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# High-temperature solution growth of intermetallic single crystals and quasicrystals

Paul C. Canfield\*, Ian R. Fisher

*Ames Laboratory and Department of Physics and Astronomy, 59 Physics, Iowa State University, Ames, IO 50011, USA*

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## Abstract

Solution growth continues to be one of the most powerful techniques for the production of single crystals for basic and applied research. It is a versatile technique that allows for the growth of congruently and incongruently melting materials with equal ease. The primary requirement for growth is that there be an exposed primary solidification surface in the appropriate equilibrium alloy phase diagram. In this paper, we will review some of the systems that we have applied this technique to over the past several years. These range from binary and ternary intermetallic compounds such as  $RFe_2$  ( $R$  = Rare earth) and  $RT_2Ge_2$  ( $T$  = Ni and Cu) to the refractory  $RNi_2B_2C$  family of magnetic superconductors to several families of quasicrystals. In each case, specific nuances of the relatively simple growth technique will be discussed. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Single crystal samples allow for the measurement of the intrinsic properties of materials. In specific, they generally provide samples with less strain, higher purity, fewer grain boundaries, and natural growth habit. For basic studies of the electronic, magnetic, thermodynamic and structural properties of new or exotic materials the size of single crystals required rarely exceeds a cubic centimeter and often (with the exception of inelastic neutron scattering) crystals with dimen-

sions of several mm on a side are more than adequate. Given that the majority of materials are incongruently melting, a technique that can grow a wide variety of congruently *and* incongruently melting materials with equal ease, with relatively simple equipment, in rather short time scales, is of great desirability. Growth from high-temperature metallic solutions is just such a technique. In addition it uses relatively small amounts of materials, making it much more economic than techniques such as Bridgman or Czochralski (CZ) growth, both of which require more substantial quantities raw material.

In this paper, we will review several recent examples of single crystals (or quasicrystals) that have been grown from metallic solutions. The

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\*Corresponding author. Tel.: +1-515-294-6270; fax: +1-515-294-0689.

*E-mail address:* canfield@ameslab.gov (P.C. Canfield).

emphasis will be on showing the versatility of this technique as well as highlighting advances that have been made in temperature range, flux, or crucible design over the past decade. This paper should be considered as an extension of two earlier papers published on this technique by Fisk and Remieka [1], and Canfield and Fisk [2].

## 2. Experimental methods

Growth of single crystals from metallic solutions requires very simple equipment: box and vertical tube furnaces, a glass bench for evacuating and sealing quartz tubes, crucible materials and, in some cases, an arc-melter for pre-alloying elements and for working with Ta. Many of these details have been covered in the earlier two articles [1,2] and will not be reviewed here.

Given the reactivity of certain elements with  $\text{Al}_2\text{O}_3$  (excessive Ce and Mg for example), a Ta crucible is sometimes needed. So as to allow for the decanting of the excess melt from the grown crystals a sealed Ta crucible with a built-in strainer is used. A simple, but effective version of such a crucible is referred to as a “3-cap crucible” because it can be made from a length of Ta tubing and three Ta caps, made of Ta sheet that have been machined to just fit inside of the Ta tube. One of the caps is arc-welded into the tube, closing it and creating a crucible, then the material is placed into the bottom of the crucible and the second cap, with holes drilled through it, is crimped into place just above the level of the solid material. Finally, the third cap is arc welded into place, sealing the crucible. Once the growth is completed the crucible can be inverted for decanting.

## 3. $\text{CeFe}_2$ and other binary compounds

$\text{CeFe}_2$  is a face centered cubic compound with the  $\text{Cu}_2\text{Mg}$  structure. Based on the binary phase diagram [3] it decomposes peritectically at  $925^\circ\text{C}$  to  $\text{Ce}_2\text{Fe}_{17}$ +liquid, passes through a second peritectic decomposition to  $\gamma\text{Fe}$ +liquid at  $1063^\circ\text{C}$ , and finally becomes a homogeneous liquid at  $\sim 1190^\circ\text{C}$ . Given the two peritectics that would

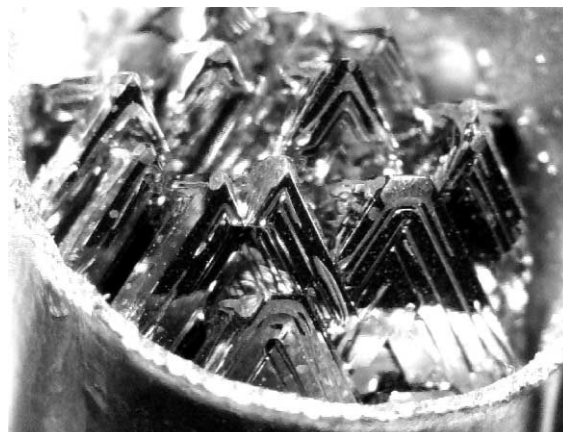


Fig. 1. Single crystals of  $\text{GdFe}_2$  in remains of 15 mm OD Ta crucible. The larger facet edges are approximately 5 mm.

have to be passed through, traditional growth methods such as Bridgman or CZ growth have proven to be impractical for this compound. On the other hand, given the relatively large, exposed  $\text{CeFe}_2$  primary solidification line which exists between 54% and 83% Ce and  $925\text{--}592^\circ\text{C}$ , there is ample opportunity to grow  $\text{CeFe}_2$  from excess Ce. Single crystals in excess of 4 g have been grown by this technique.

Elemental Ce and Fe are combined in an  $\text{Ce}_{0.55}\text{Fe}_{0.45}$  atomic ratio in the lower part of a Ta 3-cap crucible which itself is sealed into a quartz ampule. The ampule is placed in a box furnace, heated to  $1100^\circ\text{C}$  and then slowly cooled to  $950^\circ\text{C}$  over 100–200 h. When the slow cool is completed the ampule is inverted and the excess liquid is decanted.  $\text{RFe}_2$  single crystals grow with well developed [1 1 1] facets (see Fig. 1 for  $\text{GdFe}_2$ ). Neutron diffraction on samples as large as several grams reveals that the crystals have diffraction peak line widths below instrumental resolution.

In a similar manner, single crystals of  $\text{RAl}_3$ ,  $\text{RIn}_3$ ,  $\text{RSb}_2$ ,  $\text{RBi}_2$ , and many other binary compounds can be grown from binary melts [2].

## 4. $\text{RT}_2\text{Ge}_2$ (T = Cu, Ni) series

Single crystals of the  $\text{RT}_2\text{Ge}_2$  (R=rare earth and T=Cu, Ni) series can be grown via two different types of solution growth: from a ternary

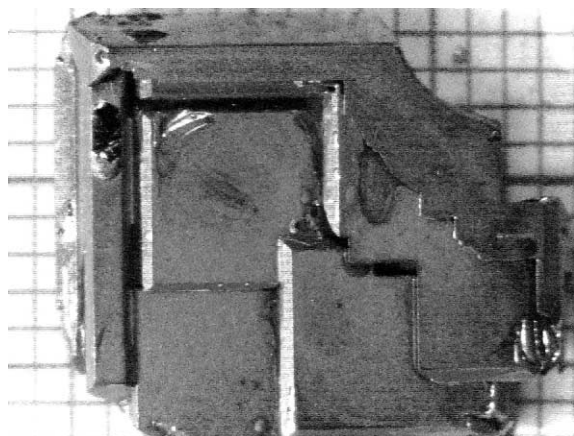


Fig. 2. Single crystal of  $\text{CeCu}_2\text{Ge}_2$  ( $m = 2.0$  g). The tetragonal  $c$ -axis is perpendicular to the plate.

rich in T–Ge or from a true flux of either Sn or In. The case of growth from the ternary melt is conceptually similar to the  $\text{RFe}_2$  growths described above. The primary difference is that there is generally inadequate information about ternary phase diagrams and therefore a bit more trial and error work is involved in optimizing a given growth. Both the Cu–Ge and Ni–Ge binary phase diagrams have relatively low melting points for  $\text{T}_{0.5}\text{Ge}_{0.5}$  mixtures. In both cases by adding roughly 5.0–7.5% R to the melt, single crystals of  $\text{RT}_2\text{Ge}_2$  can be grown. Taking the specific example of  $\text{CeCu}_2\text{Ge}_2$ , a starting composition of  $\text{Ce}_{0.05}\text{Cu}_{0.475}\text{Ge}_{0.475}$  is placed in an  $\text{Al}_2\text{O}_3$  crucible, sealed in a quartz ampule and heated to  $1190^\circ\text{C}$ . The ampule is cooled to  $825^\circ\text{C}$  over 200 h and then the excess liquid is decanted. The resulting crystal is shown in Fig. 2.

A similar technique has been used to grow virtually all of the  $\text{RNi}_2\text{Ge}_2$  series (with the glowing exception of  $\text{R} = \text{Pm}$ ) [4]. Whereas the initial composition of the growths is essentially the same the decanting temperature is higher ( $T = 950^\circ\text{C}$ ) due to the higher liquidus temperature of  $\text{Ni}_{0.5}\text{Ge}_{0.5}$ .

In the case of  $\text{YbNi}_2\text{Ge}_2$ , the crystals grown from the ternary melt exhibited a larger residual resistivity and low-temperature impurity tail in the magnetic susceptibility than is desirable. This is very likely caused by the fact that the Yb hybridizes with the conduction electrons, leading

to a mixed valent ground state, which is itself extremely sensitive to even slight ligand disorder. In order to grow more highly ordered single crystals of  $\text{YbNi}_2\text{Ge}_2$ , indium was used as a fourth element flux. A starting composition of  $(\text{YbNi}_2\text{Ge}_2)_{0.05}\text{In}_{0.95}$  was placed in an  $\text{Al}_2\text{O}_3$  crucible, heated to  $1200^\circ\text{C}$  and cooled to  $750^\circ\text{C}$  over 100 h and then decanted. The resulting single crystals were significantly smaller than those grown from the ternary melt ( $5 \times 5 \times 1$  mm in dimension) but had greatly improved magnetic and transport properties.

## 5. Icosahedral R–Mg–Zn quasicrystals

The face centered icosahedral quasicrystal family  $\text{R}_9\text{Mg}_{34}\text{Zn}_{57}$  (I-RMgZn) provides a clear example of (i) the fact that non-crystalline compounds can be grown via this technique, and (ii) the beauty of single grains with stable growth facets. Fig. 3 is a picture of a single grain of I-HoMgZn that was grown in a Ta, 3-cap crucible. The grain clearly exhibits the 5-fold symmetry associated with a quasicrystal, and more importantly the TEM and single crystal diffraction patterns are fully consistent with a highly ordered, aperiodic structure with 5-fold rotational symmetry [5].

The  $\text{RMgZn}$  series is found to be thermodynamically stable for  $\text{R} = \text{Gd} - \text{Er}$  and initial phase

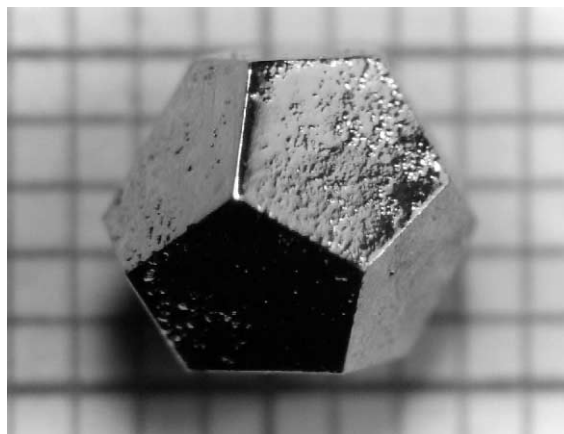


Fig. 3. Single grain of icosahedral  $\text{Ho}_9\text{Mg}_{34}\text{Zn}_{57}$  on a mm-grid [7].

diagram work on the Y–Mg–Zn system [6] indicated that there was an exposed primary solidification surface on the R-poor region. The mixture of elements  $Y_3Mg_{51}Zn_{46}$  was sealed into a 3-cap Ta crucible and subsequently in a quartz ampule. This was then heated to 700°C and cooled to 480°C over 100 h at which point the excess liquid was decanted. (Slightly different initial concentrations were needed for R=Tb and R=Gd due to inferred shifts in the primary solidification surface.)

Solution growth provided the first single grains (and to a large extent the first single phase) samples of these materials [5]. With single grains of the I-RMgZn materials a thorough investigation of magnetic and electronic properties was possible. The I-RMgZn series provides an excellent example of the spin glass ground state [7] and also exhibits many of the transport properties associated with metallic glasses. Whereas, it was previously thought that disorder was a necessary condition for the observation of spin glass or metallic glass like behavior, it is now experimentally clear that a highly ordered, aperiodic arrangement of atoms is sufficient. To this extent, the quasicrystalline samples offer a more reproducible way of examining these low-temperature states.

## 6. Icosahedral AlMnPd and decagonal AlNiCo quasicrystals

Based on our initial success at the growth of single grain, I-RMgZn quasicrystals, we examined several other stable quasicrystalline systems:  $Al_{71}Pd_{21}Mn_8$  and  $Al_{80}Ni_{11}Co_{17}$  [8,9]. In both cases, the melts are Al rich, which, due to the extreme reactivity of Al with the quartz containment ampule, leads to the need to reduce the effects of Al vapor pressure. This is done in two ways. First, two  $Al_2O_3$  crucibles are cut so as to mate as closely as possible, creating a nearly enclosed environment. Second, the quartz ampule is back filled with approximately 0.3 atm. of Ar. These two measures allow for the use of Al-rich fluxes, not only for these two specific growths, but for any Al-rich growth.

The growth of icosahedral  $Al_{71}Pd_{21}Mn_8$  (I-AlPdMn) is conceptually similar to the growth of I-RMgZn described above, but the primary solidification surface is significantly smaller and the material is much closer to being congruently melting [8]. An initial composition of  $Al_{73}Pd_{19}Mn_8$  is heated to 875°C and slowly cooled to 840°C over up to 100 h. Single grains of I-AlPdMn are similar in morphology to I-RMgZn but have linear dimensions that can exceed several cm. What is truly remarkable about the growth of these quasicrystals is that even though there is no attempt to control nucleation, and even though the initial concentration is very close to the actual concentration of the solid phase, only one or two nucleation sites occurs in a given growth. This leads to the ability to grow extremely large single grains, often crucible limited in 5, 10 and 20 ml  $Al_2O_3$  crucibles. This observation is consistent with there being a relatively large energetic cost to forming a nucleation center.

Decagonal  $Al_{80}Ni_{11}Co_{17}$  (D-AlNiCo) can be grown [9] in a manner very similar to that described above for I-AlPdMn. An initial concentration of  $Al_{77}Ni_{10.5}Co_{12.5}$  is heated to 1200°C and slowly cooled to 1000°C over 100 h and then decanted. Fig. 4a shows a picture of one of the single grains grown in this manner. The rod direction is the faster growing, periodic direction and the basal plane is the slower growing, aperiodic plane. D-AlNiCo provides a case study of the effects of width of formation of single crystals (or quasicrystals) grown from high-temperature solutions. Given that a D-AlNiCo grain grows radially at a much slower rate than it does along the periodic direction, the radial composition reflects the temperature dependent width of formation. Elemental analysis of a cross sectional area of one of the single grains is shown in Fig. 4b and qualitatively reproduces the temperature dependence of the width of formation as determined in existing phase diagrams [9,10].

## 7. $RNi_2B_2C$ magnetic superconductors

Up to this point, we have been discussing binary and ternary compounds, but quaternary compounds

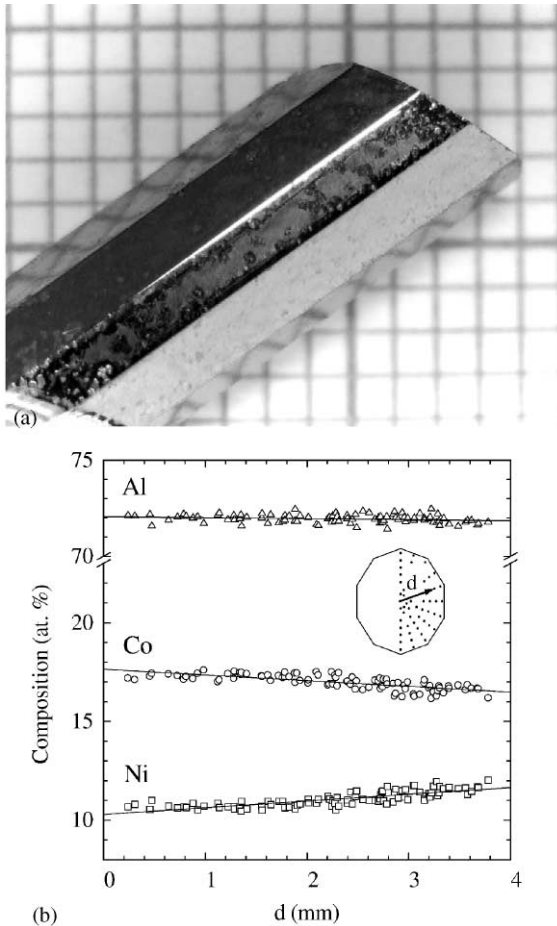


Fig. 4. (a) Single grain of decagonal  $\text{Al}_{80}\text{Ni}_{11}\text{Co}_{17}$ . Note five of ten facets visible in figure, including two with reflections of mm grid in them [9]. The rod axis is the periodic direction. (b) radial composition of sample as determined via EMPA [9].

can be grown out of solutions too. A particularly clear example of this is the  $\text{RNi}_2\text{B}_2\text{C}$  family of magnetic superconductors [11]. The discovery of these materials was announced in a series of papers in January 1994 and by March 1994 we had devised a method for the synthesis of single crystals as large as one gram of these compounds for  $\text{R} = \text{Gd-Lu, Y}$ . With such large, high purity, low strain, single phase samples a whole vista of physical measurements became possible. As a result of this, the  $\text{RNi}_2\text{B}_2\text{C}$  series is currently the most fully characterized family of intermetallic magnetic superconductors known. The physics

associated with the interplay between the local moment magnetism and the superconductivity of the conduction electrons is a rich and complex field [11]. The growth of these crystals required several modifications to the conventional techniques that are worth reviewing.

The  $\text{RNi}_2\text{B}_2\text{C}$  materials decompose peritectically just above  $1500^\circ\text{C}$ . As cast, stoichiometric samples are multi-phase, but annealing at  $1100^\circ\text{C}$  for several days leads to nearly single phase, polycrystalline materials. An examination of the Ni–B binary phase diagram [3] reveals that for compositions between approximately  $\text{Ni}_{0.85}\text{B}_{0.15}$  and  $\text{Ni}_{0.45}\text{B}_{0.55}$  the liquid–solidus line is below  $1200^\circ\text{C}$ . Indeed,  $\text{Ni}_2\text{B}$  is a binary compound that melts congruently at  $1125^\circ\text{C}$ . The use of  $\text{Ni}_2\text{B}$  as a solution for the growth of crystals of  $\text{RNi}_2\text{B}_2\text{C}$  offers the possibility of crystal growth between  $1500^\circ\text{C}$  and  $1200^\circ\text{C}$  (Fig. 5).

Polycrystalline ingots of  $\text{Ni}_2\text{B}$  and  $\text{RNi}_2\text{B}_2\text{C}$  are prepared by arc-melting stoichiometric mixtures of high purity elements. An ingot of  $\text{Ni}_2\text{B}$  is then placed at the bottom of an  $\text{Al}_2\text{O}_3$  crucible (generally a 5 ml crucible) and an ingot of  $\text{RNi}_2\text{B}_2\text{C}$  of equal mass is placed on top of the  $\text{Ni}_2\text{B}$ . The crucible is then placed in a vertical tube furnace under an atmosphere of flowing Ar [1,2], heated to  $1500^\circ\text{C}$ , and cooled to  $1200^\circ\text{C}$  over

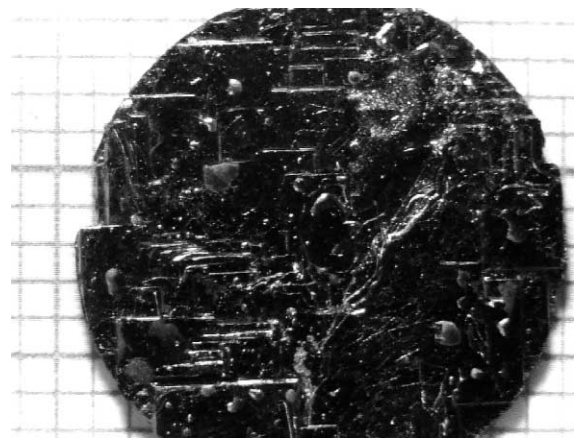


Fig. 5.  $\text{LuNi}_2\text{B}_2\text{C}$  crystal ( $m = 1.0\text{ g}$ ). The crystal was crucible limited and the cryptomorphic, circular cross section is due to the crucible walls. The tetragonal  $c$ -axis is perpendicular to the plate.

100 h. Once the furnace reaches 1200°C, it is turned off and allowed to cool. At this point, crystals can be removed from the solidified, excess material, but it is more expedient to reseal the growth crucible in a quartz ampule, reheat to 1200°C, dwell for approximately 1 h, and decant.

## 8. Summary

Each of the examples presented here illustrates some of the important points to keep in mind during the growth of intermetallic crystals from high-temperature solutions. The first and foremost point is that each crystal system is different and dictates what must be done to grow it. The desired crystal influences the type of solution to be used, the composition of the high-temperature solution determines the types of crucibles that need to be used, and the temperature range of the growth determines the choice of encapsulation, or how a protective atmosphere is to be provided.

In the cases of  $RFe_2$  and  $I-RMgZn$ , the reactivity of the melt with  $Al_2O_3$  requires the use of Ta crucibles. Three-cap Ta crucibles allow for easy decanting as well as prevent attack of the quartz ampule by metals in the vapor phase.

The growth of  $RT_2Ge_2$  crystals provides an example of a choice that sometimes exists. Larger single crystals can be grown from the ternary melt, but for some R this technique does not produce crystals with an adequate degree of order. The alternative is to grow smaller, better formed single crystals from a true, fourth element, flux.

The growth of Al-based quasicrystals reveals the importance of taking the vapor pressure of Al into account. (This is actually true of any high-temperature growth that utilizes Al as a solvent.) In addition, D-AlNiCo provides a case study of the effects of width of formation on quasicrystal (or crystal) grown from high-temperature solutions. Fortunately, many intermetallic systems manifest vanishingly small, or at least insignificant, widths of formation.

The growth of  $RNi_2B_2C$  single crystals presents several new features. First of all, it provides an example of how to grow single crystals at

temperatures well above the softening point of quartz ( $\sim 1200^\circ\text{C}$ ). Excess solution can still be decanted from grown crystals as long as the decanting temperature is equal to or less than 1200°C. It should be noted though that whereas this technique works well with the  $RNi_2B_2C$  materials, in some cases the intermediate cooling to room temperature leads to cracks and defects in other crystals: i.e., this technique does not always work. A second point to note is that whereas all the previous examples of crystal growth provided in this paper started the growth from a homogeneous liquid at the highest temperature, the  $RNi_2B_2C$  polycrystalline pellet never fully dissolves into the excess  $Ni_2B$ . Indeed this growth is probably some sort of hybrid between a traditional growth from high-temperature solution and chemical transport through a liquid phase. This was not an intentional choice, it was simply the manner in which the crystals could be best synthesized. Again, returning to the first point mentioned in the summary: each crystal system is different and dictates what must be done to grow it.

## Acknowledgements

Orson Welles once said that making films was like being a small child with a very expensive paint box. In a similar manner searching for new materials and growing single crystals of a wide variety of compounds requires an adequate and flexible materials budget. We gratefully acknowledge the US Department of Energy, Office of Basic Energy Sciences. Their unflagging support has made all of this research possible.

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