On the Nucleation and Inoculation of Metals

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Abstract
Latent heat was during recalesence and nucleation and post-recalesence temperature was analysed for refractory metals. An effect on latent heat was found by alloying the pure elements with other refractories. Latent heat was found to be 15-65% of tabulated values. Interface energy was evaluated from undercooling experiments. It was found that the dimensionless numbers β (σ_{LS}/σ_{LV}) and α can be used to classify elements into distinctive groups and crystallographic structure.

The phase diagrams for Al-Ti, Al-Ti-B and Al-Ti-C as well as inoculation were analysed. It was found that Al nucleates on Al₃Ti which nucleates on TiB₂. TiC was found to decompose into Al₄C₃ and Al₃Ti.

The inoculation of nodular cast iron with Mg, Ce; Ca and the formation of sulphides and oxides was analysed. The formation of new inclusions during the solidification as well as the formation of graphite is discussed.

Keywords
Solidification, nucleation, inoculation, undercooling, interface energy, refractory metals, latent heat, inclusions, nodular cast iron
On the Nucleation and Inoculation of Metals

This thesis contains the following supplements:

Supplement 1
Heat of Solidification in Refractory Metals Studied by Drop-Tube Experiments
L. Magnusson, B. Vinet, H. Fredriksson,
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TRITA-MG 2001:2

Supplement 2
Correlations between Surface and Interface Energies with Respect to Crystal Nucleation
B. Vinet, L. Magnusson, H. Fredriksson, P. J. Desré

Supplement 3
Study and Modelling of Nucleation and Phase Selection Phenomena: Application to Refractory Metals and Alloys from Drop-Tube Processing
Presented at Conference in Sorrento, Italy, Sept. 2000

Supplement 4
INOCULATION OF Al ALLOYS WITH Ti
L.Magnusson and H.Fredriksson
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Supplement 5
A Thermodynamic Assessment of the Inoculation Process in Al-base Alloys
L. Magnusson and H. Fredriksson
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Supplement 6
A Thermodynamic Analysis of the Inoculation Process
L. Magnusson, S. Adolfi, H. Fredriksson
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1. Introduction
The understanding of the nucleation phenomena in metals is of major importance to better control the solidification process since nucleation is the first step of the phase transition liquid→solid and thus is the first opportunity to affect the properties of the cast product. Nucleation has been extensively investigated the last centuries and still questions arise.

Inoculation of metals is used to gain the sought after properties in the final product by affecting grain size. When adding an inoculant to the melt a smaller grain size is pursued by supplying nucleating particles. The mechanism behind the inoculation effect has been discussed since the early days of developing the process and different theories, for Al [1-7] as well as for nodular cast iron [8-13] have been presented.

An analysis of the nucleation phenomena (supplements 1-3) as well as on inoculation (supplements 4-6) was performed.

The nucleation phenomena in refractories were studied in drop-tube experiments under container- and weightless conditions. The recorded cooling curves were analysed. Values for latent heat as well as for interface energies were evaluated. The latent heat for refractories was found to be 15 to 65 % of tabulated values.

The binary Al-Ti as well as the ternary Al-Ti-B and Al-Ti-C are thermodynamically calculated. It is suggested that Al is nucleated on Al₃Ti, which is nucleated on TiB₂, while TiC decomposes.

Inoculation of nodular cast iron is used to avoid formation of white structure during solidification. The effect of Mg, Ca and Ce in formation of oxides and sulphides are thermodynamically analysed. It is shown that these inoculants affect the nodule size distribution. It is proposed that oxides or sulphides form continuously during the solidification process.

2. Summary
2.1. Nucleation
During the solidification experiments in the drop-tube, Figure 1, the recalescence was recorded, by means of photodiodes, showing intensity to time.
The experiments are containerless performed in vacuum and thus the samples only lose energy through radiation. The following expression gives the heat balance for the recalescence:

\[
4\pi^2 \sigma_{SB} \varepsilon(T)(T^4 - T_0^4) = \frac{4\pi^3}{3}(\rho(T) \frac{df}{dt} L + \rho(T)C_p(T) \frac{dT}{dt})
\]

(1)

where \(\sigma_{SB}\) is \(5.67 \cdot 10^{-8}\) W/m\(^2\)K\(^4\) (Stefan-Boltzmann)
\(\varepsilon(T)\) is hemispherical emissivity (temperature dependant)
\(T\) is the actual temperature in K
\(T_0\) is the ambient temperature, in K
\(\rho\) is the density
\(df/dt\) is fraction solid per time
\(L\) is latent heat
\(C_p\) is heat capacity.

The nucleation temperature is evaluated through a heat balance for the time interval between the release of droplet until recalescence occurs. The post-recalescence temperature is calculated by the use of Wien’s law:

\[
T_n^{-1} - T_{pr}^{-1} = \frac{\lambda}{C_2} \left[ \ln \frac{s(T_n)}{s(T_{pr})} - \ln \frac{\varepsilon(\lambda, T_n)}{\varepsilon(\lambda, T_{pr})} - \ln \frac{d(T_n)}{d(T_{pr})} \right]
\]

(2)

where \(\lambda\) is the used wavelength (853 nm), chosen as to be close to the so called x-point where the spectral emissivity does not change with temperature
\(C_2\) is the second radiation constant.
s(Tᵢ) is the recorded intensity signal for the nucleation/post-recalesence event.

ε(λ,Tᵢ) is the spectral emissivity for the nucleation/post-recalesence event and

d(Tᵢ) is distance from the pyrometer for the nucleation/post-recalesence event.

The reaction rate corresponding to the fraction solid formed per time can be evaluated from expression (1). By integrating over time and temperature the latent heat can be calculated. The results for pure elements are presented in Table 1.

<table>
<thead>
<tr>
<th>element</th>
<th>w%</th>
<th>L [J/kg]</th>
<th>stdeviation</th>
<th>ΔHtab[J/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>100</td>
<td>161575</td>
<td>10041</td>
<td>190383</td>
</tr>
<tr>
<td>Re</td>
<td>100</td>
<td>144408</td>
<td>29055</td>
<td>177219</td>
</tr>
<tr>
<td>Hf</td>
<td>100</td>
<td>74370</td>
<td>4721</td>
<td>142865</td>
</tr>
<tr>
<td>Ta</td>
<td>100</td>
<td>141448</td>
<td>7816</td>
<td>198950</td>
</tr>
<tr>
<td>Zr</td>
<td>100</td>
<td>77224</td>
<td>21037</td>
<td>230213</td>
</tr>
<tr>
<td>Pt</td>
<td>100</td>
<td>53791</td>
<td>2208</td>
<td>112774</td>
</tr>
</tbody>
</table>

Table 1: Latent heat (L) evaluated from experiments and tabulated values (ΔH).

It was found that the latent heat seems to be a function of the density differences between the liquid and the solid. The values were found to be 15-65% of the tabulated values. In earlier works [14-16] the latent heat was related to the fraction of lattice defects, assumed to be vacancies. The following expression defines the relation between latent heat and fraction of vacancies:

\[ L = ΔH_{tab} - (x_v - x_v^{eq})ΔH_v \]  \hspace{1cm} (3)

where

- L is latent heat
- ΔH_v is the heat of formation for vacancies
- \( x_v^{eq} \) is the equilibrium fraction of vacancies
- \( x_v \) is fraction of vacancies.

The maximum fraction of vacancies is given by:

\[ x_v = \frac{\rho^s - \rho^L}{\rho^s} \]  \hspace{1cm} (4)

where \( \rho^{s,L} \) depicts the solid and liquid density respectively.

Inserting this into equation (3) and using the experimentally deducted values for enthalpies and the assumed value for entropy [17, 18] gives the latent heat presented in Table 2.
<table>
<thead>
<tr>
<th>Element</th>
<th>$x_v^{eq}$</th>
<th>$x_v$</th>
<th>L [J/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>4.81622E-33</td>
<td>8.82136E-05</td>
<td>190198</td>
</tr>
<tr>
<td>Ta</td>
<td>1.19585E-31</td>
<td>0.000110277</td>
<td>198715</td>
</tr>
<tr>
<td>Pt</td>
<td>2.20458E-30</td>
<td>5.70514E-05</td>
<td>112631</td>
</tr>
</tbody>
</table>

Table 2: Latent heat calculated from experimental values.

As can be seen in a comparison between Tables 1 and 2 there is a discrepancy between the measured values and the tabulated values. Mono-vacancies alone cannot explain this big discrepancy.

Most values of solid-liquid interfacial energy of metals are determined by nucleation experiments. The phenomenon of liquid undercooling gives a construction of a viable solid-liquid interface, thus giving the possibility to measure and model interface energies. According to the classical theory [19, 20]

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

where $r$ is the radius, $\sigma_{LS}$ is the interfacial energy (in J.m$^{-2}$), and $\Delta G_V$ is free energy of volume of solid from the liquid (in J.m$^{-3}$).

The critical size to form an embryo is found by deriving $\Delta G$ with respect to $r$, giving critical radius of a spherical particle

\[
r^* = -2 \frac{\sigma_{LS}}{\Delta G_V}.
\]

The nucleation rate is given by

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

where $k_B$ is the Boltzmann constant and $T$ is the temperature.

This provides a possibility to determine the interface energy from experiments. With an estimated value of $K_V$ close to $10^{39}$ s$^{-1}$, the phase boundary for homogeneous nucleation and $10^{35}$ s$^{-1}$.m$^{-3}$ at the very most for heterogeneous nucleation. By assuming $J V t = 1$ where $V$ is the sample volume, $t$ is the time to nucleation, and $K_V 10^{39}$, the nucleation barrier can be expressed as
\[ \log K_V^* = \frac{\Delta G^*}{k_B T} = \frac{C_n}{\theta^2 (1 - \theta)} \] (9)

where
\[ C_n = \frac{16}{3} \pi \frac{V_m^2 \sigma_{LS}^3}{k_B T_m^3 \Delta S_m^2} \]

\( V_m \) is the molar volume
\( \Theta = \Delta T/T_m \) is the normalised undersooling
\( \Delta S_m \) is the entropy of fusion (in J.K\(^{-1}\).mol\(^{-1}\)).

By plotting expression (9) it is found that the absolute limit for homogeneous nucleation is an intrinsic property of the material as long as no relation is introduced between the thermophysical properties appearing in \( C_n \), Figure 2.

![Figure 2: Nucleation, arrows identifying normalised amount of undercooling corresponding to different theoretical values of dimensionless \( \alpha_{LS} \).](image)

The interface energies were determined from undercooling experiments and these are compared to the cohesion energies and melting temperatures. Similar parabolic trends are found for the elements in the 3d-, 4d- and 5d-series.

For the dimensionless \( \alpha \) number \( (\alpha_{LS} = \frac{(N\gamma_m^2)^{1/3}}{\Delta S_m T_m} \sigma_{LS} = \frac{(N\gamma_m^2)^{1/3}}{\Delta H_m} \sigma_{LS} ) \), no resemblance as for the interface energies was found, instead these were found to have a relationship with the crystallographic structure, Table 3.
Table 3: The mean dimensionless $\alpha_{LS}$ for different crystallographic structures.

The dimensionless $\beta$ number ($\sigma_{LS}/\sigma_{Lv}$) [21] often considered roughly constant was found to follow the same parabolic trends as the interface energies $\sigma$. It was found that $\beta$ could be used to classify elements into groups, Figure 3.

Figure 3: The dimensionless number $\beta$ for different elements.

2.2. Inoculation

2.2.1 Aluminium

The mechanism behind the inoculation effect has been discussed since the early days of developing the process. Different nucleating agents (TiC, TiB$_2$, Al$_3$Ti) have been discussed [1-7]. These theories have been the basis for discussions of the mechanism behind inoculation.

A thermodynamic study of the reaction $3\text{Al}+\text{Ti} \leftrightarrow \text{Al}_3\text{Ti}$ was performed for the experimental values reported by [22-24]. The values in the Al-Ti system are found to be dependant on experimental conduct. A new value $\Delta G^\circ$ was evaluated and found to be $\Delta G^\circ=\text{-65246,2-156,754T J/mole}$. Latent heat was evaluated according
to expression (3) and found to be $-1.76 \times 10^5$ J/mole. The different morphologies of Al$_3$Ti are assumed related to the fraction of defects in the formed crystals. The crystals with a large fraction of defects are dissolved, giving a super-saturated liquid of Al$_3$Ti.

The possibility to form Al$_3$Ti during a normal cooling process was analysed by using the classical theory of homogeneous nucleation

$$x_{Ti} = x_{req} \exp \left( \frac{\frac{16}{3} \pi \sigma^3 (V_m)^2}{60kT} \right) \frac{RT}{} \tag{10}$$

where

- $\sigma$ is the surface energy in J/cm$^2$
- $V_m$ is the molar volume/cm$^3$
- $k$ is Boltzmann’s constant
- $R$ is the general gas constant
- $T$ is the temperature in Kelvin.

This relation was plotted against the solubility limit for Al$_3$Ti, Figure 4.

![Figure 4: Solubility line and nucleation of Al$_3$Ti.](image)

A superheat of 30 K is found to be necessary to form Al$_3$Ti during a normal casting operation, considering the Ti content is above 0.02 wt%.

The ternary system Al-Ti-B in the Al-rich corner was evaluated from the following expressions:
It was found that ~10 K in superheat is necessary for formation of TiB₂. Al₃Ti will form if the Ti content is 0.02 wt%. TiB₂ is found to form when the liquid is cooled from 680°C while Al₃Ti will form if the liquid is cooled from 800°C. It is thus assumed TiB₂ is formed by cooling and Al₃Ti is nucleating on TiB₂. At higher Ti-content the inoculation effect is larger, and it is suggested Al₃Ti is more effective than TiB₂. The ternary phase diagram at 660°C is presented in Figure 5.

![Figure 5: The ternary Al-Ti-B phase diagram at 660°C, Al-rich corner.](image-url)

The effect of TiC as an inoculant for Al has been evaluated. It has earlier been shown [25] that TiC is not stable at the melting temperature of aluminium. It is found that TiC will decompose to Al₄C₃ and Al₃Ti when cooled to from 800°C, Figure 6, to 700°C, Figure 7,
2.2.2 Nodular cast iron
The oxygen level in the melt is calculated from the equilibrium between silicon and silicon oxide, based on the low temperature and high Si content in production of nodular cast iron. The oxygen level is found to be 0.023-0.089 wt%. Approximately 0.044 to 0.14 wt% Mg is consumed for the formation of MgS and MgO. With a Mg content in the liquid of 0.04 wt% the solubility of CaO/MgO, Figure 8, shows that with a normal addition of 0.2% inoculants containing 1 wt% Ca the Ca content is on the border for formation of CaO, while Figure 9 shows that CeO$_2$ and Ce$_2$O$_3$ are easily formed.
The super-saturation was calculated with the following expression:
\[ C_M^n C_O^m = K_{eq}^0 \exp \left( -\frac{60kT}{RT} \right) \]  

(14)

where \( \sigma \) is the surface energy in J/cm\(^2\)
\( V_m \) is the molar volume/ cm\(^3\)
\( k \) is Boltzmann’s constant
\( R \) is the general gas constant and
\( T \) is the temperature in Kelvin.

The segregation of Mg, Ce and Ca was calculated using

\[ C_M^L = C_M^0 (1 - f_{y+gr} \left( k_{\gamma}^f - k_{\gamma}^L \right) f^{y} + (1 - k_{\gamma}^L f^{gr}) \]  

(15)

where \( C_M^0 \) is the original content of the metal in the melt
\( f_{y+gr} \) is fraction solidified and
\( k_{\gamma}^f, k_{\gamma}^L \) are the partition coefficients.

The segregation of oxygen and sulphur is described by the lever rule

\[ C_{S,O} = \frac{C_{S,O}^0}{1 - f_{y,gr} \left( 1 - k_{O}^{y/L} \right) f^{y} + (1 - k_{O}^{y/L} f^{gr})} \]  

(16)

where \( C_{S,O}^0 \) is the original content of sulphur, oxygen in the melt
\( f_{y,gr} \) is fraction solidified and
\( k_{O}^{y/L}, k_{O}^{y/L} \) are the partition coefficients.

By combining the expressions (14), (15) and (16) is found MgO inclusions will occur at approx. 75% solidified, while CeO\(_2\) and Ce\(_2\)O\(_3\) will form repeatedly, as can be seen in Figure 10.
3. Concluding remarks

It was found that high undercooling and low values of measured latent heat for experiments on refractories not is described by the formation of mono-vacancies. It was however found that the solid-liquid interface energy can be connected to the position in the periodic table. Trends have been found for the $\beta$ number, seemingly allowing a classification into different groups. The dimensionless $\alpha$ number can be used to classify elements into different crystallographic structures, and to predict a normalized undercooling. The absolute limit of undercooling was found to be an intrinsic material property.

The values in the Al-Ti system are found to be dependent on how experiments are performed. The large spread in solubility is suggested to depend on the formation of lattice defects in $\text{Al}_3\text{Ti}$. Calculation of the ternary phase diagrams Al-Ti-B and Al-Ti-C show that $\text{Al}_3\text{Ti}$ will form during the cooling process of a melt containing low amounts of Ti. Al is found to nucleate on $\text{Al}_3\text{Ti}$. $\text{TiB}_2$ is found to be easily formed during cooling. $\text{Al}_3\text{Ti}$ then nucleates on $\text{TiB}_2$. $\text{TiC}$ is shown to decompose into $\text{Al}_4\text{C}_3$ and $\text{Al}_3\text{Ti}$.

The size distribution of nodules in ductile iron can be related to the composition of the inoculating agent. For the nodular cast iron the nodule size measurements for the uninoculated samples show a low number of large nodules. The number of nodules then increases at a size of 20-25 µm, and an additional increase is seen at a size of 5-10 µm. This is explained by formation nucleation of nodules at the beginning and at the end of solidification, as found in the thermodynamic calculations. $\text{MgO}$ and $\text{MgS}$ inclusions are formed at the end of the solidification.
process, and graphite nodules are formed on these. The conclusion from this will be that a correctly adjusted addition of inoculants can give a continuous formation of new nodules through the whole solidification process. It is depending on the amount of Mg dissolved in the liquid prior to the inoculation process. Ca and Ce added in the proper amount will be the most efficient elements to control the formation of new nodules during the solidification process. Calciumsulphides and ceriumsulphides have been shown to be most effective compounds in his investigation.

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5. References
[7]. Arnberg, L., Bäckerud, L., Klang, H., Metals Technology 9, (11), 1-6, Jan. 1982
48 Int. Foundry Congress, 4-7 Oct 1981, Bulgarien