Solution growth of intermetallic compounds

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Abstract

In the lecture I will present principles of the solution growth technique. Common problems that are associated with this technique will be discussed.
1. M. G. Kanatzidis, R. Pöttgen, W. Jeitschko, 

2. Properties and Applications of Complex Intermetallics, 
   ed. Esther Belin-Ferré, chapter 2 by Paul C. Canfield;

3. P. C. Canfield, and Z. Fisk, 
   Philosophical Magazine Part B, 65:6, 1117 – 1123 (1992);

4. Y. Janssen, M. Angst, K. W. Dennis, R. W. McCallum, P. C. Canfield, 
   Journal of Crystal Growth 285, 670–680 (2005);

5. P. C. Canfield, I. R. Fisher, 
Outline

- Solution growth of intermetallic compounds - *principles*;
- Requirements - *what do you need*;
- Plan of the experiment - *how do you do it*;
- DTA technique - *how it can help with the experiment*;
- Unsuccessful growth;
- Conclusions.
Why the solution growth technique?

- It does not require specialized equipment;
- Lower required temperature and increased diffusion rate in comparison to other commonly used methods;
- A first choice method for exploration of systems containing highly volatile elements such as Mg, Yb or Sb.
- Your crystals can be too small for certain experiment;
- There is possibility of either flux substitution, or macroscopic flux inclusion in the grown crystals;
- The flux used should form no high temperature stable binary compounds with any of the reacting components;
- The separation of the crystals from the flux should be possible.
Basic principles

- Binary phase diagram;
- Liquidus line;
- Solidus line;
- Congruent and incongruent melting;
- Eutectic point.

Basic principles

- Co-Sn phase diagram.
- Target is CoSn$_3$.
Basic principles

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Basic principles

- Co-Sn phase diagram.
- Target is CoSn$_3$.

Source:
M. G. Kanatzidis, R. Pöttgen, W. Jeitschko,
Basic principles

Temperature

Time

400°C
1 deg/h

300°C
Requirements - *what do you need*

- Elements! Including the one which will work as **flux**;
- A crucible (something to hold it in) and a quartz tube (something to provide protecting atmosphere);
- A furnace with a **good** temperature controller;
- An idea (plan), electrical power, and patience;
- A centrifuge to remove the excess of solution;
- A hammer, all kinds of microscopes, tweezers, etchants and patience again!
Requirements - *what do you need*

- Elements! Including the one which will work as **flux**.

  Purity issue:
  99.5% or 2N5
Requirements - what do you need

- Elements! Including the one which will work as flux.

**Sn (T_m = 232 °C)** –
Tin is commonly used as a flux medium for the growth of metal-rich phosphides and arsenides.

Tends to coat the material grown out of it (Sn is superconductor). Sn tends to form MSn_3 binary compounds (increase decanting temperature).

It is the first choice for any new crystal growth project.
Requirements - *what do you need*

- Elements! Including the one which will work as **flux**.

**Pb** $(T_m = 327 \, ^\circ C)$ –

Pb is similar to Sn of its problems as a flux. Tends to coat the material grown out of it (Pb is a superconductor). Pb tends to form MPb$_3$ binary compounds (increase decanting temperature).

Easy to dissolve ($H_2O_2 +$ acetic acid).
Requirements - *what do you need*

- Elements! Including the one which will work as flux.

**In** \((T_m = 157 \, ^\circ C)\) –
Indium dissolves Si, Ge and does not form binary compounds with Ge and Si. Is used to growth CeIn\(_3\), CeTIn\(_5\), Ce\(_2\)TIn\(_8\), where \(T = \text{Co, Rh, Ir, Pd, Pt}\).

The problem with In is that it is a superconductor (again).
Requirements - *what do you need*

- Elements! Including the one which will work as **flux**.

**Sb** ($T_m = 630 ^\circ C$) –
Antimony… not easy to dissolve. Rarely used. However, very recently YbSb$_2$ superconductor grown by flux method.

Requirements - *what do you need*

- Elements! Including the one which will work as **flux**.

**Bi (T<sub>m</sub> = 271 °C)** –

Bismuth – rarely used,
but… that is why U<sub>3</sub>Bi<sub>4</sub>M<sub>3</sub> compounds were not reported

Requirements - *what do you need*

- Elements! Including the one which will work as **flux**.

**Ga** ($T_m = 29.8 \, ^\circ \text{C}$) –
Gallium Gallium is an interesting flux metal. Two problems: liquid Ga tends to wet surface of your crystals (not easy to decant); in the case of RE it often forms compounds with the solutes that preclude the desired material from growing.

A good choice for the actinide compounds: e.g. **PuCoGa$_5$**.
Requirements - *what do you need*

- Elements! Including the one which will work as *flux*.

Other fluxes:
- Al ($T_m = 660 \, ^\circ\text{C}$),
- Zn ($T_m = 419.5 \, ^\circ\text{C}$),
- Li ($T_m = 180.5 \, ^\circ\text{C}$),
- Na ($T_m = 98 \, ^\circ\text{C}$),
- Cu ($T_m = 1084 \, ^\circ\text{C}$).

- NaCl ($T_m = 801 \, ^\circ\text{C}$)!
- FeAs ($T_m = 1030 \, ^\circ\text{C}$)!
- NiAs ($T_m = 968 \, ^\circ\text{C}$)!
Requirements - *what do you need*

- Elements! Including the one which will work as flux.

  - **Self flux method:** (reacting solvent)
  - **Non-self flux method:** (non reacting solvent)
Requirements - what do you need

- Crucibles!

The most popular for intermetallic growth is dense (!!) \( \text{Al}_2\text{O}_3 \) crucible. It is because it is cheap and can be used when common metal fluxes are used: Bi, Pb, Sb, Sn, In, Ga, Ge, Zn, Cu, Al.

Should not be used if your experiment requires more than 10 at. % of RE, or Mg and some transition metals (in particular from group IV: Ti, Zr and Hf). Possibly releases Al and O, when Ca, Sr and Ba are employed.
Requirements - *what do you need*

- A quartz tube…

Nothing special, just an amorphous silica with a diameter larger than the diameter of your crucible. However…
1. you should be familiar with using a blow torch;
2. you should work in a fume-hood;
3. you need a pumping station for evacuating back your ampoule.
Requirements - *what do you need*

- Silica wool…
  ... and sometimes you also use (for safety reason) an additional alumina crucible.
Requirements - *what do you need*

- A high temperature furnace.

  If you use quartz tubes, the highest temperature is limited to 1220°C.

  Your furnace should hold up at least one tube in vertical (or close to) position.
Requirements - *what do you need*

- A high temperature furnace… and a programmable controller (!).

- T set point = 600°C
- T ramp = 6 deg/h
- or:
- Target T = 600°C
- Time = 100 h.
Requirements - *what do you need*

- A centrifuge!!!
  (decanting process)
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Requirements - *what do you need*

- A hammer, all kinds of microscopes, tweezers, etchants and patience again!
Requirements - *what do you need*

- A hammer, all kinds of microscopes, tweezers, *etchants* and patience again!
Requirements - *what do you need*

- Etchants.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Etchant</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>$\text{H}_2\text{O}/\text{HF}$</td>
<td>1:1</td>
</tr>
<tr>
<td>Antimony</td>
<td>$\text{H}_2\text{O}/\text{HCl}/\text{HNO}_3$</td>
<td>1:1:1</td>
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<tr>
<td>Bismuth</td>
<td>$\text{H}_2\text{O}/\text{HCl}$</td>
<td>10:1</td>
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<tr>
<td>Chromium</td>
<td>$\text{H}_2\text{O}/\text{HNO}_3$</td>
<td>3:1</td>
</tr>
<tr>
<td>Cobalt</td>
<td>$\text{H}_2\text{O}/\text{H}_2\text{O}_2$</td>
<td>1:1</td>
</tr>
<tr>
<td>Copper</td>
<td>$\text{H}_2\text{O}/\text{HNO}_3$</td>
<td>3:1</td>
</tr>
<tr>
<td>Gold</td>
<td>Hot $\text{H}_2\text{O}/\text{H}_2\text{O}_2$</td>
<td>20:1:1</td>
</tr>
<tr>
<td>Hafnium</td>
<td>Hot $\text{H}_2\text{O}/\text{HNO}_3$</td>
<td>3:1</td>
</tr>
<tr>
<td>Indium</td>
<td>Hot $\text{H}_2\text{O}/\text{HNO}_3$</td>
<td>3:1</td>
</tr>
<tr>
<td>Iridium</td>
<td>Hot $\text{H}_2\text{O}/\text{HNO}_3$</td>
<td>3:1</td>
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<tr>
<td>Iron</td>
<td>$\text{H}_2\text{O}/\text{HNO}_3$</td>
<td>1:1</td>
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<tr>
<td>Lead</td>
<td>Acetic $\text{H}_2\text{O}$</td>
<td>1:1</td>
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<tr>
<td>Magnesium</td>
<td>Hot $\text{H}_2\text{O}/\text{NaOH}$ followed by $\text{H}_2\text{O}/\text{Cr}_2\text{O}_7$</td>
<td>10:1 by weight 5:1 by weight</td>
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<td>Molybdenum</td>
<td>$\text{HCl}/\text{H}_2\text{O}_2$</td>
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<td>Nickel</td>
<td>$\text{H}_2\text{O}/\text{HNO}_3$</td>
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<td>Niobium</td>
<td>$\text{H}_2\text{O}/\text{HNO}_3$</td>
<td>1:1</td>
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<tr>
<td>Palladium</td>
<td>Hot $\text{HCl}/\text{HNO}_3$</td>
<td>3:1</td>
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<tr>
<td>Platinum</td>
<td>Hot $\text{HCl}/\text{HNO}_3$</td>
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<tr>
<td>Rhenium</td>
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<td>3:1</td>
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<td>Rhodium</td>
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<td>Ruthenium</td>
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<tr>
<td>Silver</td>
<td>$\text{NH}_4\text{OH}/\text{H}_2\text{O}$</td>
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<td>Tantalum</td>
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<tr>
<td>Tin</td>
<td>$\text{H}_2\text{O}/\text{HCl}$</td>
<td>1:1</td>
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<tr>
<td>$\text{H}_2\text{O}/\text{HNO}_3$</td>
<td>1:1</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>$\text{H}_2\text{O}/\text{H}_2\text{O}_2$</td>
<td>1:1</td>
</tr>
<tr>
<td>Tungsten</td>
<td>$\text{H}_2\text{O}/\text{HNO}_3$</td>
<td>1:1</td>
</tr>
<tr>
<td>Vanadium</td>
<td>$\text{H}_2\text{O}/\text{H}_2\text{O}_2$</td>
<td>1:1</td>
</tr>
<tr>
<td>Zirconium</td>
<td>$\text{H}_2\text{O}/\text{H}_2\text{O}_2$</td>
<td>1:1</td>
</tr>
</tbody>
</table>
Planning experiment

- Solution growth of intermetallic compounds - *principles*;
- Requirements - *what do you need*;
- **Plan of the experiment** - *how do you do it*;
- DTA technique - *how it can help with the experiment*;
- Unsuccessful growth;
- Conclusions.
Planning experiment

- How to plan your experiment.

Have an idea!
Read papers, listen talks, talk to people, do not stop asking questions.
Check phase diagrams and chemical and crystallographic data bases.
CeIn$_3$ – Ce:In 10:90;
$T_{\text{max}} = ? \, ^oC$
$T_{\text{dec}} = ? \, ^oC$
DTA technique

- Solution growth of intermetallic compounds - *principles*;
- Requirements - *what do you need*;
- Plan of the experiment - *how do you do it*;
- **DTA technique** - *how it can help with the experiment*;
- Unsuccessful growth;
- Conclusions.
DTA technique

- Derivative thermo analysis (DTA)

Based on:


We have found that the use of DTA can greatly facilitate the optimization of the growth, and can play a role in selecting the right crucible material.
DTA technique

- Derivative thermo analysis (DTA)

Unsuccessful growth

- Solution growth of intermetallic compounds - *principles*;
- Requirements - *what do you need*;
- Plan of the experiment - *how do you do it*;
- DTA technique - *how it can help with the experiment*;
- **Unsuccessful growth**;
- Conclusions.
Unsuccessful growth

- Nothing left in a crucible (total spin);
- Nothing leaves a crucible (no spin);
- Problem with crucible (all kind of damage);
- Growth of a second phase;
- Small crystals.

Safety and some more hints

- Think twice before starting your experiment.

- Work safely!
  Use protective glasses, gloves, long trousers, long coat, closed shoes.

- Use your imagination!

- Read papers and ask people.

- Never give up!

- No guts, no glory!
Summary

- “Using liquid metals as fluxes, to carry out synthetic explorations, could serve as a great way to discovering (without having to predict) a large variety of intermetallic compounds.”


- “Although this lack of a precise method or recipe for growing crystals from a flux might strike some as a large hurdle to surmount, it is precisely this imprecision and reliance on either intuition or luck that gives this technique so much of its charm and power. The accidental growth of second phase is more often the source of interesting new materials than the intentional plotting of any specific course.”