Nucleation studies on undercooled refractory metals and alloys: a review

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1. Experimental approach - containerless processing
2. Nucleation studies on pure refractory metals
   - statistical analysis on nucleation events
   - comments on the limit to crystal nucleation
3. Metastable phases
   - pure metals
   - Refractory alloys (Re-W and Re-Ta systems)
4. Conclusion - acknowledgments - references
1. Experimental approach: liquid undercooling (1)

The state of **liquid undercooling** is discovered by **Fahrenheit** (1724) on water when working on the thermometer; observed by **Cavendish** in Hg protected by nitric acid and fats (bef. 1800).

**Undercooling water down to -20°C, Despretz** noticed a **rapid solidification** that caused the destruction of the glass vessel (ard 1820).
The French word “germination” is introduced by Gernez (1865), a student of Pasteur: nucleation is favoured by introducing isomorphous solid particles; Van Riemsdyk (1880) observed the detrimental effect of stirring and discontinuous cooling.

**1. Experimental approach: heterogeneous nucleation (2)**

- **heterogeneous nucleation**
  - extraneous interfaces (e.g. impurities, container walls)

- **homogeneous nucleation**
  - favourable thermodynamic fluctuations in the bulk
  - theoretical limit

**containerless processing**

**free-fall methods**
1. Experimental approach: dispersion methods (3)

**Mendenhall** and **Ingersoll** (1908) obtained very large undercoolings on minute particles of Pt (375 K) placed upon the surface of a Nernst glower, whose temperature could be controlled with suitable rheostat and examined with a microscope of low power.

**Vonnegut** (1948) demonstrated that heterogeneous nucleation sites can be isolated by dividing the melt into small particles: suitable way to investigate the undercooling behaviour.

**dispersion & emulsification methods**

**Turnbull, Perepezko, Bosio, Rasmussen, Skripov,**...
1. Experimental approach: containerless processing (4)

Containerless processing is introduced by Shiraishi and Ward (1964) for thermophysical properties measurements. Based on the monitoring of temperature/time profiles, it is well suited for undercooling experiments on high-temperature and refractory materials (free-fall conditions).

- aerodynamic lev.: CRMHT - Orléans (F. Millot)
- electrostatic lev.: NASDA - Tsukuba (J.F. Paradis)
- electromagnetic lev.: DLR - Cologne (D.M. Herlach)
- 1st drop-tube: NASA - Huntsville (W.H. Hofmeister)

space transfer of containerless processing

1. Experimental approach: refractory metals (5)

Undercooling experiments have essentially dealt with elements ranging between Hg and Fe in melting temperature, thus considering in a common approach elements characterized by very different physical and chemical properties (e.g. Fe, Al, Si, Bi, Au, etc.).

<table>
<thead>
<tr>
<th>3d-</th>
<th>Ti</th>
<th>1660°C</th>
<th>V</th>
<th>1890°C</th>
<th>Cr</th>
<th>1857°C</th>
<th>Mn</th>
<th>1244°C</th>
<th>Fe</th>
<th>1535°C</th>
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<th>1495°C</th>
<th>Ni</th>
<th>1453°C</th>
<th>Cu</th>
<th>1083°C</th>
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<td>fcc</td>
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<tr>
<td>4d-</td>
<td>Zr</td>
<td>1852°C</td>
<td>Nb</td>
<td>2468°C</td>
<td>Mo</td>
<td>2617°C</td>
<td>Tc*</td>
<td>2172°C</td>
<td>Ru</td>
<td>2250°C</td>
<td>Rh</td>
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<td>10.5</td>
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<td>fcc</td>
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<td>fcc</td>
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<tr>
<td>5d-</td>
<td>Hf</td>
<td>2231°C</td>
<td>Ta</td>
<td>2985°C</td>
<td>W</td>
<td>3410°C</td>
<td>Re</td>
<td>3180°C</td>
<td>Os</td>
<td>3045°C</td>
<td>Ir</td>
<td>2443°C</td>
<td>Pt</td>
<td>1772°C</td>
<td>Au</td>
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<td>16.65</td>
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<td>22.4</td>
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<td></td>
<td>fcc</td>
<td></td>
<td>fcc</td>
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</tr>
</tbody>
</table>

Importance of transition refractory metals:

- fundamental: correlation with the periodic table (atomic number)
- practical: outstanding properties (severe environments), new alloys
Gibbs proposed in 1873 a thermodynamic analysis of phase stability. In the case of classical nucleation, metastability corresponds to the situation where a critical size exists within a localized fluctuation beyond which growth occurs. Through the capillary formalism, the Gibbs free-energy difference of a spherical nucleus in the melt is the sum of:

\[
\Delta G = 4\pi r^2 \sigma_{\text{LS}} + \frac{4}{3} \pi r^3 \Delta G_v
\]

where \( \sigma_{\text{LS}} \) is the solid-liquid interface energy and \( \Delta G_v \) is the negative free enthalpy change in forming a unit volume of solid from the liquid.

The diagram illustrates the Gibbs free energy \( \Delta G \) as a function of the radius \( r \). The activation barrier \( \Delta G^* \) is shown at the critical radius \( r^* \). At 1 nm, there are 250 atoms.
Improving the Volmer and Weber approach (1926) for nucleation in a supersaturated vapour, Becker and Döring (1935) assumed that embryos of critical size are formed by a sequence of bimolecular processes involving vapour molecules and subcritical embryos, some of which are dissolved. A theory of the rate of homogeneous nucleation in condensed systems is realized by Turnbull and Fisher (1949).

\[ J = K_v \exp \left( - \frac{\Delta G^*}{k_B T} \right) \]

\[ \Delta G^* = \frac{16}{3} \pi \frac{\sigma_{LS}^3}{\Delta G_V^2} \]

\[ \Delta G_V = \Delta S_m \Delta T \]

\[ \Delta S_m = \frac{\Delta H_m}{T_m} \]

\[ \Theta = \frac{\Delta T}{T_m} \]

\( \Delta S_m \): entropy of fusion

\( \Delta T \): liquid undercooling

\( J \): frequency of the formation of crystal nuclei per unit volume of an undercooled liquid (nucleation rate)
2. Nucleation studies: undercooling results (3)

**Turnbull** and **Cech** (1950) remarked that the normalized amounts of undercooling ($\theta = \Delta T / T_m$) are roughly constant ($0.18 \pm 0.02$). The systematic use of a scaling of $\Delta T$ against $T_m$ allows comparisons between experiments but promotes the speculation of a defined, relatively unique, $\theta$ limit for metals.
2. Nucleation studies: Cn-θ scaling (4)

Assuming the classical assumptions, the critical nucleus is unique ($JV_t = 1$) and $K_v \approx 10^{39}$ s$^{-1}$m$^{-3}$, a graphic interpretation for homogenous nucleation using a new Cn-θ scaling shows that the absolute limit is an intrinsic property of the material under consideration.

\[
JV_t = K_v V_t \exp\left(-\frac{\Delta G^*}{k_B T}\right) = 1
\]

\[
K_v^* \exp\left(-\frac{\Delta G^*}{k_B T}\right) = 1
\]

\[
\log K_v^* = \frac{\Delta G^*}{k_B T} = \frac{Cn}{\theta^2(1 - \theta)}
\]

\[
Cn = \frac{16}{3} \pi \frac{\Delta S_m}{R} \alpha_{LS}^3
\]

\[
\alpha_{LS} = \left(\frac{NV_m^2}{\Delta H_m}\right)^{1/3} \sigma_{LS}
\]
2. Nucleation studies: statistical analysis (5)

The determination of $K_v$ is considered the clearest way to distinguish properly between homogeneous and heterogeneous processes. This can be undertaken by studying the effect of sample size on nucleation or, by analysing the full width at half maximum of the distribution of nucleation events (Skripov, 1977). *evidences for refractory metals*

![Graph showing statistical analysis on nucleation studies](image)

*See also Hoffmeister’s work*

Statistical analysis on a double recrystallisation phenomena: A15 metastable phase in the Re-W system (see page 16).
As for numerous physical properties, the solid-liquid interface energy $\sigma_{LS}$ derived from undercooling experiments is found to be correlated with the atomic number (not $\alpha_{LS}$). The trends are identical to those obtained for the liquid-vapour surface energies $\sigma_{LV}$. A classification of the elements into different groups is obtained by considering the $\sigma_{LS}/\sigma_{LV}$ number, the main division being between metals and nonmetals.
2. Nucleation studies: dimensionless $\alpha_{LS}$ (7)

The majority of transition metals are around the classical value of 0.45. Clear correspondances are found with the crystallographic structure. The average values for the compact fcc and hcp structures are in excellent agreement with the recent simulation from molecular dynamics* (i.e. 0.51 for fcc).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Elements</th>
<th>$\alpha_{LS}$</th>
<th>$\Delta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A4</td>
<td>Ge, Si</td>
<td>0.40</td>
<td>0.5</td>
</tr>
<tr>
<td>bcc (A2)</td>
<td>Cr, W, V, Nb, Mo, Ta</td>
<td>0.43</td>
<td>8.6</td>
</tr>
<tr>
<td>bcc</td>
<td>Ti, Zr, Hf</td>
<td>0.47</td>
<td>1.5</td>
</tr>
<tr>
<td>hcp</td>
<td>Ti, Zr, Hf</td>
<td>0.47</td>
<td>1.5</td>
</tr>
<tr>
<td>fcc (A1)</td>
<td>Al, Pt, Pd, Cu, Ni, Ir, Rh, Au, Ag, Pd</td>
<td>0.48</td>
<td>12</td>
</tr>
<tr>
<td>hcp (A3)</td>
<td>Cd, Zn, Ru, Os, Tc, Re</td>
<td>0.50</td>
<td>8.6</td>
</tr>
<tr>
<td>others</td>
<td>In (A6), Ga (A11), Hg (A10)</td>
<td>0.65</td>
<td>5</td>
</tr>
</tbody>
</table>

Spaepen analysis: fcc (0.86), bcc (0.71)!

3. Metastable phases: pure metals (1)

The nucleation of metastable phases of pure metals (f.c.c.-Re and A15-Ta) is observed through favourable heterogeneous nucleation events. The melting temperature of the metastable phase is the only property that can be both measured or calculated, especially by first-principles calculations (FPLMTO and pseudopotential methods)

![Graph](image)

**Tantalum**

- 2660°C
- 2480°C
- 2620°C
- 3020°C

**Signal (V)**

**Free-fall time (s)**

**Structural energy differences**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
</tr>
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<tbody>
<tr>
<td>fcc</td>
<td></td>
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<td>hcp</td>
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<tr>
<td>bcc</td>
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<tr>
<td>A15</td>
<td></td>
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</tbody>
</table>

**ΔE_{x-fcc} (kJ.mol^{-1})**

- 2630°C
3. Metastable phases: sequences (2)

A **systematic study** is carried out for both 4d- (Nb, Mo, Tc and Ru) and 5d- (Ta, W, Re and Os) metals: the sequence of phase appearance is bcc $\rightarrow$ A15 $\rightarrow$ $\sigma$ $\rightarrow$ $\chi$ $\rightarrow$ fcc $\rightarrow$ hcp when increasing $\Delta T$ (reverse for a hcp metal). With a common origin (atomic coordination and level-splitting of the d-like states), this sequence is also observed with composition in many binary metallic systems based on refractory metals (e.g. Os-Nb).
3. Metastable phases: Re-W system (3)

Weak heteroatomic interactions favour the formation of solid solutions (entropic effects). The A15 phase shows a metastable behaviour in a tremendously wide range of composition (two sublattice description to simulate order-disorder phenomena).
Alloying effects are stronger in the Re-Ta system, which promote the stability of t.c.p. phases. The (Ta) solid solution is affected by the metastable behaviour displayed again by the A15 phase as well as by a primary nucleation of the $\sigma$-phase around 15 at% Re due to an uncommon site inversion between its two 12-fold coordinated sites*.

*Cluster Variation Method calculations have been performed by M. Sluiter (University of Sendai)
4. Conclusion (1)

“Nucleation, essentially, the *initiation of a phase transformation*, is of *central importance* in physics, chemistry, biology and materials science. Many of the pioneers in the study of nucleation processes were metallurgists…”*

The study of undercooled refractory metals leads to establish that the *solid-liquid interface energy* can be connected to the position of the element in the *periodic table*. No significant unexplained anomaly is identified making believe that the *classical theory* furnishes a *robust support* to describe crystal nucleation. The 5d-series, that does not present any physical anomaly, shows the most perfect parabolic trends for dimensional properties. This context allows to develop an experimental strategy for studying alloys.

*From a lay report of the discussion meeting 6-7 June 2002 on “Nucleation Control” (The Royal Society, London)*
Kinetics measurements are of a central importance when dealing with alloys, due to the possibility in getting significant variations of $K_v$ (complex phases, multicomponent alloys). First-principles based calculations of the structural stability have been successfully developed to identify the intervening metastable phases (sequences).

Acknowledgements

The drop-tube experiments have been performed within an agreement between CNES and CEA. The author is indebted to Pierre Jean Desré (LTPCM-Saint-Martin d’Hères) and Alain Pasturel (LPNSC/ CNRS) for their invaluable help. Many thanks to


Investigations with European teams have also received a financial support from ESA. Many thanks to Hasse Fredriksson, Lena Magnusson (KTH - Stockholm), Lindsay Greer (University of Cambridge), Hans Fecht (University of Ulm), Dieter Herlach (DLR - Cologne), Wolfgang Löser (IFW - Dresden) and László Gránásy (ISPPO, Budapest) for their scientific collaboration.
Related work (1)

1. Last overview, process
B. Vinet; Solidification of undercooled refractory metals and alloys by containerless processing. Special Issue: Emerging process in metal casting, science and technology, International Journal of Materials Product and Technology (2003), in press.

2. Nucleation studies / pure metals
L. Cortella, B. Vinet; Undercooling and nucleation studies on pure refractory metals processed in a ultrahigh vacuum drop-tube, Philosophical Magazine B 71(1995) 11.
Related work (2)

3. Phase selection phenomenon in refractory alloys (Re effect)


C. Berne, B. Vinet, E. Rolland, A. Pasturel; Comparative study from drop-tube experiments and ab-initio calculations of the nucleation of the sigma phase in the Re-W systems during solidification far from equilibrium, Journal of Metastable and Nanocrystalline Materials 8 (2000) 3.


4. Multicomponent systems
