Applications of Phase Equilibria in Aluminium Alloy Products and Processes

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Introduction

Aluminium alloys are generally not used in a state of thermodynamic equilibrium
- many contain metastable precipitates or intermetallic phases
- with process routes designed to avoid attainment of equilibrium

Even alloys relying on solid solution strengthening are usually in a metastable state at their operating temperatures.

However equilibrium can be of relevance during earlier stages of production, and at high temperature stages.

Bright field TEM image of metastable \( \beta'' \) precipitates in AA6061 (Al-Mg-Si alloy)

High resolution image down \( \beta'' \) needle

Equilibrium during processing aluminium

In some cases the thermodynamic understanding is embedded in the practices...

...in other cases it comes back to haunt us!

We will consider a few of examples drawn from the aluminium process stream:

1. virtually all aluminium undergoes some form of treatment whilst molten
   - measurement and removal of dissolved hydrogen can be problematic
2. extrusion: a process stream designed around attainment of equilibrium *in situ*
3. rolled product development: *a case of being wise after the event*
1) Hydrogen in aluminium

Aluminium melt treatment generally focuses on improving 3 quality attributes
- dissolved hydrogen, inclusions, alkali metals

Hydrogen is the major contaminant controlled by equilibrium considerations

Hydrogen is far more soluble in liquid aluminium *cf.* solid aluminium
- solidification of a melt containing too much hydrogen results in porosity

example of internal porosity visible on machined engine face

surface blistering after homogenisation
Effects of porosity

Fatigue life is also reduced as porosity increases.

fatigue life variation with pore size


fatigue failure surface and pore initiation
Porosity in wrought alloys

Porosity also causes problems during subsequent fabrication in wrought alloys, e.g. hot mill edge cracking.
Hydrogen solubility

The solubility of hydrogen in pure liquid aluminium is now well established

- dating back to pioneering work of Ransley, Talbot and others
- note hydrogen concentration usually expressed as ml. H₂ per 100g aluminium

Data shown for solubility in contact with an atmosphere of pure hydrogen

D.E.J. Talbot
Expected relationship

Equilibrium constant for the reaction between gaseous hydrogen and hydrogen dissolved in molten aluminium

\[ H_2 \text{(gas)} \rightleftharpoons 2H_{Al} \text{(solution in metal)} \]

\[ K_{eq} = \frac{S^2}{p_{H_2}} \]

- \( S \) = activity ~ concentration of hydrogen (ml/100g)
- \( p_{H_2} \) = partial pressure hydrogen

So we expect the following form for hydrogen solubility:

\[ S = \sqrt{K_{eq}} \sqrt{p_{H_2}} = S_o \sqrt{p_{H_2}} \]

(Sieverts’ Law)

where \( S \) is Hydrogen concentration in ml / 100g, partial pressure is in atmospheres

\( S_o \) is the \text{equilibrium solubility} in contact with pure hydrogen
What about alloying additions?

Some elements influence the solubility of hydrogen in liquid aluminium
➤ relatively sparse data available, and even fewer for the effect in solid aluminium

Magnesium, titanium and lithium increase hydrogen solubility in liquid aluminium...

...whilst iron, copper, silicon and zinc reduce the solubility levels

So Mg containing alloys pick up hydrogen more readily…

…and harder to degas

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data from
P.N. Anyalebechi,
Scripta Met and Mater.,
33 (8), p1209 (1995)
Alloy correction factors

The simple solubility equation for hydrogen in liquid aluminium needs to be corrected for the alloy composition

- generally use interaction coefficients for excess solution free energy

\[
\log(f_H) = k'_Mg W_{Mg} + k'_Cu W_{Cu} + k'_Si W_{Si} + k'_Zn W_{Zn} \ldots
\]
\[
+ k''_Mg W_{Mg}^2 + k''_Cu W_{Cu}^2 + k''_Si W_{Si}^2 + k''_Zn W_{Zn}^2 \ldots
\]

\(f_H = \) hydrogen activity coefficient
\(W_x = \) wt.% of x
\(k' = 1^{\text{st}}\) order interaction
\(k'' = 2^{\text{nd}}\) order interaction


Published experimental data extensively reviewed

- some first order coefficients reliable, second order more variable
  - some concern over Mg data
- temperature dependence not available for all elements

Alloy hydrogen solubility treated with a correction factor \(C_{alloy} = 1/f_H\)

\[
S_{alloy} = C_{alloy} S_o \sqrt{p_{H_2}}
\]
But where does hydrogen come from?

The solubility of hydrogen is expressed on the basis of equilibrium between the melt in contact with $\text{H}_2$ gas

- but the partial pressure of hydrogen in the atmosphere is vanishingly small

Water vapour provides the source of hydrogen

- aluminium can react with water vapour to form alumina and dissolved hydrogen
Molten aluminium will pick up hydrogen from atmospheric humidity

But melting furnaces are usually gas-fired

\[7.5N_2 + CH_4 + 2O_2 \rightarrow 7.5N_2 + CO_2 + 2H_2O\]

Combustion products comprise ~15% water vapour H₂O (allowing for excess air)

It gets worse...

- **Furnace**: combustion water vapour
- **Summer**: 45°C, 80% humidity
- **Winter**: 20°C, 50% humidity
Typical hydrogen levels exiting a furnace

Example shows measured hydrogen levels in melt (ml/100g) exiting furnace, sampled over many hundreds of casts

- commercial purity aluminium, furnace running at 725-750°C

Generally found that hydrogen levels in melting and holding furnaces are dominated by equilibrium with furnace atmospheres
How much hydrogen can we live with?

Furnaces are quite turbulent environments. The melt rapidly achieves equilibrium with the local atmosphere. For nearly all applications, the level of dissolved H₂ exiting furnace is too high... and must be reduced before casting.

"Degassing" is the process by which the melt is treated to lower H₂ levels.

The acceptable level of hydrogen varies depending on product and application.

- Holding furnace hydrogen levels
- Melting furnace hydrogen levels
- Typical commodity wrought products
- Demanding products
- Aerospace products

H₂ (ml/100g)
Hydrogen removal: batch degassing

The degassing process bubbles a dry inert gas through the melt

- the melt tries to reach equilibrium with the gas by mass transfer of hydrogen

The kinetics are controlled by local equilibrium at the bubble-melt interface
Mass transfer between the melt and the bubbles

Hydrogen is transferred into gas bubbles, recombining as $H_2$ molecules

- partial pressure of hydrogen in the bubble stays in *local equilibrium*…
- …with concentration of hydrogen in the boundary layer around the bubble, $H_i$

This establishes a difference in hydrogen concentration between

- the bulk liquid, $H_b$  and the boundary layer, $H_i$

which then drives mass transfer from the bulk melt to the bubbles

$$\text{hydrogen flux} = k_i A_i (H_b - H_i)$$

$k_i =$ hydrogen mass transfer coefficient (m/s)

$A_i =$ surface area of bubble

$p_{H_2}$ hydrogen partial pressure in bubble (atm.)

$H_b$ hydrogen concentration in bulk liquid

$H_i = S_o \sqrt{P_{H_2}}$ hydrogen concentration in boundary layer
Batch degassing kinetics

The mass transfer and associated local equilibrium boundary conditions, along with re-absorption from the atmosphere, is built into process models.

- quantitative understanding of local equilibrium at the bubble-melt interface is crucial.

Comparison of kinetic model with trial degassing Al-9% Si

Web base degassing model developed for Foseco

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Large furnaces... the need for in-line degassing

Batch degassers work well for small melts (e.g. < 1 tonne)

But modern wrought plants cast from 30-130 tonne furnaces

- casts can take 1-2 hours duration
- ample time for the melt to up-gas once more in the furnace
- furnace degassing has become ineffectual and largely abandoned

Degassing and up-gassing kinetics in a holding furnace

In–line degassing

Wrought aluminium plants generally use in-line degassers
- just before casting, allows no time to up-gas before solidification

Continuous process where metal flows through a reaction chamber
- characterised by an average residence time (chamber volume/metal flow rate)

In line SNIF degasser
www.pyrotek.com
Just how do we measure hydrogen?

The levels of hydrogen we are dealing with in solution are rather low:

- 0.1 ml/100g ~ 0.09 ppm or ~ 0.1 gram of hydrogen per tonne of aluminium

And yet these levels are measured on line, in real time: all rely on equilibrium

A small volume of carrier gas re-circulates through a porous probe in the melt:

- hydrogen diffuses to the gas and recombines as \( \text{H}_2 \) reaching equilibrium

**AISCAN hydrogen measurement**
All on-line hydrogen measurement methods entail measuring the partial pressure of hydrogen in equilibrium with the melt.

- we are not measuring hydrogen in the melt directly

In order to estimate the concentration of hydrogen dissolved in the melt:

1. temperature used to calculate the equilibrium solubility for H$_2$ in pure Al
2. measured $p_{H_2}$ used to calculate the H level in the melt (assuming pure Al)
3. calculated concentration corrected for effect of alloying elements on H solubility

0.05 atm. H$_2$ pressure converts to three different H levels, depending on the melt composition

...so measurement devices rely entirely on knowledge of equilibrium H solubility, and its variation with alloy
Current issues: aluminium and hydrogen

Uncertainty over interaction parameters affects our ability to both measure gas levels on line reliably, and control degassing processes

- the effect of magnesium is probably the most worrying

There are a reasonable amount of data concerning hydrogen solubility in pure liquid aluminium, and some data for a selection of binary alloys…

- but hardly any for fully commercial alloys

Binary interaction coefficient contributions are assumed additive…

- very limited evidence suggests this may not always be the case:

2) Extrusion processing
Most common extrusion alloys are based on the Al-Mg-Si system (AA6xxx)

- often with additions of Cu, Mn

Precipitation hardening system, based on the Al-Mg$_2$Si pseudo-binary
Al-Mg-Si phase diagrams

The area of interest is the aluminium rich corner of the Al-Mg-Si system

Aluminium solid solution isotherms

Pseudo-binary section

“balanced” alloys

Extrusion process route: homogenisation

Extrusion logs are homogenised after casting, typically >570°C
- dissolution of soluble Mg₂Si eutectic (quick)
- formation of Mn dispersoids, and phase transformation of cast intermetallics (slow)

Cooling after homogenisation

Note: no formal solution heat treatment stage in the process route

It might be thought quenching rapidly after homogenisation would be desirable

- preserving Mg and Si in solid solution
- retaining it during extrusion and quenching, maximising the ageing response

Perhaps surprisingly, a slower cooling rate is usually deliberately applied

- resulting in extensive fine re-precipitation of β’-Mg$_2$Si needles
- (note these would be very over-aged in terms of final mechanical properties)

Quenched after homogenisation: Mg and Si retained in solid solution

Controlled cool after homogenisation (350°C/hr): nucleation of β’-Mg$_2$Si needles

R.A. Ricks et al, Extrusion Technology 1992, pages 57 - 69
So what is the point of encouraging precipitation prior to extrusion?

The extruders have come up with a cunning plan:

Having the solute out of solution before extrusion lowers the flow stress

- so they can extrude faster on a given extrusion press

But a correct selection of billet preheat temperature, combined with the heat of deformation, will carry the extrudate above the solvus

- re-dissolving the precipitates, just before the extrudate is quenched
Effect of cooling rate from homogenisation on flow stress

In situ re-solutionising

This process allows maximum press productivity
- whilst still ensuring maximum strengthening potential during subsequent ageing

Hence precipitates formed after homogenisation must not be too coarse
- otherwise they won’t re-dissolve in short time available above the solvus
Potential problems (1)

The amount of deformation heating depends on the details of the extrusion:
- mainly the extrusion ratio (strain)
- and the strain rate (extrusion speed)

So operating practices need to be fine tuned for each product…
- to ensure the extrudate achieves a temperature above the solvus…
- but below the solidus: otherwise incipient melting is observed

…and more concentrated alloys have a diminishing operating window:

![Graph showing temperature vs. wt% Mg2Si for AA6060, AA6061, and AA6063 alloys]

Potential problems (2)

Example of speed cracking, showing underlying re-melted eutectic colonies

3) Practical alloy development

Brazing sheet is a clad aluminium rolled product widely used in heat exchangers

- core typically AA3xxx, cladding typically Al-10%Si

A very elegant product, with one small problem...
Scrap

What to do with the inevitable process scrap (ingot crops, edge trims, etc.)?

The core and clad are metallurgically bonded: can’t separate

- re-melted average composition typically: Al -1.4%Si -0.8%Mn -0.1%Mg
- this is x10 more Si than can be tolerated in most rolled products

The more successful the sales of brazing sheet, the more scrap created

Solution: register a new alloy designed to absorb the scrap: AA4015

- typical application: low cost (painted) building sheet

Only problem: mechanical properties rather poor cf. normal building sheet
(Blind?) Alloy development

This is a cold rolled product, deriving its strength from a combination of work and solute hardening

- not feasible to increase cold rolling reductions (start and end gauges fixed)
- only option: increase level of solid solution

Our client proposed increasing magnesium (and/or manganese) in the alloy

- (wrought metallurgists rule of thumb: if in doubt, increase Mg for work hardening)

The base alloy contains 0.1%Mg

off line process used to investigate: 0.3% and 0.5%Mg hoping to close the gap
Mechanical properties

Experimental alloys were cast up, homogenised, then hot and cold rolled

The results were surprisingly disappointing

Rolled to a common final gauge (strain), all A4015 variants showed ~identical strength

And exactly the same behaviour seen on making Mn additions

We were invited to consider whether the client’s strategy made sense…
…and could we explain why it was all going wrong?
The thermodynamic equilibrator

After homogenisation, slabs are hot rolled to ~3mm intermediate gauge

For this client, the final 3 passes are coil to coil
- ~50% reductions, with many minutes between passes at ~350°C

On reflection, you would be hard pressed to find a process better designed to drive an alloy to equilibrium in the solid state!
Al-Mg-Si again

The diagram shows the limit of solid solubility at 350ºC

- data taken from Phillips (1961) and Feufel et al. (1997)

Increasing Mg in this alloy simply advanced into the 3 phase region at 350ºC

- with a Mg solid solution level pegged to the corner of the triangle

What else can we add?

If Mn and Mg are ruled out because of the high Si in the alloy, what could we add (cheaply) that would be retained in solution?

- Cu was a candidate, provided the Mg level was also kept low (avoiding Q phase)
- potentially could retain e.g. 0.4-0.8 %Cu in solution

Calculations undertaken by Chart Associates (2005)
A series of alloys were cast based on AA4015 with Cu additions
- containing 0.3, 0.5 and 0.8 wt.% Cu

For a fixed strain, 0.8% Cu alloy achieved ~75MPa strength increase
- in reasonable agreement with strain hardening prediction
Strength ok, but corrosion?

Not surprisingly, although Cu additions addressed the strength issue...

...they also degraded the corrosion resistance of the product

Not as much of an issue as might be expected: it is a coated product

➢ but would limit its application as a bare product

0% Cu  0.3% Cu  0.5% Cu  0.8% Cu

corrosion test samples, 500 hours acidified salt spray (ASTM B287)
(overlaid with image analysis of pitting corrosion)
Conclusions

- These application examples have been chosen to try and demonstrate the importance of setting phase equilibria predictions in a larger context.
- There are times when thermodynamic equilibrium is achieved, either unavoidably or by design...
- ...and other times when the process route has evolved to avoid equilibrium at all costs.
- One of the most important application areas of phase equilibria relate to the provision of realistic local equilibrium boundary conditions.
  - increasingly required by microstructural kinetic models during processing.
- Understandably there are gaps in the availability of reliable experimental data concerning metastable phase equilibria...
- ...but some equilibrium data also very sparse for molten aluminium alloys.
  - e.g. relating to hydrogen in ternary or higher alloys.
  - e.g. interactions of molten salts with molten aluminium alloys (alkalis).
  - e.g. solubility of carbon in molten aluminium, and precipitation of carbides.