flux at the end of the rotation when the crucible set is rotated to the “six o’clock” position. From the vertical axis perspective, this puts the grown crystals above the
filter and the “catch” crucible. Therefore it is possible that some remnant liquid is pulled by the force of gravity, wetting and solidifying in some filter holes. Figure 5c shows Al\textsubscript{1.67}B\textsubscript{22} grown in a graphite crucible set and decanted \textit{in situ} using the same temperature profile as the one used for YbB\textsubscript{4}, whereas the filter and the “catch” crucible are shown in Figure 5d. Different color on the crucible filter (Figure 5d) suggests reaction of the filter (and probably crucible walls) with aluminum vapors during the crystal growth.

Unit cells of grown Al\textsubscript{1.67}B\textsubscript{22} and YbB\textsubscript{4} crystals were successfully refined using the space groups \textit{P}4\textsubscript{1}2\textsubscript{1}2 \#92 and \textit{P}4/\textit{mbm}, respectively (Figure 6). The obtained lattice parameters were $a = 1.0184(2)$ nm and $c = 1.4285(2)$ nm for Al\textsubscript{1.67}B\textsubscript{22} and $0.7062(2)$ and $0.3985(2)$ nm for YbB\textsubscript{4}. This is in a good agreement with the published values [8,9].

The HTF-ISD method of crystal growth can also be used for single crystal synthesis involving all commonly used metallic fluxes. Additionally, with the proper choice of crucibles used, many other transition metals and elements (such as Si) with melting points above 1200°C can now be used as solvents. The same method can also be modified and applied for oxide fluxes. The effects of crucible rotation and shaking during the growth on solubility of various hardly soluble materials and subsequent single crystal nucleation can also be studied and optimized. With appropriate choice
of the materials for the rotating tube, support structure and crucibles, it is possible to use other gases besides inert Ar or gas mixtures that would introduce volatile elements in the melt and enable crystal growth of materials such as metal nitrides.

4. Conclusions

The HTF-ISD crystal growth method enables stable intermetallic flux decanting inside the furnace. The method utilizes crucible sets with built-in filters, reducing the probability for contamination from the silica wool. We have demonstrated successful in-situ decanting of Sb flux below (650°C) and Al flux (1280°C) above the silica melting point. This method provides means for decanting of crystals very close to solidification lines in the alloy phase diagrams since there is no need to remove the crystal from the furnace during the decanting process. This provides the means for exploration of intermetallic phases that have a very narrow range of coexistence with the liquid. When compared to the common practice of decanting outside the furnace, the method reduces the possibility of oxidation during the decanting and crystallization of impurity phases. More materials (pure elements as well as compounds) can be used as a flux. Thus, the important and largely unexplored synthesis space opens up, particularly at the alloy phase diagrams containing high melting and low vapor pressure elements of significant importance for science and technology such as B, C, Fe, Mo, Si and Ti. This paves the way for not only new correlated electron materials in basic science but also for high temperature and lightweight alloys.

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