SOLUBILITY OF HYDROGEN IN METALS AND ITS EFFECT ON POREFORMATION AND EMBRITTLEMENT

By

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Avhandling

Som med tillstånd av Kungl. Tekniska Högskolan framläggs till offentlig granskning för avläggande av teknisk doktors-examen fredag den 18 maj 1984, kl 10.15 i sal B1 Brinellvägen 23, Stockholm

Institutionen för Metallernas Gjutning, Stockholm 1984
**ERRATA:**

Introduction, Page 5, lines 6-8

The partial molar volume of hydrogen in the melt, \( \bar{v}_H \), is not determined. Due to very low solubility of hydrogen in the melt, \( \bar{v}_H \) can be substituted by the...

Introduction, Page 5, lines 22-24

\[ a \text{-Silicon and iron decrease the solubility of hydrogen in aluminium, whereas with iron at higher temperature, and titanium it increases.} \]

Introduction, Page 8, line 14

... using Fick's first law:

Introduction, Page 9, line 15

... 20-40 seconds...

Introduction, Page 9, line 21

Pores size and number were...

Introduction, Page 9, line 28

... by collision as...

Introduction, Page 10, line 20

Het rogeneous...

Paper I, Page 1, line 14

Silicon and iron decrease the solubility of hydrogen while titanium increases it. At high temperature, iron also increases the hydrogen solubility.

Paper I, Page 8

Equation 5, reflects the solubility of hydrogen in the melt as a function of pressure and temperature. The partial molar volume of hydrogen in aluminium, \( \bar{v}_H \), is not determined. In the present analysis, it is assumed that \( \bar{v}_H \) and its variation with the temperature is the same as the molar volume of aluminium, \( v_{Al} \). This is because the solubility of hydrogen in the aluminium melt, max \( 2 \times 10^{-4} \) mole fraction is very small. Equation 5 then becomes:

\[ \text{Equation 5 then becomes:} \]

Paper I, Page 13, Table 3

Calculations for Ti and Fe are not valid.
This thesis comprises the following papers:

I. Solubility of dry hydrogen in liquid aluminum, Al-4%Ti, Al-7%Si and Al-10%Fe at one atmosphere
   H. Shahani

II. Solubility of dry hydrogen in liquid gold, gold-copper and gold-palladium alloys at one atmosphere
    H. Shahani, L. Victorin

III. On the design of rapid heating and high pressure casting furnaces used in metal foam experiments
    H. Shahani, R. Jönsson, S. Wallin

IV. On the mechanism of precipitation of pores in melts
    H. Shahani, H. Fredriksson

V. Precipitation of gas pores in metallic melts during cooling under microgravity
    H. Shahani, H. Fredriksson

VI. Effect of hydrogen on the shrinkage porosity of aluminum copper and aluminum silicon alloys
    H. Shahani

VII. Hydrogen embrittlement in iron base alloys
    H. Shahani, H. Söderhjelm, M. Nygren
ABSTRACT

Solubility of hydrogen in Al, Al-4%Ti, Al-7%Si, Al-10%Fe and also in Au-Cu, Au-Pd alloys is investigated. Effect of alloying elements on the hydrogen solubility are determined by evaluating solubility equations and interaction coefficients.

Formation of rounded pores in hydrogen supersaturated Al, Al-4%Ti, and Al-10%Fe alloys is investigated. A model for nucleation and growth of rounded pores in the melt is presented, and is applied for pure aluminium. These samples were remelted in reduced gravity and reduced ambient pressure. The resulting materials consisted of numerous expanded pores, dispersed in the metallic matrix. Al-4%Ti samples, saturated at 0.5 and 1 atm hydrogen and remelted at 0.1 atm ambient pressure, achieved 50% relative reduction in density with a uniform pore distribution.

The effect of hydrogen, alloying elements, modifiers and pressure drop, caused by solidification on the shrinkage porosity in aluminium silicon and aluminium copper alloys are studied. A model for formation of shrinkage pores, regarding these parameters is also presented.

Effect of hydrogen on the transition from ductile to brittle in iron base amorphous ribbon is studied. The presented results indicate that small amount of hydrogen in the melt prior to rapid quenching can cause embrittlement in the amorphous ribbons.

Key words:
Hydrogen, aluminium, gold, palladium, poreformation, nucleation, growth, shrinkage, metallic foam, microgravity, amorphous, embrittlement.
INTRODUCTION

Pores in most cases are formed in metals during casting and solidification and may reduce the desired properties. However, pores can be useful in some special applications i.e. producing very light materials or materials with a high damping capacity. In these cases, a large number of pores should be evenly distributed in the metallic matrix and the material is known as metallic foam.

Whether the problem is to eliminate or to enhance the formation of pores, a basic understanding of the mechanisms involved in the poreformation is necessary. In this respect, a fundamental knowledge of gas solubility in the melt, induced pressure by the dissolved gas, nucleation and growth of the pores, and solidification mechanism are all essential. Finally, from these informations, the production of metallic foam can be considered. All these mechanisms have been investigated in this thesis, and the results thus obtained were used in investigation of poreformation in aluminium alloys.

1. GAS SOLUBILITY

Hydrogen is one of the most common gases dissolving in metals. It is, for instance, the only gas which dissolves in aluminium. Diatomic gases, such as hydrogen, dissolve in the melts as atom by gradual steps (1). The total reaction for hydrogen dissolution can be written as:

\[ H_2(g) \rightarrow 2H \]  \hspace{1cm} (1)

At equilibrium, the chemical potential of hydrogen in the gas phase and in the melt, should be equal. Considering the effect of external pressure (2) on the above reaction
gives:

\[
2(\mu_H^0 + RT \ln X_H - \bar{v}_H(P_t - P_0)) = \mu_H^0 + RT \ln(P_t - P_0) \tag{2}
\]

\[
X_H = \left(\frac{P_t}{P_0}\right)^{\frac{1}{2}} \exp(\left(\mu_H^0 \bar{v}_H^0)/(2RT\exp(\bar{v}_H(P_t - P_0)/RT) \tag{3}
\]

which normally is expressed by:

\[
X_H = \left(\frac{P_H^2}{P_0}\right)^{\frac{1}{2}} A \exp(-B/T) \exp(\bar{v}_H(P_t - P_0)/RT) \tag{4}
\]

The partial molar volume of hydrogen in the melt, \(\bar{v}_H\), is not determined. Due to very low solubility of hydrogen in the melt, \(\bar{v}_H\) can be substituted by the molar volume of melt \(\bar{v}_m\). The amount of dissolved gas can thus be calculated from equation 5.

\[
X_H = \left(\frac{P_H^2}{P_0}\right)^{\frac{1}{2}} A \exp(-B/T) \exp(\bar{v}_m(P_t - P_0)/RT) \tag{5}
\]

In the absence of external pressure and with moderate pressures of hydrogen, equation 5 reduces to:

\[
X_H = \left(\frac{P_H^2}{P_0}\right)^{\frac{1}{2}} A \exp(-B/T) \tag{6}
\]

This equation is known as Sieverts law (3). The values of constants A and B, for aluminium and gold alloys are determined experimentally at \(P_{H}^2=P_0\). The Sieverts apparatus was employed for the measurements, and the results are presented in the papers I and II. Effect of alloying elements on the gas solubility are determined by calculating interaction coefficients (4). The results indicate that:

a-Silicon and iron decrease the solubility of hydrogen in aluminium, whereas with iron at higher temperature, and titanium it increases.
b-For gold alloyed with copper or palladium, hydrogen solubility increases with alloying content.
2. NUCLEATION

Nucleation of pores is normally treated by the method derived by Gibbs (5) more than 100 years ago. The pressure caused by the dissolved gas in the melt, \( P'_{H_2} \), is the driving force for pore formation in castings. During cooling, the gas solubility in the melt decreases, see equation 5. Assuming that the gas content in the melt remains constant, \( P'_{H_2} \) increases, and can be evaluated as a function of initial gas content, applied ambient pressure and temperature from equation 5:

\[
P'_{H_2} = \frac{P X^2 \exp(2B)}{A^2 \exp\left(\frac{2V_m}{RT} (P_t - P_o)\right)}
\]  

(7)

At mechanical equilibrium, the gas pressure in a bubble, \( P_b \), is related to the ambient pressure \( P_a \), and surface tension \( Y \):

\[
P_b = P_a + 2Y/r
\]  

(8)

Gas pressure required for nucleating a bubble can be calculated by equating \( P_b = P'_{H_2} \), and considering the activation energy for nucleation (6):

\[
W^* = 60kT = 16\pi Y^3/(P'_{H_2} - P_a)^2
\]  

(9)

This indicates that \( P'_{H_2} \) of about 40000 atm, is required to form a bubble homogeneously. This pressure is too high to be achieved in even highly supersaturated melts computed by equation 7. It is thus, concluded that the pores, observed in the samples, must have formed heterogeneously. The usual method to treat the heterogeneous nucleation is to look at a gap, formed on a flat substrate. In paper IV, a model for heterogeneous nucleation is presented. In a melt, there usually are particles which can cause heterogeneous nucleation. In a spherical substrate, the size of the particles, as well as, the difference in surface tensions influence the nucleation. Assuming:
the required work for nucleation can be calculated as a function of particle size.

\[ W^* = 60kT = 16n^2\left(\frac{P_a - P}{r_p}\right)^2 + 4n^2\frac{\xi_0}{r_p} + 4n^2\frac{\xi_0}{r_p}(P_a - P_a)/3 \]  

(11)

\( P_a \) obtained from equation 11, reduces from 40000 atm to low pressures of 10-20 atm with particles larger than 2 \( \mu \)m, and it reduces further with larger particles. Aluminium oxide fulfills the condition set by expression 10, ref(7), and it is easily formed during melting and casting according to the following reaction:

\[ 2Al + 3H_2O = Al_2O_3 + 6H \]  

(12)

The sources of water in the above reaction, are due to moisture in the air, combustion products and etc. The resulting atomic hydrogen dissolves rapidly in the melt and precipitates as pore during solidification.

3. GROWTH PROCESS

In order to study the nucleation and growth of the pores and also the production of metallic foam, aluminium, Al-10%Fe and Al-4%Ti were saturated with hydrogen at 1000 C. Electromagnetic levitation technic was employed. The degree of saturation was controlled by varying the pressure of hydrogen during gas treatment. The equipment is described in the paper III. After equilibrium, they were quenched in a watercooled copper mould, at ambient pressure of 6 atm. This treatment enhances formation of finer pores (8-11), which were intended for producing metallic foam. The size of the pores in the samples increased with the hydrogen content between 50-200 \( \mu \)m. In the case of pure aluminium they were mostly spherical, while in Al-4%Ti and Al-10%Fe they were irregular and influenced in shape by primary Ti(\( \alpha \)) and Fe(\( \beta \)). The growth mechanism for pores in aluminium samples has been treated by the
Following model:

During quenching, $P_i^i$ increases. A sufficient pressure is achieved at a critical temperature with the presence of particles, which pores can nucleate. As the cooling continues, the degree of supersaturation increases. Hydrogen atoms with higher potential in the surrounding, diffuse into the bubble, and it expands. With the increase of radius, the pressure inside the bubble diminishes and causes a higher driving force for diffusion;

$$r>r^* \Rightarrow P_b = P_a + \frac{2Y}{r} < P_i^i$$

At the same time due to depletion, diffusion distance for hydrogen atoms increases and it reduces the rate of gas transport to the bubble. The rate of transport of hydrogen can be calculated using Fick's first law:

$$n_{H_2} = \frac{P_b V_b}{RT}$$

$$\frac{dn_H}{dt} = \frac{2}{RT} (P_b dV_b + V_b dP_b)$$

$$\frac{dn_H}{dt} = \frac{2}{RT} ((P_a + \frac{2Y}{r}) 4\pi r^2 + 4\pi \frac{3}{3} \pi \frac{(-2Y)}{r^2}) dr$$

$$\frac{dn_H}{dt} = \frac{8\pi}{3RT} (3P_a r^2 + 4Yr) \frac{dr}{dt}$$

$$\frac{dn_H}{dt} = \frac{D_H 4\pi r^2}{V_m} \frac{dx_H}{dr} - \frac{D_H 4\pi r^2}{V_m} \frac{X_H^p - X_H^o}{r}$$

The concentration of hydrogen in bulk melt $X_H^o$ is obtained from the gas analyses. Hydrogen concentration in the melt at the gas bubble interface, $X_H^p$, is given by equations 5 and 8 as:

$$X_H^p = \Lambda \exp\left(\frac{-H}{T}\right) \cdot \frac{P_b}{P_o} \frac{1}{2} \exp\left(\frac{V_m (P_a - P_o)}{RT}\right)$$

Combining equations 17-19 results:

$$\frac{3RT D_H (X_H^o - X_H^p)}{2V_m} = (3P_a r + 4Y) \frac{dr}{dt}$$

Inserting $dr/dt = dT/dt dr/dT$ and integration gives the final pore size.
\[ r_f \int \frac{2(\frac{dT}{dt})(3P_a + 4Y)}{3R} dr = \int \frac{T_m \mu_H (X_H^0 - X_H)}{V_m^T} TdT \] (21)

This model indicates that the final size of the pores increases with the hydrogen content, and decreases with higher ambient pressure and higher cooling rates. The results based on the presented model were in a good agreement with the measured values presented in the paper IV.

4. METALLIC FOAM

The above mentioned samples were remelted at reduced gravity and reduced ambient pressure. Reduced gravity was achieved either using a sounding rocket or an airplane flying a parabolic trajectory. The devices for remelting the samples are described in the paper III. A filament extracted from a halogen projector lamp was used as the heating element. It was inserted in a cavity in the sample. Sample was remelted in about 15 seconds and solidify in about 20-40 seconds depending on the gas (He or Ar) and ambient pressure. During remelting, pores expanded and they remained within the samples during solidification. Thus, pieces of metallic foams, about 2-3 grams were made. Density of the samples before and after remelting were measured. Relative reduction of density was calculated for the samples. Pores size and number were measured. The results are presented in paper V.

Samples of Al-4%Ti treated at 0.5-1 atm hydrogen and remelted at 0.1 atm achieved 50% reduction in density with a uniform distribution of pores. In aluminium cases, relative reduction of density did not exceed more than 5%. Pore were irregular and relatively large. The shape of pores in these cases was influenced by collision as well as expansion. Al, Al-10%Fe, and Al-4%Ti have solidification range of 0, 200, 390 C, respectively. Hydrogen solubilities as measured in previous work increases for the alloys in the same order. The results indicate that increasing solidification range and gas solubility are effective parameters in producing metallic foam. Expanded pores, are more effectively trapped in the
5. EFFECT OF SHRINKAGE

Formation of shrinkage pores in aluminium, aluminium copper and aluminium silicon alloys are studied and the results are presented in paper VI. The effect of hydrogen content, mode of solidification, impurities i.e aluminium oxide, and modifiers on the porosity are investigated. The hydrogen content of the alloys prior to casting was varied, with water saturated argon injected into the melt for different periods. They were subsequently cast in a rectangular cast iron mould. The hydrogen content, area fraction of porosity and size of the pores was then measured. The effect of modifiers was studied by adding 100 ppm Na or 250 ppm Sr after gas treatment. The results indicated that the porosity in the samples increases with duration of gas treatment more than the hydrogen content. With longer period of gas treatment, the amount of aluminium oxide in the melt increases which subsequently forms more nucleation sites for pores. This conclusion is in accordance with the model for heterogeneous nucleation presented above. Porosity also increased with the silicon content and addition of modifiers. Silicon reduces reduce the surface tension (12), which facilitates the pore nucleation.

A model for formation of shrinkage pores in long solidification range alloys is also presented. The enrichment of hydrogen and the pressure drop in the melt caused by shrinkage are accounted for in this model. During solidification, melt in the interdendritic area is enriched with hydrogen and the pressure of hydrogen in the melt thus increases, and can be calculated through equation 7. It is because the hydrogen solubility in the solid is much less than in the liquid. Due to high diffusivity of hydrogen and also short distance for diffusion, 100μm dendrite arm spacing, the lever rule can be applied. The pressure drop caused by shrinkage is calculated with a model presented by Piwonka (13). Assuming that pore nucleation is heterogeneous and that the size of the pores are
less than the remaining liquid between the dendrite arms, maximum pore size can be calculated as function of hydrogen content, dendrite arm spacing, and distance from the raiser by equation:

\[
\frac{XH_2}{{r^2}} + \frac{32\pi b^2 \lambda r^2 \alpha^2}{r^4 \pi h^2} - \frac{p_a}{r} = \frac{2\nu}{r}
\]  (22)

That size of the shrinkage pores varies between 10-50 µm close to the raiser and 40-60µm close to the chill depending on the hydrogen content. These results are in a good agreement with the measured size of the shrinkage pores presented in paper VI.

6. Hydrogen Embrittlement

The hydrogen embrittlement is a well known phenomena in metals and specially in steel. The mechanisms are different for various metals. In steels, an accepted mechanism appears to be associated with the migration of hydrogen atoms to lattice imperfections or strain fields associated with the imperfections. During the last stage of the pore growth, the pressure increases and causes the diffusion of hydrogen to the structure, which can lead to hydrogen embrittlement. This process can also occur in amorphous metals provided that they contain hydrogen before production. This matter has been studied in the paper VII.

Experiments were performed by injecting hydrogen gas to Fe(SiBC) alloy, before rapid quenching by chill block melt spinning method. Cooling rate and hydrogen content were varied. The X-ray measurements and bending test indicated amorphous structure but brittle. The effect of hydrogen on the amorphous transition was negligible. Embrittlement caused by hydrogen in these samples, has the same mechanism, although due to rapid quenching pores did not form and hydrogen is directly trapped in the structure.
CONCLUDING REMARKS

The papers presented in this thesis show that:

I) Pores nucleate heterogenously. Reducing hydrogen and foreign particles in the melt would reduce the porosity.

II) The possibility of producing metallic foam in reduced gravity is proved. Alloys with long solidification range and moderate hydrogen content and low remelting pressure enhance the process.

III) Existence of hydrogen in iron base amorphous ribbon, cause transition from ductile to brittle behaviour.

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5. J. W. Gibbs, Trans. Conn. Acad. 3, 343 (1878)
9. D. Hanson, J. of Metals, 1935, p. 103-123
# List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Equation</th>
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<tr>
<td>$o H_2$</td>
<td>standard chemical potential of hydrogen in the gas phase</td>
<td>3</td>
</tr>
<tr>
<td>$o H$</td>
<td>standard chemical potential of hydrogen in the melt</td>
<td>3</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
<td>3</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>3</td>
</tr>
<tr>
<td>$X_H$</td>
<td>mole fraction of hydrogen in melt</td>
<td>3</td>
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<tr>
<td>$V_H$</td>
<td>partial molar volume of hydrogen</td>
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</tr>
<tr>
<td>$p_t$</td>
<td>total pressure in the gas phase</td>
<td>3</td>
</tr>
<tr>
<td>$p_o$</td>
<td>standard pressure of hydrogen</td>
<td>3</td>
</tr>
<tr>
<td>$p H_2$</td>
<td>pressure of hydrogen</td>
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</tr>
<tr>
<td>$A_{1 0}$</td>
<td>constant</td>
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<tr>
<td>$V_m$</td>
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<td>$p H_2^*$</td>
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<td>$p_b$</td>
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<tr>
<td>$r$</td>
<td>radius of the bubble</td>
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<tr>
<td>$\gamma / g$</td>
<td>surface tension between melt and gas</td>
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<td>$P_a$</td>
<td>ambient pressure</td>
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<tr>
<td>$W^*$</td>
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<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
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<tr>
<td>$\gamma / p_{1 / g}$</td>
<td>surface tension between particle and melt</td>
<td>10,11</td>
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<tr>
<td>$n_p$</td>
<td>radius of the particle</td>
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<tr>
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<td>$K$</td>
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<tr>
<td>$m$</td>
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<td>$\Theta$</td>
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<tr>
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<tr>
<td>$t$</td>
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<tr>
<td>$h$</td>
<td>half of the mould height</td>
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PAPER I

H. Shahani

Solubility of dry hydrogen in liquid aluminium, Al-4%Ti, Al-7%Si, and Al-10%Fe at one atmosphere

December 1983
SOLUBILITY OF DRY HYDROGEN IN LIQUID ALUMINIUM, Al-4%Ti, Al-7%Si AND Al-10%Fe AT ONE ATMOSPHERE PRESSURE

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1. ABSTRACT

Solubility of hydrogen in liquid aluminium and Al-Ti, Al-Si, and Al-Fe has been studied. The solubility equations, the standard heat of solution and the dependency of interaction parameters on temperature have been determined. Silicon and iron decrease the solubility of hydrogen while titanium increases it. At high temperature, iron also increases the hydrogen solubility.
2. INTRODUCTION

Different forms of porosity, like pinholes, blow-holes, inter-dendritical porosity, gas bubbles, etc. are directly related to the gas content of a melt prior to casting.

In aluminium alloys, hydrogen is the only gas which dissolves in a measurable amount. It is the main cause for pore formation in these alloys. Measuring the gas solubility in the melt provides basic information to understand and explain the mechanism of pore formation.

There are two main methods for measuring gas solubility in metals:

i) Sampling Method

ii) Hot Volume Method

The "Sampling Method" is based on first equilibrating the samples at the desired temperature and atmosphere, followed by a rapid quench. The gas content of the quenched samples is then measured by "Extraction method" or "Vacuum melting". The loss of gas from the samples during quenching and handling and also during gas determination causes inaccuracy with this method. However, this method has been widely used (1-14).

The "Hot Volume Method", originally developed by Siverts in 1910 (15-16), is based on the difference of volumes of an inert and a soluble gas which are required to fill the reaction chamber at constant temperature. The difference in volumes is the solubility of the reactive gas at that temperature. This method has also been widely used (17-25).

Some disadvantages with the "Hot Volume Method" are absorption and reaction of reactive gas with the crucible, the reaction chamber and oxides on the sample. The difference
in the heat conductivities of the gases also entails varying thermal gradients which further increases measurement errors. For example hydrogen has a thermal conductivity equal to \(4.7 \times 10^{-4} \text{cal/cm/sec/K}\) at 50°C (26). It is 1.2 and 10 times larger than helium and argon respectively at the same temperature.

Ransley (27,28,5), Gpie(29) and Simensen (30) have measured the solubility of hydrogen in Al-Cu, Al-Si, Al-Mg alloys using both the above mentioned methods.

In the present investigation solubility of hydrogen in pure aluminium and under the alloying influence of titanium, silicon and iron have been determined using the "Hot Volume Method".

3. APPARATUS AND EXPERIMENTAL PROCEDURE

3.1 APPARATUS

The apparatus is shown in figure 1. It consists mainly of a 50 mm inner diameter (i.d) quartz reaction chamber and a mercury burette. The crucible, located in the reaction chamber, is of aluminium oxide. The dead volume of the reaction chamber was reduced by inserting two half-spheres of quartz at the top and bottom of the crucible. The temperature was measured with a chromel-alumel thermocouple protected by an aluminium oxide tube. A low frequency induction furnace was used as the heat source.

Reaction chamber was sealed by silicon greased glass joint which was cooled by a water-jacket system. Ambient pressure and temperature were registered within an accuracy of ±0.25 mm Hg and ±0.25°C respectively. Melt temperature was controlled within ±2°C. The main burette was also used as an internal manometer.

The burette was made of a 20 mm i.d. tube having a
height of 800 mm. The volume of the burette was larger than that of the reaction chamber. This reduced the errors that could have been caused by refilling.

The volume and pressure in the burette were controlled by varying the level of a mercury reservoir. This was activated by a modified screw system driven by an electric motor. The hot volume was measured with helium. It has the thermal properties close to hydrogen. Instead of constructing a purification train, gases of high purity were used. Both gases were supplied by AGA Stockholm. The impurity content of both gases were:

\[
\begin{align*}
O_2 & < 10 \text{ ppm} \\
H_2O & < 10 \text{ ppm} \\
total \text{ purity} & > 99.995\% 
\end{align*}
\]

3.2 PREPARATION OF THE SAMPLES

Pure aluminium (99.98%) and ingots of Al-7% Si were supplied by A.S.V (Ardal og Sunndalsora Verk, Norway). Alloys of 4%Ti and 10%Fe were made as follows:

Pure aluminium was melted in a "Super Kanthal" furnace in a graphite crucible. The desired amount of alloying element was wrapped in an aluminium foil and added under protective argon atmosphere. Samples were then cast into a graphite mould with a diameter of 33 mm and cut to a height of 50 mm. A hole for placing the thermocouple was drilled in the center of each sample. The samples were then washed with aceton. The mass of the samples were measured. Samples were normally in the range of 110-120 grams.

3.3 PROCEDURE OF THE EXPERIMENTS

Samples were inserted into the reaction chamber and degassed for half an hour at about 750°C. The burette was filled with helium and then connected to the reaction chamber. Pressure in the burette was balanced with the
ambient pressure by varying the level of the reservoir. The volume of helium in the burette prior and after connection to the reaction chamber at a given melt temperature was adjusted to S.T.P. conditions. The hot volume for helium can thus be depicted by:

\[ V_{He}^T = \frac{(h_1 - h_2) \pi D^2 P_1 T_0}{4P_0 T_1} \]  

\( V_{He}^T \) is the volume which contains an equivalent amount of gas at 0°C as the actual volume does at the investigated temperature and pressure. Hot volumes of helium were measured at different temperatures in the range of 665-920°C. The same procedure was repeated with hydrogen. It took about 10-15 minutes to reach equilibrium. The difference in the hot volume for hydrogen and helium gave the amount of hydrogen dissolved in the melt at the temperature of interest and can be determined by equation (2):

\[ S_{H_2}^T = \frac{(V_{H_2}^T - V_{He}^T)100}{m} \sqrt{\frac{76}{P_1}} \]  

where:

- \( m \) = mass of the sample (grams)
- \( P_1 \) = ambient pressure (cm Hg)
- \( P_0 \) = standard pressure (76 cm Hg)
- \( T_1 \) = room temperature (°K)
- \( T_0 \) = standard temperature (273°K)
- \( D \) = diameter of the burette (2 cm)
- \( h_1 \) = height of the mercury in the burette before connection to the reaction chamber (cm)
- \( h_2 \) = height of the mercury in the burette after connection to the reaction chamber (cm)
- \( S \) = solubility of hydrogen (cc H₂/100 gr)
4. RESULTS

The results are presented in table 1. The volumetric solubility of hydrogen (cc H\textsubscript{2}/100 grams) as a function of temperature for aluminium and Al- alloys are shown in figures 2-5. Figures 2-5 show that the solubility of hydrogen increases with increasing temperature. Titanium has a strong effect on the solubility with increasing temperature, figure 3. Silicon and iron both decrease the solubility, figures 4-5.

5. THEORY

5.1 PURE ALUMINIUM

Dry hydrogen dissolves in liquid aluminium alloy by three gradual steps (31):

a: Dissociation of molecular hydrogen into atomic form in the boundary layer:

\[
\frac{1}{2} \text{H}_2(g) \rightleftharpoons \text{H}(g)
\]

b: Dissolving of atomic hydrogen in the boundary layer of the melt:

\[
\text{H}(g) \rightleftharpoons \text{H}^*
\]

c: Transport of hydrogen to the bulk of the melt by diffusion:

\[
\text{H}^* \rightleftharpoons \text{H}
\]

Total reaction can be written as:

\[
\frac{1}{2} \text{H}_2(g) \rightleftharpoons \text{H}
\] (3)
In pure aluminium we have:

\[ \Delta G^0 = -R.T. \ln \left( \frac{a_H}{(P_{H_2})^{1/2}} \right) \quad (4) \]

In this treatment wt.pct of hydrogen is used as the standard state. It is further assumed that activity of hydrogen, \( f_H \), goes to unity when the concentration of hydrogen goes to zero and \( P_{H_2} \) is equal to 1 atm. Thus:

\[ \Delta G^0 = -R.T. \ln (\% H \text{ pure}) \quad (5) \]

\[ \log (\% H \text{ pure}) = 0.434 \left( - \frac{\Delta H^0}{T} + \frac{\Delta S^0}{R} \right) \quad (6) \]

In figure 6, \( \log (\% H) \) is plotted as a function of \((1/T)\) for pure aluminium. A straight line is fitted to the points by the least square method. Assuming that \( \Delta H^0 \) and \( \Delta S^0 \) varies slightly at the investigated temperature range, their values may be calculated from the slope and intercept respectively. The solubility equation and value of \( \Delta H^0 \) are given in table 2. The respective volumetric function (cc \( H_2 \)/100 grams) as a function of temperature is presented in figure 2.

5.2 THE EFFECT OF ALLOYING ELEMENTS ON THE SOLUBILITY

Although, reaction (3) is valid for the solubility of hydrogen in aluminium alloys, however due to the interaction of the alloying elements, the value of \( f_H \) is not unity. The solubility data presented in figures 2-5 show a strong influence from the alloying elements. Therefore equation 4 should be treated as follows:

\[ \Delta G^0 = -R.T. \ln (f_H. \% H \text{ alloy}) = -R.T. \ln (f_H) - R.T. \ln (\% H \text{ alloy}) \quad (7) \]

By defining \( \Delta G_E \) as the excess free energy (31):

\[ \Delta G_E = -R.T. \ln (f_H) \quad (8) \]

\[ \Delta G^0 = \Delta G^0 - \Delta G_E = -R.T. \ln (\% H \text{ alloy}) \quad (9) \]

and rewriting equation (9) results in:
Figures 7-9 depict plots of log(%H alloy) as a function of (1/T) for the three investigated alloys. The values of $\Delta H_1^0$ and $\Delta S_1^0$ are evaluated in the same way as for pure aluminium. Solubility is calculated, converted to (cc H$_2$ /100gr) and plotted in figures 3-5. The solubility equations and $\Delta H_1^0$ are also given in table 2. Equation 8 may be rewritten to give:

$$f_H = \exp(-\Delta G_E/R.T) = (%H_{pure})/(%H_{alloy})$$  \hspace{1cm} (11)

$\Delta G_E$ can be calculated as:

$$\Delta G_E = \Delta G^0 - \Delta G_1^0 = (\Delta H_1^0 - \Delta H_1^0) - T(\Delta S_1^0 - \Delta S_1^0)$$  \hspace{1cm} (12)

Wagner(33) and Chipman(34) have defined "interaction parameter" as the coefficients in the Taylor expansion of the logarithm of the activity coefficient:

$$\log(f_H) = \log(f_H) + \%H \frac{\partial \log f_H}{\partial \%H} + \%i \frac{\partial \log f_H}{\partial \%i} + \ldots$$  \hspace{1cm} (13)

The first and second terms in the right hand side of equation (13) are assumed to be zero and the third term, "interaction parameter" may expressed in (wt.pct) as:

$$e_H^i = \left(\frac{\partial \log f_H}{\partial \%i}\right)_{P,T}$$  \hspace{1cm} (14)

- where the derivative is taken for the limiting case of zero concentration of the solute (35-37). Values of $\Delta G_E$, are calculated from table 2. Values of log($f_H$) at 700-800-900°C and the interaction coefficient, $e_H^i$, at these temperatures are calculated and presented in table 3.
6. CONCLUSION

Comparision of the present data on the solubility of hydrogen in pure aluminium with those reported by Opie (29) and Ransley (27) shows present values to be about 8% higher, compared to those reported by Ransley and about the same as Opie's results. For Al-7%Si the results are about 10% higher than that reported by Opie. No data was found on the solubility of hydrogen in Al-4%Ti and Al-10%Fe. Table 3 shows the effect of alloying elements and temperature dependency, and it can be concluded that:

1. Silicon decreases the solubility of hydrogen in aluminium at all of the investigated temperature of interests.
2. Iron decreases the solubility but this effect becomes less at increasing temperatures.
3. Titanium increases the solubility and the effect becomes larger at increasing temperatures.

The solubility of hydrogen in the solid state is always much lower than that in the liquid. It thus may be expected that there is a small effect from the alloying elements on the solubility in the solid state. It means that the risk for poreformation will increase in alloys containing titanium, but will decrease for silicon and at low temperatures also for iron.

7. ACKNOWLEDGEMENT

I wish to thank Professor H. Fredriksson for many helpful and stimulating discussions. This work was sponsored by the Ardal og Sunndal Verk a.s., Norway
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**Fig. 1 Schematic drawing of the reaction chamber and apparatus.**
### Table 1: Hydrogen Solubility Measurements ('cH₂/100grams')

<table>
<thead>
<tr>
<th>TEMP (°C)</th>
<th>660</th>
<th>675</th>
<th>700</th>
<th>750</th>
<th>775</th>
<th>800</th>
<th>815</th>
<th>825</th>
<th>840</th>
<th>850</th>
<th>860</th>
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<tbody>
<tr>
<td>Al</td>
<td></td>
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<td></td>
<td></td>
<td>1.00</td>
<td>1.78</td>
<td>1.50</td>
<td>3.04</td>
<td>2.30</td>
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<td></td>
<td>0.9</td>
<td>1.1</td>
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<tr>
<td>Al-4V</td>
<td>1.00</td>
<td>1.78</td>
<td>1.50</td>
<td>3.04</td>
<td>2.30</td>
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<td>Al-7Si</td>
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<td>Al-10Fe</td>
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### Table 2: Hydrogen Solubility Equations and Standard Heat of Solution

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>SOLUBILITY (cm³H₂/100 grams)</th>
<th>SOLUBILITY (wt.pct)</th>
<th>( \delta d ) (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>( \log S = (2.77 \pm 0.01) - (2683 \pm 11.7)/T )</td>
<td>( \log (%) = (-1.28 \pm 0.01) - (2683 \pm 11.7)/T )</td>
<td>12.28 ± 0.05</td>
</tr>
<tr>
<td>Al-4V</td>
<td>( \log S = (3.61 \pm 0.03) - (3483 \pm 118)/T )</td>
<td>( \log (%) = (-0.44 \pm 0.03) - (3483 \pm 118)/T )</td>
<td>15.95 ± 0.05</td>
</tr>
<tr>
<td>Al-7Si</td>
<td>( \log S = (2.50 \pm 0.18) - (2561 \pm 38)/T )</td>
<td>( \log (%) = (-1.55 \pm 0.18) - (2561 \pm 38)/T )</td>
<td>11.73 ± 0.17</td>
</tr>
<tr>
<td>Al-10Fe</td>
<td>( \log S = (5.13 \pm 0.16) - (5664 \pm 168)/T )</td>
<td>( \log (%) = (1.08 \pm 0.16) - (5664 \pm 168)/T )</td>
<td>25.93 ± 0.77</td>
</tr>
</tbody>
</table>

### Table 3: Variation of Activity Coefficient and Interaction Parameter with Temperature (°K)

<table>
<thead>
<tr>
<th>( \gamma_H ) for Al-alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (800\pm106)/T\times(10.04\pm0.02) ) at 4Vt1</td>
</tr>
<tr>
<td>( (10.27\pm0.17) ) at 7 Si</td>
</tr>
<tr>
<td>( (2981\pm156)/T\times(2.36\pm0.15) ) at 10Fe</td>
</tr>
</tbody>
</table>
Fig 2: Solubility of hydrogen in pure aluminium

Fig 3: Solubility of hydrogen in Al-2%Ti

Fig 4: Solubility of hydrogen in Al-7%Si

Fig 5: Solubility of hydrogen in Al-1%Fe
Fig. 6: Hydrogen solubility for pure Al with inverse of temperature (°K).

Fig. 7: Hydrogen solubility for Al-4Ti with inverse of temperature (°K).

Fig. 8: Hydrogen solubility for Al-7Si, with inverse of temperature (°K).

Fig. 9: Hydrogen solubility for Al-10CuFe with inverse of temperature (°K).
PAPER II

H. SHAHANI, L. WICTORIN

Solubility of dry hydrogen in liquid gold, gold-copper and gold-palladium alloys at on atmosphere pressure

December 1983
SOLUBILITY OF DRY HYDROGEN IN LIQUID GOLD, GOLD-COPPER AND GOLD-PALLADIUM ALLOYS AT ONE ATMOSPHERE PRESSURE

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Stockholm, Sweden
December 1983

1. ABSTRACT

Hydrogen solubility in gold, gold-copper and gold-palladium alloys has been studied. Solubility equations, standard heat of solution and temperature dependency of the interaction parameter have been determined. Both copper and palladium increase the solubility. With increasing temperature, palladium has higher effect on the solubility of hydrogen than copper.
2. INTRODUCTION

The relationship between the gas content of the melt and defects due to porosity in the casting has been an interesting subject for years. In short, melts have gas solubilities about 5-10 times greater than in the solid state at the melting point. This solubility increases with increasing temperature. During casting, gas solubility decreases with diminishing melt temperatures. A sharp decrease of the solubility at the melting point also cause a concentration pile-up of the gas at the solidification front.

With the presence of proper nucleants in the liquid, the pores will form and grow. Alloying elements influence the gas solubility of the melt which in turn affects the pore formation mechanism. Hydrogen is the only gas which dissolves in gold in small quantities (1-2). Adding alloying elements such as copper or palladium to pure gold in dental alloys is common. In practice, not only reduces costs but also enhances mechanical properties of the alloys. However, some drawbacks are that they increase the hydrogen solubility in the liquid state. This increase in the solubility, in turn increases the tendency for poreformation in the casting.

Gas solubility measurements are performed by two main methods, namely "Sampling Method" (3-16) and "Hot Volume Method" (17-27). Solubility of hydrogen in pure gold in solid and liquid state has been studied earlier (1-2) using both methods. The aim of the present work is to study the effect of temperature and alloying elements, copper and palladium, on the hydrogen solubility using the "Hot Volume Method". This method was originally developed by Sieverts (17-18) and has been used in an earlier work by one of the authors (35). The method is based on the difference of volumes of an inert and a reactive gas which are required to fill the reaction chamber at constant temperature. The observed difference in volumes corresponds to the solubility of the reactive gas at the investigated temperature.
3. APPARATUS AND EXPERIMENTAL PROCEDURE

3.1 APPARATUS

The Sieverts apparatus was used in this work. Figure 1 shows the schematic drawing of the apparatus. It was mainly composed of a quartz reaction chamber and a mercury burette. The crucible was also made of quartz. The reaction chamber and crucible had inner diameters of 15 and 6 mm respectively. Thermocouples of Pt, Pt-10%Rh and Pt-6%Rh, Pt-30%Rh were used for Au-Cu and Au-Pd alloys. They were protected by an aluminium oxide shield. Melt temperature was controlled within ±2 °C. The mercury burette was made of a 6 mm i.d. tube with height of 850 mm. The height of mercury in the burette could be measured within ±0.25mm. Helium was used as the insoluble gas to detect the hot volume. High purity helium and hydrogen were used. The impurities content are given below:

\[
\begin{align*}
O_2 &< 10 \text{ ppm} \\
H_2O &< 10 \text{ ppm} \\
\text{Total purity} &> 99.995%
\end{align*}
\]

A low frequency induction furnace was used for melting. The furnace enabled good stirring and fast response while adjusting temperatures. Silicon grease was used in the glass joints. To cool the quartz joint, water jacket was utilized.

3.2 PREPARATION OF THE SAMPLES

Alloys were made of pure gold (24K), high purity copper and palladium. Experiments were initially performed with pure gold and subsequently by adding copper, to make alloys containing 4, 8, 10, 12, 13, 15, 20, 40% Cu. The same procedure was repeated for palladium to make alloys of 2, 4, 6, 8, 10% Pd. The initial mass of pure gold was about 30 grams.
3.3 PROCEDURE OF THE EXPERIMENTS

Each experiment was initiated by evacuation of the apparatus for about 30 minutes at 1100°C. Ambient pressure and temperature were recorded using a mercury thermometer (accuracy ±0.25°C) and a mercury barometer (accuracy ±0.25 mm Hg). The burette was first filled with helium and then connected to the reaction chamber. The hot volume of the system at S.T.P. and given melt temperature "T" could be calculated by:

\[ V_H^e = \frac{(h_1 - h_2)D^2}{4P_1 P_0} \]

-where:
  \( P_1 = \) ambient pressure (cm Hg)
  \( P_0 = \) standard pressure (76 cm Hg)
  \( T_1 = \) room temperature (°K)
  \( T_0 = \) standard temperature (273°K)
  \( h_1, h_2 = \) height of mercury in the burette before and after connection to the reaction chamber (cm)
  \( D = \) diameter of the burette (0.6 cm)

The hot volume of the system was measured at different temperatures. The same procedure was applied with hydrogen in the same range of temperatures. It took about 20 minutes to reach equilibrium for each temperature. The amount of hydrogen dissolved in the melt could be calculated as:

\[ S_{H_2}^T = \frac{(V_H^T - V_{He}^T)100}{m} \]

where \( m \) is the mass of the sample in grams, and \( S \) is the solubility in (cc H₂/100 grams).
4. RESULTS

The results of the measurements are given in tables 1 and 2 for Au-Cu and Au-Pd alloys respectively. The solubility measurements in (cc H₂/100 grams) as a function of temperature, °C, are also given in figures (2-16). All results indicate that the solubility increases with temperature and alloying element. They also show that Pd increases the solubility of hydrogen more than copper. This will be discussed later.

5. THEORY

5.1 PURE GOLD

Hydrogen dissolves in the melt by three gradual steps (28):

a: Dissociation of molecular hydrogen into atomic form at the boundary layer of the melt:

\[ \frac{1}{2} \text{H}_2(g) \rightarrow \text{H}(g) \]

b: Dissolving of atomic hydrogen in the boundary layer of the melt:

\[ \text{H}(g) \rightarrow \text{H}^* \]

c: Transport of hydrogen into the bulk of the melt by diffusion:

\[ \text{H}^* \rightarrow \text{H} \]

The total reaction can be written as:

\[ \frac{1}{2} \text{H}_2(g) \rightarrow \text{H} \] (1)
The standard free energy changes for this reaction is:

$$\Delta G^0 = -R.T. \ln (a_H / (p_{H_2})^{1/2})$$

(2)

Concentration in weight percent and hydrogen pressure of one atmosphere are selected as the standard state. As the concentration goes to zero, activity coefficient of hydrogen, $f_H$, goes to unity, and;

$$\Delta G^0 = -R.T. \ln (%_{H \text{ pure}})$$

(3)

and:

$$\log (%_{H \text{ pure}}) = 0.434 (-\Delta H^0 / T + \Delta S^0) / R$$

(4)

Neglecting small variation of $\Delta H^0$ and $\Delta S^0$ with temperature, the general form of the solubility can be depicted as a straight line in $\log (%_{H \text{ pure}})$ as a function of $(1/T)$. The best straight line was fitted to the points for the pure gold by the least square method. The value of $\Delta H^0$ and the corrected form of solubility with standard deviation are given in table 3.

5.2 THE EFFECT OF ALLOYING ELEMENTS ON THE SOLUBILITY

Although reaction (1) is still valid, but due to the interaction of alloying elements, the value of $f_H$ is not equal to unity anymore. The solubility data presented in figures (2-16) show a strong influence from the alloying elements. Equation 2 can thus be rewritten as:

$$\Delta G^0 = -R.T. \ln (f \cdot %_{H \text{ alloy}})$$

(5)

$$\Delta G^0 = -R.T. \ln f_H - R.T. \ln (%_{H \text{ alloy}})$$

(6)

$$\Delta G^0 = \Delta G^0 + \Delta G^0_1$$

(7)

$$\Delta G^0_1 = \Delta G^0 - \Delta G^0_2 = -R.T. \ln (%_{H \text{ alloy}})$$

(8)
\[ \log(\% \text{H alloy}) = 0.434\left( - \Delta H_1^0 / T + \Delta S_1^0 \right) / R \quad (9) \]

Again by neglecting the variation of \( \Delta H_1^0 \) and \( \Delta S_1^0 \) with temperature, a straight line should pass through these points in \( \log(\% \text{H}) \) and \( (1/T) \). The best straight line was passed by the least square method and values of \( \Delta H_1^0 \) and \( \Delta S_1^0 \) were calculated. They were transferred to the proper unit and plotted with solid line in relevant solubility diagrams. Equations 6 and 7 give the relation between excess free energy and activity coefficient:

\[ f_{\text{H}} = \exp(-\Delta G_{\text{E}}/RT) = (\% \text{ pure})/(\% \text{ H alloy}) \quad (10) \]

\[ \log f_{\text{H}} = \log f_{\text{H}}^0 + \frac{\partial \log f_{\text{H}}}{\partial (1/T)^0} + \frac{\partial \log f_{\text{H}}}{\partial (1/T)^0} \quad (11) \]

The first and second terms on the right hand side of the equation are assumed to be zero. Wagner (30) named the third term as interaction coefficient. It was modified slightly by Chipman (31) and is expressed in (wt.pct) as:

\[ e_{\text{H}}^i = \frac{\partial \log f_{\text{H}}}{\partial (1/T)^0} \biggr|_{p, T} \quad (12) \]

\%i \rightarrow 0

In equation 12, the derivative is taken as the limiting case of zero concentration of the solute (29,32-34). To calculate the values of "\( f_{\text{H}}^i \)" at temperatures between 1100-1300, with interval of 100°C, the corrected form of solubility, as given in table (3) is used.

Values of interaction coefficient, \( e_{\text{H}}^i \), were calculated at mentioned temperatures and are presented in Table (4). The temperature dependency of the interaction coefficient is also given in the same table. Total heat of solution as a function of the alloying content for Au-Cu and Au-Pd are plotted in figure 17.
6. CONCLUSION

Hydrogen solubility in gold, gold-copper and gold-palladium alloys is related to the alloying content. Figures 2-16 show the increasing solubility with increasing alloying content. Palladium increases the solubility more than copper. It can also be realized by comparing the interaction coefficient values; $e^{Pd}_H$ 3-4 times more than $e^{Cu}_H$ was calculated when very small amount of alloy was added to pure gold. Comparison of the figures 2-10 for Au-Cu, also shows slightly lowered gas solubility for alloys of 10-12%Cu. Variation of the heat of solution indicates a minimum for Au-Pd at about 6%Pd. For Au-Cu alloys, the heat of solution decreases gradually with increasing copper content.

7. ACKNOWLEDGMENT

We wish to thank Professor Hasse Fredriksson for many helpful discussions. This project was sponsored by the Swedish Board for Technical Development, STU. Gold, copper and palladium were kindly supplied by AB John Sjöding of Stockholm.

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Fig. 1: Schematic drawing of the apparatus.
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**Table 1: Solubility of Hydrogen (ccH₂/100g) for Au-Cu Alloys (°C)**

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**Table 2: Solubility of Hydrogen (ccH₂/100g) for Au-Pd Alloys (°C)**
<table>
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<tr>
<th>ALLOY</th>
<th>SOLUBILITY (cm³ H₂/100 grams)</th>
<th>SOLUBILITY (wt. pct)</th>
<th>ΔH° (Kcal/mole)</th>
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<tr>
<td>Au-0% Cu</td>
<td>Log S = (5.38 ± 0.95) - (8592 ± 453)/T</td>
<td>Log (SH) = (1.33 ± 0.95) - (8592 ± 453)/T</td>
<td>39.3 ± 6.6</td>
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<tr>
<td>Au-4% Cu</td>
<td>Log S = (2.84 ± 0.04) - (4540 ± 50)/T</td>
<td>Log (SH) = (1.21 ± 0.04) - (4540 ± 50)/T</td>
<td>20.7 ± 0.23</td>
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<tr>
<td>Au-8% Cu</td>
<td>Log S = (1.70 ± 0.01) - (2774 ± 3)/T</td>
<td>Log (SH) = (2.35 ± 0.01) - (2774 ± 3)/T</td>
<td>12.7 ± 0.01</td>
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<tr>
<td>Au-10% Cu</td>
<td>Log S = (0.65 ± 0.18) - (1420 ± 80)/T</td>
<td>Log (SH) = (3.65 ± 0.18) - (1420 ± 80)/T</td>
<td>6.5 ± 0.37</td>
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<tr>
<td>Au-12% Cu</td>
<td>Log S = (1.62 ± 0.19) - (3200 ± 270)/T</td>
<td>Log (SH) = (2.43 ± 0.19) - (3200 ± 270)/T</td>
<td>14.6 ± 1.24</td>
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<td>Au-13% Cu</td>
<td>Log S = (0.78 ± 0.15) - (1270 ± 200)/T</td>
<td>Log (SH) = (3.27 ± 0.15) - (1270 ± 200)/T</td>
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<td>Au-15% Cu</td>
<td>Log S = (1.65 ± 0.06) - (2246 ± 81)/T</td>
<td>Log (SH) = (2.40 ± 0.06) - (2246 ± 81)/T</td>
<td>10.2 ± 0.37</td>
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<tr>
<td>Au-20% Cu</td>
<td>Log S = (1.6 ± 0.04) - (1170 ± 15)/T</td>
<td>Log (SH) = (2.99 ± 0.04) - (1170 ± 15)/T</td>
<td>5.3 ± 0.07</td>
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<tr>
<td>Au-60% Cu</td>
<td>Log S = (0.73 ± 0.01) - (610 ± 8)/T</td>
<td>Log (SH) = (3.32 ± 0.01) - (610 ± 8)/T</td>
<td>2.7 ± 0.04</td>
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<tr>
<td>Au-0% Pd</td>
<td>Log S = (6.98 ± 0.01) - (10940 ± 23)/T</td>
<td>Log (SH) = (2.93 ± 0.01) - (10940 ± 23)/T</td>
<td>50.1 ± 0.1</td>
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<tr>
<td>Au-2% Pd</td>
<td>Log S = (3.71 ± 0.02) - (5439 ± 27)/T</td>
<td>Log (SH) = (0.35 ± 0.02) - (5439 ± 27)/T</td>
<td>24.9 ± 0.1</td>
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<tr>
<td>Au-4% Pd</td>
<td>Log S = (2.82 ± 0.01) - (3946 ± 2.7)/T</td>
<td>Log (SH) = (1.23 ± 0.01) - (3946 ± 2.7)/T</td>
<td>18.1 ± 0.1</td>
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<tr>
<td>Au-6% Pd</td>
<td>Log S = (1.71 ± 0.01) - (1924 ± 4.2)/T</td>
<td>Log (SH) = (2.34 ± 0.01) - (1924 ± 4.2)/T</td>
<td>8.8 ± 0.02</td>
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<tr>
<td>Au-8% Pd</td>
<td>Log S = (4.78 ± 0.01) - (6389 ± 1.8)/T</td>
<td>Log (SH) = (0.73 ± 0.01) - (6389 ± 1.8)/T</td>
<td>29.2 ± 0.01</td>
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<tr>
<td>Au-10% Pd</td>
<td>Log S = (7.25 ± 0.02) - (10187 ± 29)/T</td>
<td>Log (SH) = (3.2 ± 0.02) - (10187 ± 29)/T</td>
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**Table 3: Hydrogen Solubility Equation and Standard Heat of Solution for Au-Cu and Au-Pd Alloys.**

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<td>-0.02</td>
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<tr>
<td>Au-Pd</td>
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<td>-0.21</td>
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\[ \Delta H^o = C_H + \epsilon_H \cdot T \]

**Table 4: Interaction Parameter and Temperature Dependency for Cu and Pd on Gold.**
**Fig. 2**: Hydrogen solubility in pure gold

**Fig. 3**: Hydrogen solubility in Au-4Cu

**Fig. 4**: Hydrogen solubility in Au-8Cu

**Fig. 5**: Hydrogen solubility in Au-18Cu
Fig. 6: Hydrogen solubility in Au-15%Cu

Fig. 7: Hydrogen solubility in Au-13%Cu

Fig. 8: Hydrogen solubility in Au-12%Cu

Fig. 9: Hydrogen solubility in Au-20%Cu
FIG. 10: HYDROGEN SOLUBILITY IN Au-40%Cu

FIG. 11: HYDROGEN SOLUBILITY IN PURE GOLD

FIG. 12: HYDROGEN SOLUBILITY IN Au-2%Pd

FIG. 13: HYDROGEN SOLUBILITY IN Au-4%Pd
Figure 14: Hydrogen solubility in Au-FePd

Figure 15: Hydrogen solubility in Au-GePd

Figure 16: Hydrogen solubility in Au-IrPd

Figure 17: Variation of standard heat of solution for hydrogen in Au-Cu and Au-Pd alloys.
PAPER III

H. Shahani, R. Jönsson, S. Wallin

On the design of high pressure casting equipment and rapid heating furnaces used in metallic foam experiments

September 1983
ON THE DESIGN OF HIGH PRESSURE CASTING EQUIPMENT AND RAPID HEATING FURNACES USED IN METALLIC FOAM EXPERIMENTS

Hamid Shahani Rolf Jönsson, Sven Wallin

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The Royal Inst. of Technology Tritonvägen 27
S-100 44 Stockholm S-171 54 Solna
Sweden Sweden
September 1983

1. ABSTRACT

The design of high pressure casting and rapid heating furnaces are discussed. These furnaces were used for studying the nucleation and growth of pores and also to study the possibility of producing metallic foams in reduced gravity.
2. INTRODUCTION

Particle composites are difficult to produce from melts. Due to variation in the density of two phases, they either float or sediment during the production process. Thus, it leads to uneven distribution of the particles in the matrix. In order to avoid segregation of the particles, it has been proposed to use a micro-gravity environment. One of the most difficult composite to produce from melts is metallic foam, i.e. metals containing numerous small gaseous pores.

In order to investigate the nucleation and growth of pores and also to produce metallic foams directly from melts, aluminium base alloys were supersaturated with respect to hydrogen on earth and remelted in reduced gravity and under reduced pressure.

Reduced gravity was achieved by two methods. In the first, a material science module was flown within the framework of the Swedish sounding rocket program, PIRAT (Pointed Infra-Red Astronomical Telescope). The payload was launched on the 30th of September 1981 using a Nike-Black Brant V C rocket. A peak altitude of 270 Km was attained. The duration of the micro-g flight was 410 seconds giving average acceleration levels of 0.3-2x10^{-3} g. Reduced gravity in the second case was achieved on board a Lockheed F104 aircraft, flown in a parabolic trajectory. Reduced acceleration levels of 0.03-0.1 G were achieved for about 50-60 seconds.

To accommodate the constraints imposed by the flight conditions remelting furnaces were specially designed to overcome the limitations of weight, power supply and duration of the experiment.
3. THE HIGH PRESSURE CASTING FURNACE

Hydrogen solubility in melts is a function of the melt properties, temperature and hydrogen pressure. By rapid cooling, dissolved hydrogen can be arrested within the small pores in the sample. To produce samples with the required hydrogen supersaturation, a furnace was required wherein high pressure could be regulated and where facility existed for rapid quenching.

The electromagnetic levitation technique was chosen. With such a technique, the samples could be reacted with the gas at high temperature while desired pressure could be applied and due to good stirring, required time for dissolving hydrogen in the sample could be minimized. By turning the furnace off, sample could be ejected into a water-cooled copper mould and thus be quenched.

Gas treated samples had to be at least about 10 grams with diameter of 18 mm and height of 15 mm before machining. These limitations were imposed by the flight conditions. Figure 1 shows a schematic drawing of the levitation equipment built for this purpose using a 15 kHz induction furnace. It consists of a quartz tube with the inner diameter 46 mm, the wall thickness 2.5 mm and the height 400 mm. A copper tube with five turns (Ø=6 mm) functioned as the induction coil.

The lower section of the furnace housed a graphite crucible and a water-cooled copper mould. The quartz tube was sealed at the top and the sample was inserted from the bottom with the help of a pneumatic device. The water-cooled copper mould was soldered to the bottom section. A stomatite cylinder was used as heat and electric insulator and was inserted between the crucible and the mould. A graphite table was placed in the crucible just above the outlet. The table supported the melt in the center of the induction-field where the lifting force was at its minimum.
The wall thickness of the crucible was critical. Thick walls reduce the levitation force and thin walls lift the sample out of the induction field. The thickness in the present work was about 3 mm, which was found optimal in this application. The position of the table was also crucial. It was imperative that it should be placed exactly where the induction field balanced the gravity field. This, in turn, was influenced by the mass and the alloy composition. The latter, was due to change of the electrical resistance of the sample and the related effect on the eddy currents.

3.1 EXPERIMENTAL PROCEDURE

The candidate alloys, Al, Al-4%Ti and Al-10%Fe were cast into a water cooled copper mould with the diameter 18 mm and the height 20 mm. They were subsequently machined to a height of 15 mm and washed with acetone.

Clean specimens were placed on the graphite table inside the crucible. The reaction chamber was then closed, evacuated and refilled with hydrogen to a predetermined pressure. The pressure of hydrogen was varied between 0.5 to 5 atm. With this technique, different quantities of hydrogen could be dissolved within the sample. Once the sample had melted the process was continued for further six minutes before the furnace was switched off. The melt was ejected through the channel under the table and via the outlet hole into the copper mould beneath the crucible. To enhance the formation of smaller pores, the ambient pressure during quenching, was increased to 6 atm by addition of argon. The melt temperature was measured by a pyrometer and was about 1000°C for all the runs. The total solidification time in the mould was between 5-7 seconds dependent on the alloys. After casting the samples were stored in liquid nitrogen except during machining to proper dimensions. The structure of the pores formed in this work are discussed in reference 1.
4. THE RAPID HEATING FURNACES

The power package in the material science module was built of 28 silver-zinc cells of 5 Ah capacity which gave a nominal voltage 36 V at a current load of 11 amp. This allowed about 400 W capacity for each furnace during the heating sequence. For the heating elements under the existing conditions, a novel solution was resorted to. A filament was extracted from a halogen projector lamp, Philips 7787, 36 V, 400 W. This element had the appropriate dimension and the power capacity to meet the required heating rate. To prevent rapid vaporization and prolong the life of the filament, argon or helium atmosphere was employed. The applied voltage was also restricted to 30 volts. The life time of the filaments was now well above the duration of the experiment. The current through the filament was about 10 amperes at 30 volts giving a power output of about 300 W. To prevent short circuiting of the filament by the melted sample a thin boron nitride cap was inserted between the sample and filament. Boron nitride is an electrical insulator with good thermal properties. The samples should be melted within 15 seconds. Equation 1 depicts the appropriate mass that could be melted within the limited time and power for pure aluminium;

\[ m \left( C_p^S \Delta T^S + C_p^L \Delta T^L + L_m \Delta t \right) = P \cdot t \]  

where:
- \( m \) mass of the sample (gram)
- \( \Delta T^S \) change of temperature in the solid phase, 640 (°C)
- \( \Delta T^L \) melt over heat, 50 (°C)
- \( C_p^S, C_p^L \) the specific heat of solid and liquid aluminium, 0.215 and 0.26 (cal/g/K)
- \( L_m \) heat of fusion of aluminium 95 (cal/g)
- \( \Delta t \) total heating and melting time, 15 sec
- \( P \) power delivered to the sample, 240 (W)

\( m = 3-4 \) grams, volume = 2.5-3 cm
The shape and dimension of the samples were based on the design of the filament and allowed mass as calculated above. Figure 2 shows the furnace assembly consisting of the filament, the boron nitride cap and the sample. The furnace and sample were assembled by attaching the sample directly to the mounting plate by a screw, figure 3. The boron nitride cap was then placed in the cavity of the sample and the heating filament was subsequently lowered into the cap. Each furnace had a height of 50 mm and diameter of 63 mm. The temperature was monitored by chromel-alumel thermocouple inserted into the sample through a drilled hole, figures 2, 4. Three of these furnaces were incorporated in a cannister shown in the figure 4. System pressure was monitored by an IC pressure transducer mounted on a PC-board at the bottom of the cannister. Four cannister were incorporated in the module for the eventual flight.

4.1 ACTIVATION OF THE FURNACES

Acceleration during the flight was monitored by accelerometers (G-sensors). When entering into the low g level part of the flight, the G-sensors started the control electronics for the furnaces in the cannisters. When the first sample had reached a predetermined temperature, the power was switched off after a programmed delay (3-6 seconds) and the next furnace was then switched on. This procedure was repeated for all the furnaces. Depending on the gas and pressure used in the cannister it took 20-40 seconds for the samples to solidify.

4.2 EQUIPMENT FOR VIDEO OBSERVATION

The experiments were repeated on board a Lockheed aircraft with similar equipment. The processes were monitored by a motor driven camera. Illumination of the samples was provided by six incandescent lamps (24v, 10W). The melting,

...
expansion and solidification of the samples were photographed at a rate of three frames per second. The equipment is shown in figure 5. Totally nine flights were performed and 27 samples were processed. The results of this investigation are presented in reference 2.

5. ACKNOWLEDGEMENT

We would like to thank Prof. Hasse Fredriksson for his valuable advises in developing the equipments. This project was financed by the Swedish Board for Space Activities.

6. REFERENCES

Figure 1. Schematic drawing of the high pressure casting equipment.
Figure 2. Schematic drawing of the sample, cap and filament.

Figure 3. Rapid heating furnace assembly.
Figure 4. Complete assembly of furnaces and electronics.

Figure 5. Cannister with remelting equipments and camera unit used in the aircraft experiments.
PAPER IV

H. Shahani, H. Fredriksson
On the mechanism of precipitation of pores in melts

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ON THE MECHANISM OF PRECIPITATION OF PORES IN MELTS

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1. ABSTRACT

Precipitation of rounded pores in aluminium, Al-4%Ti and Al-10%Fe has been studied. Samples were equilibrated with hydrogen at 1000°C and subsequently quenched at an ambient pressure of 6 atm. During quenching, due to increasing hydrogen pressure in the melt, pores were formed. A model for nucleation and growth of these pores in pure metals has been presented. In accordance to this model, existence of foreign particles in the melt is necessary for pore formation and pore size increases with the initial hydrogen content. The measured size of the pores in pure aluminium are in a good agreement with computed values.
2. INTRODUCTION

Pores are usually formed in cast metals during cooling and solidification processes. In general, the various types of pores can be related to the gas content of the melt prior to casting and they can be classified into three groups:

A) Rounded Pores;
When the gas content of a melt is greater than its gas solubility these pores may precipitate in the melt. They are mostly spherical and due to the buoyancy forces, usually located in the upper section of castings.

B) Elongated Pores;
When the initial gas content is below the gas solubility of the melt, at the ambient pressure and solidification temperature, this type of pores nucleate at the solidification front and grow in an eutectic-like reaction (1-4).

C) Shrinkage Pores;
They form in parts of the melt that solidify last and are often termed as shrinkage pores. They are formed due to the pressure drop caused by the solidification shrinkage and their shape is influenced by the dendrite structure (4-7).

In the present investigation, formation of rounded pores has been studied. Aluminium alloys were equilibrated at 1000 °C with hydrogen at various pressures. After equilibration, the specimens were quenched at an ambient pressure of 6 atm. This treatment enhances formation of smaller pores (8-16). These pores were metallographically examined and in the case of pure aluminium, theoretically analysed.

In a follow up investigation (17), samples produced by the above method were remelted at the reduced ambient pressures and reduced gravity. This treatment enabled the pores to expand and resulted in a metallic foam. Reduced gravity was achieved by either using a sounding rocket or an
aircraft flying in a parabolic trajectory.

3. EXPERIMENTAL WORK

Samples of pure Al, Al-4\%Ti and Al-10\%Fe, weighing about 12 grams each, were electromagnetically levitated at 1000 °C for about 6 minutes in a hydrogen atmosphere. The levitation equipment is shown in figure 1 and is described in detail in references (17,18). The investigation was carried under hydrogen pressures of 0.5, 1, 3 and 5 atm. At the termination of each run, the furnace was switched off and the sample was quenched in a water-cooled copper mould located beneath the crucible. The mould diameter and height were 18 and 20 mm respectively. During the quenching step, the ambient pressure in the reaction chamber was increased to 6 atm by applying argon. Cooling rate of the melts during quenching was about 50-70 °K/sec.

4. EXPERIMENTAL RESULTS

The density of the samples was measured by immersing them in the water. The total volume of the pores, \( V_p \), was then computed by equation 1:

\[
\%V_p = (1 - \frac{\rho}{\rho_0}) \times 100 \quad (1)
\]

where \( \rho_0 \) and \( \rho \) are densities of the sample in the pore-free state and the treated state respectively. Samples were subsequently sectioned into two halves along the vertical axis and prepared for metallographic investigations. The area fraction of porosity, the average and also the largest size of the pores for each case were measured using a False Color TV Analyser. The average number of the pores was calculated from the measured pore size and total volume of porosity. Examination of the samples indicated that pore size distribution in the castings were not uniform. Small pores (20-50um) tended to concentrate at the periphery, while larger pores tended to accumulate along the center.
Figures 2a-c, show micro-graphs taken from the central area of samples treated at 5 atm hydrogen. In the case of pure aluminium pores were mostly spherical while in Al-4%Ti and Al-10%Fe alloys they were irregular and influenced in shape by primary Ti(β) and Fe(θ), figures 3a-c. A trace of aluminium oxide could be detected at the periphery of the pores, figure 3a.

Hydrogen content of the samples was between 1 to 4 ppm. The measurements, as presented in table I, indicate that the hydrogen content, as well as porosity and size of the pores increased with the pressure of hydrogen during gas treatment. These values were higher for the investigated alloys than the respective ones in pure aluminium.

5. THEORETICAL ANALYSIS

Hydrogen dissolves in melts as atoms (19);

\[
H_2(g) = \text{solid} \quad \text{(2)}
\]

Chemical potential of hydrogen in the gas phase and in the melt at the equilibrium must be equal. The effect of external pressure on the system (20) can be considered as:

\[
2(\mu_{H_2}^0 + RT \ln X_H - \sqrt{V_H (P_t - P_o)}) = \mu_{H_2}^0 + RT \ln (P_{H_2}^t / P_0) \quad \text{(3)}
\]

where:

\( \mu_{H_2}^0 \) = standard chemical potential of hydrogen in the gas phase (J/mole)

\( \mu_H^0 \) = standard chemical potential of hydrogen in the melt (J/mole)

\( X_H \) = hydrogen concentration in the melt (mole fraction)

\( P_o \) = standard pressure of hydrogen (1E5 N/m²=1 atm)

\( P_{H_2}^t \) = equilibrium pressure of hydrogen during gas treatment (N/m²)

\( P_t \) = total pressure in the system, equal to \( P_{H_2}^t \) during gas treatment at 1000 C (N/m²)
\( V_H \) = partial molar volume of hydrogen in the melt 
\( (m^3/mole) \)

\( T = \) melt temperature \((K)\)

\( R = \) gas constant, 8.314 \((J/mole/K)\)

This gives:

\[ X_H = \left( \frac{P_H}{P_O} \right)^{\frac{1}{2}} \exp\left( \left( \frac{\Delta H^0}{2} \right) / RT \right) \exp\left( \frac{V_H}{P_t - P_O} \right) \]  (4)

Equation 4 can be rewritten as:

\[ X_H = \left( \frac{P_H}{P_O} \right)^{\frac{1}{2}} A \exp\left( \frac{-B}{T} \right) \exp\left( \frac{V_H}{P_t - P_O} \right) \]  (5)

Equation 5, reflects the solubility of hydrogen in the melt as a function of pressure and temperature. The partial molar volume of hydrogen in aluminium, \( V_H \), is not determined. In the present analysis, it is assumed that \( V_H \) and its variation with the temperature is the same as the molar volume of aluminium, \( V_m^{Al} \). This is because the solubility of hydrogen in the aluminium melt, max. 2x10^{-4} mole fraction is very small. Equation 5 then becomes:

\[ X_H = \left( \frac{P_H}{P_O} \right)^{\frac{1}{2}} A \exp\left( \frac{-B}{T} \right) \exp\left( \frac{V_m^{Al}}{P_t - P_O} \right) \]  (6)

The molar volume of aluminium, used in equation 6, as a function of temperature \((21)\) is calculated by:

\[ \rho_{Al} = 2646.2 - 0.28T \]  (kg/m^3)  

\[ V_m^{Al} = 27 \times 10^{-3} \rho_{Al} \]  (m^3/mole)  (8)

The constants \( A \) and \( B \) in equation 6, can be determined experimentally. Their values, for the case of hydrogen solubility in pure liquid aluminium \((22,23)\) are equal to 1.42x10^{-2} (mole fraction) and 6178 \((K)\) respectively. For \( Al-4\%Ti \) and \( Al-10\%Fe \), \( A \) and \( B \) have also been determined \((23)\). The dissolved hydrogen content in pure aluminium, table I, were 1.5 to 3 times less compared with the calculated values.
Hydrogen equilibrium pressure in the melt, \( P_{H_2} \), during quenching as a function of melt temperature can be calculated with equation 6. The total pressure in the system \( P_t \), is equal to the pressure of argon during quenching. Equation 6 may be rewritten as:

\[
P_{H_2} = \frac{P \chi H^2 \exp\left(\frac{2B}{T}\right)}{A \exp\left(\frac{2V_m}{RT}(P_t - P_0)\right)}
\]  

Equilibrium pressure of hydrogen in the pure aluminium melt, as a function of temperature is plotted in Fig.4. This pressure, at its solidification temperature, varies between 10 to 25 atm, depending on the initial gas content.

The pressure balance for a bubble in mechanical equilibrium with a liquid phase gives the required pressure of hydrogen in the melt for homogeneous nucleation;

\[
r_b = \frac{2Y}{P_b - P_a}
\]

where:

- \( r \) = radius of the bubble (m)
- \( Y \) = surface tension between liquid and gas (N/m)
- \( P_b \) = pressure inside the bubble (N/m²)
- \( P_a \) = ambient pressure (N/m²)

The work expended for the formation of a bubble of size \( r_b \), (24) is described by:

\[
W = 4\pi r_b^2 Y - 4\pi r_b^3 (P_b - P_a)/3
\]

Substituting equation 10 into equation 11 gives:

\[
W = 16\pi Y^2/3/(P_b - P_a)^2
\]

Mechanical and chemical equilibrium co-exist at the nucleation of a bubble. Accordingly \( P_b \) becomes equal to \( P_{H_2} \). Equation 12 can be thus rewritten as:
Where $W^*$ is the activation energy for nucleation (24) equal to $60kT$; $k$, is the Boltzmann's constant. $T_H^*$ as a function of melt temperature for different values of surface tension is calculated then, figure 5. For aluminium with surface tension (25) of 0.914(N/m), homogeneous nucleation occurs at hydrogen pressures of about 40000 atm, see Fig. 5. For pore nucleation to take place at hydrogen pressures of 10 to 25 atm, the surface tension must be below 0.01 (N/m). It is therefore concluded that all the "rounded pores", observed in the present investigation must have been formed by heterogeneous nucleation.

In a melt, there usually are particles; such as oxides, which can cause heterogeneous nucleation of the pores. The mechanism of this nucleation is normally treated by considering the gap formed on a flat substrate, which is shown in figure 6. In a spherical substrate, the size of particles as well as the difference in surface tensions influence the spread of the gas around the particle. In order to simplify the problem, we have assumed that $Y_{L/P}Y_{L/G} = n$, where $Y_{L/P}$ and $Y_{L/G}$ are surface tension of liquid-particle and liquid-gas, respectively. If $n$ is greater than 1, (26) the bubble will spread around the particle and the condition described by figure 7 will be obtained. Activation energy for the pore nucleation can now be written as:

$$W^* = 4\pi(r_b^2nr_p^2)Y_{L/G} - \frac{4}{3}\pi(r_b^3-n^3p)(P_{H_2}-P_a)$$

where:

$r_b^*$ = critical bubble radius (m)
$r_p$ = particle radius (m)
$n = \frac{Y_{L/P}}{Y_{L/G}}$

Substituting $r_b^*$ and $W^* = 60kT$ into equation 14 yields

$$W^* = \frac{16\pi(Y_{L/G})^3}{3(P_{H_2}-P_a)^2} - \frac{4\pi n r_p^2 Y_{L/G}}{3} \frac{4r_p^3}{3} (P_{H_2}-P_a)$$
From this the pressure of hydrogen, $P_{H_2}$, required for heterogeneous nucleation as function of the particle size, $r_p$, can be calculated at $P_a = 6$ atm, figure 8. With the presence of the particle sizes larger than $2 \mu m$ in the melt, the required hydrogen pressure for the nucleation reduces to about 10 atm. With this pressure the critical melt temperature for nucleation, $T^*$, is determined depending on the initial hydrogen content, its values ranging between 680-750 $^\circ$C. The critical size of the pores is then evaluated to 12 $\mu m$ at $P_{H_2} = 10$ atm.

With progressive cooling, the nucleated bubble grows by diffusion of hydrogen from the surrounding supersaturated liquid. The growth process, using Fick's first law, is described by;

$$\frac{dn_i}{dt} = \frac{8\pi}{3RT}(3P - 4Yb) \frac{dr}{dt} = \frac{4\pi r^2 b H}{v m} \frac{X^o_i - X^p}{r_b} \quad (16)$$

where $X^o_i$ and $X^p_i$ are concentrations of hydrogen in bulk liquid and at the liquid-bubble interface, respectively. The former, $X^o_i$, is the measured hydrogen content, and the latter $X^p_i$ obtained from equation 6. When $r > 1$ $\mu m$, $P_b \approx P_a$, and equation 6 becomes;

$$X^p_i = \left(\frac{P}{P_0}\right)^{1/2} A \exp(\frac{-B}{T}) \exp(\frac{V^m}{RT} (P_a - P)) \quad (17)$$

Inserting the hydrogen diffusivity (27), $D_H = 3.8 \times 10^{-6} (m/sec)$, and the change of variable; $dr/dt = dr/dT$, $dT/dt = -50$, $dr/dT$, equation (17) is then integrated to;

$$r_f \int_{r_b}^{r_f} \frac{-100(3P + 4Y)}{3R} dr = \int_{T^*}^T \frac{D_H (X^o_i - X^p_i)}{V^m} TdT \quad (18)$$

From equation 18, the pore size, $r_f$, as a function of critical temperature and initial hydrogen content can be determined, Fig. 9.
Area percent and total volume of porosity for the other investigated alloys also increased with the hydrogen content and were greater than in the pure aluminium cases. This can be related to the dendritic solidification, existance of primary phases in the melt during pore nucleation, and also greater hydrogen solubility in these melts. However, due to the change in the melt composition during solidification, the pressure of hydrogen can not be evaluated.

6. CONCLUDING REMARKS

In this paper, we have presented a model for formation and growth of the pores in the melt. This model indicates that the presence of particles in the melt, for formation of pores is necessary. These particles are mostly aluminium oxide. Moreover, the size of the pore increases with the higher hydrogen content. The computed size of the pores are in a good agreement with the experimental results. The hydrogen content of the samples was about one to five times less than those calculated during hydrogen treatment. This has been ascribed to insufficient quenching and the high diffusivity of hydrogen during handling and preparation for gas analysis treatments. Pore size is inversely proportional to the cooling rate and it reduces with higher cooling rate.

7. ACKNOWLEDGEMENT

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<table>
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<th>Pressure of hydrogen during gas treatment (atm.)</th>
<th>Hydrogen content (ppm)</th>
<th>Measured density (g/cm³)</th>
<th>Total volume of porosity (%)</th>
<th>Average area fraction of porosity (%)</th>
<th>Measured pore diameter (μm)</th>
<th>Number of pores per mm of the sample</th>
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Figure 1. Schematic drawing of the high pressure casting equipment.
Figure 2a. Pure Al treated at 5 atm hydrogen.

Figure 2b. Al-4 Ti treated at 5 atm hydrogen.

Figure 2c. Al-10 Fe treated at 5 atm hydrogen.
Figure 3a. Pure Al.

Figure 3b. Al-4Ti.

Figure 3c. Al-10Fe.
Figure 4. Pressure of hydrogen in the melt during cooling.

Figure 5. Required pressure of hydrogen for nucleation with varying surface tensions.
Figure 6. Heterogeneous nucleation on a flat substrate

Figure 7. Heterogeneous nucleation on a spherical particle
Figure 1. Required pressure of hydrogen for nucleation of pores with particles.

Figure 2. Calculated size of the pores as a function of critical temperature of the melt.
PAPER V

H. Shahani, H. Fredriksson

Precipitation of gas pores in metallic melts during cooling under microgravity

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 Precipitation of Gas Pores in Metallic Melts During Cooling Under Microgravity

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Abstract

In the Swedish rocket program for Material Science research a series of experiments in pore formation in Al-base alloys have been performed. The alloys were melted under high pressure H2-atmosphere on earth and remelted at low pressure in space. Due to the pressure difference pores were formed. The nucleation and growth of the pores were analysed as a function of the pressure difference and also as a function of the alloy composition. The results of the experiment will be discussed in the paper. The growth of pores will be theoretically discussed.

Keywords: Metallic Foam, Hydrogen, Microgravity

1. Introduction

Particle composites are difficult to produce from the melt. The particles often have another density than the liquid. Due to this they will floatate or sediminate during the production process. One thus gets an uneven distribution of the particles in the matrix. In order to avoid movement of the particles it has been proposed to use a microgravity environment.

One of the most difficult composites to produce from a melt is metal foams, metals containing a lot of small gas pores. In order to investigate the possibility to produce metal foams directly from the melt a series of experiments with aluminium alloys supersaturated with hydrogen were performed in space. The alloys were produced on earth at a high pressure of hydrogen and after that remelted at a reduced helium pressure in a microgravity environment. The experiments were performed in a rocket campaign and in an aircraft with a parabolic path.

2. Experimental Work

Three different alloys were investigated, namely pure Al, Al with 4% Ti and Al with 10% Fe. The addition of Ti and Fe was made in order to investigate the effect of a second phase in the liquid on the pore growth. The solubility of hydrogen (ref. 1, 2) in the three alloys is presented in Fig. 1 at a hydrogen pressure of one atmosphere. The figure shows that the solubility is about 10 times higher in the liquid than in the solid at the melting point. Siever's law tells us that the solubility increases with the square root of pressure. It will thus be possible to get a high hydrogen content in an alloy by melting it at a high hydrogen pressure and at a high temperature. It will be possible to store hydrogen in the alloy by rapid quenching of a melt treated under those conditions.

In produce the samples an equipment, schematically shown in Fig. 2, was constructed.

The sample, which was cast in a copper mould (dimensions diameter 18 mm and height 20 mm), was placed on the graphite table in the crucible. The crucible was mounted on a water cooled copper mould by a cylindrical insulator.

(a) At the beginning all the valves shown in Fig. 2 were closed. The valve (1) was opened and argon with 6 atm pressure closed the quartz tube with a pneumatic device.

(b) Valve (3) was opened and the chamber was evacu-
Figure 2. Equipment for producing hydrogen supersaturated samples

(a) Valve (4) was opened for 3-4 minutes. The valve (3) was closed again.

(c) Valve (4) was opened to let the hydrogen fill the chamber to the desired pressure. After adjusting the pressure this valve was closed again.

(d) The induction furnace was switched on and the melting process started after 3-4 minutes. The sample was heated to ca 1000°C and kept at this temperature for 6 minutes. This was enough for the hydrogen to react with the melt, since the sample was partly levitated, fig. 3, and that the melt was heavily stirred and kept at a high temperature. During this process the pressure usually increased slightly in the chamber. By controlling the valve (3), the pressure could be adjusted.

(e) After the dissolving reaction had taken place, valve (5) was opened and argon at 6 atm pressure was applied to the melt in order to prevent hydrogen from leaving the sample. The furnace was switched off and the levitated melt was dropped through the hole in the bottom of the graphite crucible into the copper mould. A measurement showed that it took 5-7 seconds for the sample to solidify.

For the remelting of the sample in space an equipment, shown in fig. 4, was constructed. The sample size and form are shown in the figure. The sample was placed on a lampfilament. The filament was extracted from a 400 watt halogen lamp. The sample and the filament were electrically isolated from each other by a boron nitride cap. This type of furnace was developed in order to have a solid skin around the sample as long as possible to prevent a loss of hydrogen during the remelting process.

Figure 3. Levitation melting in the equipment shown in fig. 2

Figure 4. Drawing of sample and space melting equipment

Three melting equipments of the type shown in fig. 4 were placed in a canister, fig. 5. Two different types of canisters were built. One for the aircraft experiment and one for the rocket experiment, fig. 6. The chamber was evacuated and filled with Ar or He to a predetermined pressure before the experiments. A pressure transducer measured the pressure inside the canister. In the aircraft experiment a motor driven camera was added. The process was photographed each 0.3 seconds.

The temperature of each sample was measured by a Chromel-Alumel thermocouple, which would send the signals to the unit control of the same furnace. The furnace switched off after a predetermined delay and the next furnace switched on automatically.

3. RESULTS

3.1 Original samples
The alloys were melted under a pressure of 0.5, 1.0, 3.0 and 5.0 atm hydrogen. The pressure was increased with Ar to 6 atm just before quenching. The samples were machined to the proper dimensions. The side of each sample was metallographically prepared and analysed. Fig. 7, 8 and 9 show the microstructure in each alloy. All the figures are taken from samples produced under a hydrogen pressure of 5 atm. Fig. 7 shows that the sample of pure aluminium contains a lot of small rounded pores. Fig. 8 shows that the alloy with 4% Ti also contains rounded pores. The figure also shows that the structure contains crystals of Al₃Ti.

Many of these crystals have contacts with very small pores. This structure might have been formed in the following way. During the quenching gas pores have started to grow in the liquid. After this a precipitation of Al₃Ti has started. New pores have then been formed in contact with the Al₃Ti crystals. Fig. 7 shows the structure in the alloy with 10% Fe. The structure consists of Al₃Fe crystals with a plate-like morphology. Gas pores are
situated between the plates. This structure has probably been formed by a precipitation of AlFe-
crystals followed by a gas pore precipitation.

For each alloy and for each hydrogen pressure a series of samples were produced, in one sample
from each series the pore size and number were evaluated. The density of the sample as well as
the hydrogen content were also evaluated. All those data will be presented together with the
flight data.

3.2 Aircraft samples

Twentyseven experiments were performed. The samples were processed during the parabolic flight ac-
cording to the time-temperature curve shown in fig. 10. The samples were melted under different
He pressures (0.1, 0.4 and 1.0).

![Figure 10. The temperature-time curve for sample](image)

The camera started to take pictures after nine
seconds. Fig. 11 gives an example of the melting
and expansion process of one sample. After the
flight all the samples were photographed from six
different directions, and fig. 12 and 13 show one
sample before and after the flight process.

All the samples were then cut and metallograph-
ically prepared. Fig. 14, 15 and 16 show a cross
section of three different samples, one from each
alloy.

The area fraction of pores was measured, the
number and the size were evaluated. The density of
each sample was also determined. All the evaluated
data is presented in table 1.

3.3 Rocket flight

Nine successful experiments were performed. All
the samples were treated and evaluated in the same
way as in the aircraft experiments. Table 1 shows
the results (they are marked with A).

One of the samples (number 8) was only partly re-
 melted in space. Fig. 17 shows a cross section of
this sample. The melting border is shown in the
upper part of the figure. The figure shows that
the small pores are expanding at the melting of
the alloy.

![Figure 11. Melting and expansion of the sample](image)

![Figure 12. Top and side view of sample 85 before](image)

4. DISCUSSION

The alloys were melted under a high hydrogen pres-
 sure on earth and after that rapidly solidified in
a copper mould. When the melt was quenched in the
copper mould a solid skin formed immediately. Dur-
ing the solidification process solubility of hydro-
gen decreases sharply, as can be seen from Fig. 1.
Due to this pores are formed. However, the solid
skin and the rapid cooling lead to entrappment of
pores and the samples are supersaturated with
hydrogen.

A comparison of the solubility of hydrogen at high

pressure and high temperature, fig. 1 and the
amount of hydrogen kept in the samples, table 1,
shows that some hydrogen must have left the samples
during the quenching process. However, the amount
of hydrogen kept in the samples is higher than the
equilibrium value of the remelting pressure.

The samples are thus supersaturated with hydrogen,
when remelting in space. The samples contain a lot
of small pores. Those pores will grow and the
sample will expand during the remelting process un-
til equilibrium is reached.

The number of pores as a function of pore size and
Figure 13. Top and side view of sample EES after remelting \( P_{H_2} = 1 \text{ atm}, \text{Al} + \text{Ti}, \) \( P_{H_4} = 0.1 \) atm. \( P_{H_2} = 0.1 \) atm, \( \text{Al} + \text{Ti}, \) \( P_{H_4} = 0.1 \) atm.

Figure 14. Metal foam of pure Al-Ti-N. Remelting pressure 0.2 atm. Super saturation pressure 0.2 atm. R.R.D. = 1.0. Pores are spherical.

Figure 15. Metal foam of Al-Ti-N. Remelting pressure 0.2 atm. Super saturation pressure 0.2 atm. R.R.D. = 1.0. Pores are spherical.

Hydrogen content and remelting pressure can be calculated by the following equation:

\[ \frac{R_{eq}}{V_0} = \frac{(P_a + R - \sigma)}{R} = \sqrt{\frac{a}{R}} \]

where

- \( P_a \) = equilibrium pressure (1 atm)
- \( V_0 \) = amount of hydrogen stored in the super saturated sample given by table 1 (cc H2/gram)
- \( T_0 \) = equilibrium temperature (273 K)
- \( P_0 \) = remelting pressure (0.1 - 0.4 - 1 atm)
- \( \sigma \) = surface tension 0.914 N/m
- \( R \) = radius of the pores (cm)
- \( \delta_a \) = solubility of hydrogen at the remelting temperature given by fig. 1
- \( T_a \) = solidification temperature (933 K)
- \( N \) = number of pores per gram

Figure 16. Metal foil of Al 10% Fe (E). Remelting pressure 0.2 atm. Super saturation pressure 1 atm. R.R.D. = 24. Pores are affected by second phase.

Figure 18 and 19 show the number of pores per gram as a function of the radius of pores with \( P_a \) equal to 0.1 and 1 atm., with hydrogen content varying from 1.0 to 340.100 gr. The data presented in table 1 is also given in the figures.

Equation 1 can also be used to calculate the density of the sample, as a function of \( P_a \) and \( V_0 \). The calculated density is changed to Relative Reduction of Density (R.R.D.) and given in figures 20-22 for three different values of \( P_a \) (0.1-0.4-1 atm).

The figures show that the density will decrease with decreasing remelting pressure \( (P_a) \), decreasing radius and increasing solved hydrogen.

The figures can be used to compare the experimentally measured density with the theoretically measured. A comparison shows that the theoretical R.R.D. is higher than the experimental one. The comparison also shows that one has come closest to the theoretical density in the sample containing small and large amounts of pores such as the samples alloyed with titanium. The reason for this might be as follows:

Both in the aircraft and in the rocket some gravity is left during the experiments. In the aircraft the
The expansion process was studied using the following models:

- **Figure 15:** The expansion process during pouring of the sample.
- **Figure 16:** The number of pores per grain as a function of time and temperature.
- **Figure 17:** The relationship between the number of pores and the grain size.
- **Figure 18:** The relationship between the radius of pores and the number of pores.

The expansion process was found to be influenced by the following factors:

- **Grain size:** Smaller grains tend to have more pores due to the increased surface area.
- **Temperature:** Higher temperatures lead to a decrease in the number of pores.
- **Porosity:** The porosity of the sample affects the expansion process, with higher porosity leading to more expansion.

The results of the experiments showed that the expansion process is a complex interplay of factors, and further studies are needed to fully understand the mechanisms involved.
Figure 21. Variation of Relative Reduction of Density as a function of pore radius at $P_a=0.4$ atm and $v_o=1.5-3.5$ ppm

Figure 22. Variation of Relative Reduction of Density as a function of pore radius at $P_a=1$ atm and $v_o=2-3.5$ ppm

Table 1. Properties of Gas in Metallic Melts

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Table 3. Properties of Gas in Metallic Melts

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the gravity vector is not constant and this will decrease the possibility for the pores to leave the sample.

5. CONCLUDING REMARKS

It has been shown that it will be possible to produce metal foams in space. Due to the low solubility of hydrogen in Al the density was in this case only reduced by a factor of two. This can be overcome by using metals with a higher solubility of gases.

6. ACKNOWLEDGEMENT

Grants were given by the Swedish delegation of space research. The furnaces were constructed by the Swedish Space corporation. We are grateful to Rolf Jonsson and Sven Malin for their help with the experiments. We are also grateful to D.F.R.F., NASA for the possibility of performing the aircraft experiments.

7. REFERENCES


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PAPER VI

H. Shahani

Effect of hydrogen on the shrinkage porosity of aluminium-copper and aluminium silicon alloys

January 1984
EFFECT OF HYDROGEN ON THE SHRINKAGE POROSITY OF ALUMINIUM COPPER AND ALUMINIUM SILICON ALLOYS

Hamid Shahani

Dept. of Casting of Metals
The Royal Institute of Technology
S-100 44 Stockholm
Sweden

January 1984

1. ABSTRACT

The effect of hydrogen content on shrinkage porosity of Al-Cu and Al-Si alloys was studied. A model for formation of shrinkage porosity is presented. Experiment and theory show that the amount of shrinkage porosity in castings is dependent on the gas content, pressure drop due to shrinkage and amount of foreign particles in the melt. Modifiers facilitate formation of these types of pores.
2. INTRODUCTION

Existence of porosity in metals, in general, reduces the mechanical properties of the products (1-2). It has been shown earlier that initial gas content of the melt (3-4), mode of solidification (5) and shrinkage caused by solidification (6-9) are among the parameters which may influence the porosity. Due to good mechanical and machining properties, aluminium-copper and aluminium-silicon alloys are widely used in industry. Hydrogen is the only soluble gas in aluminium alloys (10) and thus is the leading contributor to porosity in these alloys. In nearly all cases, the source of the hydrogen is some form of water. Water sources in foundaries are numerous but the main ones are moisture in the air, combustion products in gas burner furnaces during melting, and holding and moisture absorbed on the surfaces of charge components. Water, in contact with aluminium melt, dissociates to hydrogen and oxygen according to the following reaction:

\[ 2 \text{Al} + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6 \text{H} \]  

(1)

Hydrogen dissolves in the melt as atoms and oxygen remains as dross. The reaction rate increases rapidly with temperature and is even more rapid when Mg is present (10). Hydrogen solubility in the melts decreases with lowering temperature and falls sharply from 0.7 ppm to 20 times less during solidification (11). When hydrogen content in the melt exceeds the solubility limit, with the presence of proper nucleants (12), pores form and grow. Pores can either form prior or during the solidification. The former are spherical and relatively large. The latter are small and irregular in shape and are known as shrinkage porosity (13). Their formation is influenced by the hydrogen enrichment and shrinkage pressure in the interdendritic area (14).

The present work was aimed at studying the effect of hydrogen on the shrinkage porosities in pure aluminium, Al-4.5%Cu and Al-2%, 4%, 7% Si. Hydrogen content of the melts,
were varied by injecting argon saturated water and purging with argon. In the case of Al-4.5%Cu samples, AlLiH powder and hydrogen gas were also applied.

Alloying elements, temperature and modifiers influence melt properties such as surface tension, viscosity (29-31) and the solidification mechanisms. In aluminium alloys, silicon decreases the surface tension of pure aluminium from 0.9 (N/m) to 0.8 (N/m), while Cu has no influence (30,32,33). Modifiers such as sodium also decrease the surface tension (30). Increasing temperature reduces both the surface tension and viscosity of the alloys.

The effect of modifiers Na and Sr (15-28) on the porosity of Al-Si alloys was studied. They were added to the melt after gas treatment and prior to casting. In the case of Al-4.5%Cu, effect of aluminium oxide powder on pore nucleation was studied.

3. EXPERIMENTAL PROCEDURE

Materials investigated in the present study were:

1- Pure aluminium (99.8%)
2- Al-2%Si
3- Al-4%Si
4- Al-7%Si,0.3%Mg
5- Al-4.5%Cu

Al-7%Si,0.3%Mg, SIS4244, was supplied by Ardal og Sundal Verk a.s Norway. Alloys of 2%, 4% Si were made by adding pure aluminium (99.8%) to alloy SIS4244. Al-4.5%Cu was made by adding electrolytic copper to pure Al. Alloys were melted in a graphite crucible at temperatures about 100 C above their respective liquidus temperatures. Hydrogen content of the melts was varied by the equipment shown in figure 1, as follows:

1- Injecting water saturated argon at different time
intervals, with 22 mm Hg partial pressure of water in the gas mixture.

2- Purging the melt with argon.

3- Injecting directly hydrogen and AlLiH4, for Al-4.5%Cu (AlLiH decomposes easily and generates hydrogen)

Hydrogen flame was formed around the lance after 10 minutes injecting watersaturated argon. It indicated that melt was saturated with hydrogen. In the case of Al-Si alloys, 250 ppm Sr and 100 ppm Na were also added to the melt after gas treatment and prior to casting. For Al-4.5%Cu, 0.5 wt.pct aluminium oxide powder was sprayed into the melt after 20 minutes of gas treatment with water saturated argon. Table 1 summarizes the treatments performed on the samples. Treated melts were cast in a mould as shown in figure 2. The top and bottom sections of the mould as well as the chill were made of cast iron. The side walls and the raiser were of asbestos.

4. EXPERIMENTAL RESULTS

The hydrogen analysis of the samples is presented in Table 1 and indicates that:

Hydrogen content of the samples Z1 to Z3 (Al-4.5% Cu), treated with argon, AlLiH and hydrogen was unaffected and remained at 0.18 ppm. Hydrogen content increased for the samples Z4-Z8 treated with the argon saturated water.

These results can be explained by the dissolving mechanism of hydrogen in melts. Hydrogen dissolves in the melts as atoms (\(\text{H}_2\)). The dissociation rate of the molecular hydrogen to atomic at the treatment temperature (750°C) is extremely low (35). Thus, change of hydrogen content was not achieved and it behaved as an inert gas, argon. In the other hand, the standard free energy change for reaction 1 is very high (\(\Delta G^\circ\)) and the values for the activity quotient \(a_{\text{H}_2} a_{\text{H}_2O}\) is so high that for practical purposes it implies the complete conversion to hydrogen for all traces of water vapour contacting the metal. The resulting atomic hydrogen is readily soluble in the melt.
up to its solubility.

In order to study the effect of extra solid particles on the poreformation, Al₂O₃ powder was added to sample Z8. The hydrogen content, compared to the similar gas treated sample Z7, reduced from 0.43 ppm to 0.35 ppm. Variation of hydrogen content in Al-4.5%Cu samples as a function of reaction time is presented in figure 3.

Variation of hydrogen content in aluminium and Al-Si alloys are presented in figures 4-7. Hydrogen content in these samples also increased with the reaction time. In order to study the effect of modifiers, 250 ppm Sr or 100 ppm Na were added at the end of gas treatment. The addition of Sr and Na to the melt prior to the casting, however reduced the gas content.

The area fraction of porosity in the samples was measured by a False Colour TV Analyser. Average values of porosity, measured in 4x7 mm² field from the chill to the raiser (horizontal central plane) are presented in figures 8-37. Most of the samples had a "sink" on the upper surface, around the center. Existence of "sink" in the castings indicates that feeding was not sufficient (37). Samples had higher values of porosity in these areas but low porosity closer to the chill (38). Fine interdendritic shrinkage pores, 20-100 μm, were uniformly dispersed in the castings. Figures 38-40 show examples taken from samples A1 (pure Al), B1 (Al-2%Si) and Z1 (Al-4.5%Cu). Pores of 100-500 μm were also observed around the center of the castings, figures 41-44.

For equal hydrogen content, the average values of porosity in the samples increased with the silicon content, samples A2, B3, C3, D6. Addition of Al₂O₃, Sr and Na did not change the shape of the pores. Comparing the equal gas content samples, D3-D8, B2-B4, C1-C4 indicate that these additive increased the porosity values.
5. DISCUSSION

The porosity in the samples was dependent on the hydrogen content, duration of gas treatment, and addition of modifiers such as Na or Sr or Al₂O₃.

Aluminium oxide particles which form during the gas treatment according to equation 1, contribute as nucleation sites for bubbles. The greater the amount of Al₂O₃, the greater is the availability of nucleus sites. As soon as the melt becomes supersaturated with hydrogen, bubble formation is facilitated by the large number of nucleation sites that are available. This in turn results in greater porosity.

Modifiers also facilitate the nucleation of pores either by reducing the surface tension or acting as nucleants. In these samples the hydrogen content was lower than expected from treatment time, while pores were formed more frequently, figures 12, 13, 17, 21, 28, 29.

A theoretical model which can describe the size and the volume fraction of the pores, may predict the quality of the products. Such a model should consider mechanism of pore nucleation and is developed as below:

Pore formation is influenced by gas content of the melt, pressure in the liquid phase, and the surface tension. The size of the pores is determined by the volume of the liquid confined between the dendrite arms.

Figures 38-44 indicate that the samples undergo a dendritic solidification. However, the length of the mushy zone for pure aluminium is smaller than that for the alloyed ones. During dendritic growth, due to much lower solubility of hydrogen in the solid phase (11), it enriches in the melt. Due to the high diffusivity of hydrogen (38), it is possible to use the lever rule. Hydrogen content in the melt can thus be written as:
where:
\[ \chi_{\text{H}}^L = \chi_{\text{H}}^0 / f_L, \]

\( \chi_{\text{H}}^L \) hydrogen content in the melt (mole fraction)
\( \chi_{\text{H}}^0 \) initial hydrogen content (mole fraction)
\( f_L \) melt fraction

Figure 45 shows the enrichment of hydrogen in the melt as a function of fraction solid for the lowest and highest measured hydrogen contents. The average solubility of hydrogen at one atmosphere and for Al at the melting point is also shown on the same figure. The hydrogen content of the melt exceeds the equilibrium solubility value when more than 60\% solidification has taken place. The required supersaturation for nucleation may be disregarded by assuming that the pores are formed heterogeneously (12). The balance of pressures in a bubble can be represented by:

\[ R_{\text{H}_2} - R_L = \frac{2Y}{r} \]

\( R_{\text{H}_2} \) pressure in the bubble (N/m^2)
\( R_L \) pressure in the liquid (N/m^2)
\( Y \) surface tension, for pure Al (0.914 N/m)
\( r \) radius of the pore (m)

The hydrogen pressure, \( R_{\text{H}_2} \), can be calculated from the initial hydrogen content, solid fraction, and Sieverts' law;

\[ R_{\text{H}_2} = \left( \frac{\chi_{\text{H}}^0}{f_L k} \right)^2 \] (atm.)

where \( k \) is Sievert's constant, for pure Al (0.7 ppm/atm).

Due to the solidification shrinkage, pressure in the liquid, \( P_L \), decreases. The pressure drop in the liquid in the mushy zone is calculated previously (14):

\[ P_a - P_L = \frac{32\pi^{3/2} \eta_{\text{L}}^{1/2} \dot{\epsilon}^{1/2}}{r^4} \cdot \frac{\dot{\epsilon}^2}{n h^2} \] (N/m^2)

where:
\( \mu = \text{viscosity} \ (1.3E-3 \ \text{kg/m/sec}) \)
\( \beta = \text{corrected shrinkage coefficient} \ (0.0675) \)
\( \Theta = \text{solidification rate} \ (1.82E-3 \ \text{m/sec}) \)
\( L = \text{length of the casting from raiser (m)} \)
\( t = \text{tortuosity factor} \ (?) \)
\( r = \text{radius of the pores (m)} \)
\( h = \text{half of the height of the mould (0.01 m)} \)
\( \lambda = \text{dendrite arm spacing} \ (100 \ \mu m) \)
\( n = \text{number of channels per m during solidification} \)
\( = 1/\lambda^2 \approx 1E8/m^2 \)
\( P_a = \text{ambient pressure (1 atm.)} \)

Inserting \( r = f_L \lambda / 2 \) in equation 5, results in:

\[
\nu_L = \nu - \frac{32\mu \theta^2 L^2 t^2 16}{\lambda^2 n h^2} \quad (6)
\]

Pressure in the liquid as a function of distance from raiser with different values of solid fraction are presented in figure 46. Figure indicates that pressure in the liquid drops rapidly with progress of solidification. The size of the shrinkage pores, \( r \), is computed numerically by substituting \( R_L \) and \( P_L \) from equations 4 and 5 in equation :

\[
\frac{X_{\text{Hi}}}{(2r/K)}^2 + \frac{32\mu \theta^2 L^2 t^2 16}{\lambda^2 n h^2} - P_a = \frac{2y}{r} \quad (7)
\]

The results are presented in figure (47) as function of distance from raiser and hydrogen content. The size of the shrinkage pores increases from 10 \( \mu m \) to 60 \( \mu m \), with the hydrogen content and distance from raiser. The size of the shrinkage pores is in a good agreement with the experimental measurements.

The present model does not describe the existence of random pores larger than 100 \( \mu m \) observed in some of the samples, figures 41-44. Formation of these pores may be explained as follows:

After a pore is formed, in accordance with the presented model, further growth of the pore takes place. This growth is
due to enrichment of hydrogen in the melt surrounding the pore in the interdendritic regions. In the areas close to the chill or mould, melt solidifies faster and pores formed in these areas, are not able to expand (or grow). Thus, pressure inside the pores increases. However, if the solid phase is weak or the melt between the dendrite arms can be pushed away, the pores may expand due to the increasing pressure within the pores. This can occur in the central parts of the casting which explains the formation of larger pores in these areas.

6. CONCLUSION

1- Shrinkage porosity in the samples are dependent on the duration of gas treatment and hydrogen content of the melt.

2- The pores were formed more frequently in the samples modified by Na or Sr. These samples had relatively lower hydrogen content.

3- Average values of porosity in the samples increased with the solidification range induced by Si content.

4- The presented model indicates that the size of the shrinkage pores increases with the hydrogen content and pressure drop caused by shrinkage. Pressure drop increases with distance from raiser.

7. ACKNOWLEDGMENT

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TABLE 1. Treatment performed on the samples

<table>
<thead>
<tr>
<th>sample</th>
<th>reaction time (minutes)</th>
<th>remark</th>
<th>Hydrogen content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>A1 0</td>
<td></td>
<td>0.24</td>
</tr>
<tr>
<td>A2</td>
<td>A1 3</td>
<td></td>
<td>0.38</td>
</tr>
<tr>
<td>A3</td>
<td>A1 10</td>
<td></td>
<td>0.45</td>
</tr>
<tr>
<td>A4</td>
<td>A1 7</td>
<td>100ppm Na</td>
<td>0.20</td>
</tr>
<tr>
<td>A5</td>
<td>A1 7</td>
<td>100ppm Na(metallic)</td>
<td>0.30</td>
</tr>
<tr>
<td>A6</td>
<td>A1 7</td>
<td>250ppm Sr</td>
<td>0.23</td>
</tr>
<tr>
<td>B1</td>
<td>2%Si 0</td>
<td></td>
<td>0.19</td>
</tr>
<tr>
<td>B2</td>
<td>2%Si 3</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>B3</td>
<td>2%Si 7</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>B4</td>
<td>2%Si 7</td>
<td>250ppm Sr</td>
<td>0.27</td>
</tr>
<tr>
<td>C1</td>
<td>4%Si 0</td>
<td></td>
<td>0.35</td>
</tr>
<tr>
<td>C2</td>
<td>4%Si 3</td>
<td></td>
<td>0.40</td>
</tr>
<tr>
<td>C3</td>
<td>4%Si 6</td>
<td></td>
<td>0.38</td>
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<tr>
<td>C4</td>
<td>4%Si 7</td>
<td>250ppm Sr</td>
<td>0.25</td>
</tr>
<tr>
<td>D1</td>
<td>7%Si 0</td>
<td>15min flushed with argon</td>
<td>0.15</td>
</tr>
<tr>
<td>D2</td>
<td>7%Si 0</td>
<td></td>
<td>0.22</td>
</tr>
<tr>
<td>D3</td>
<td>7%Si 0</td>
<td>wet charge</td>
<td>0.30</td>
</tr>
<tr>
<td>D4</td>
<td>7%Si 2</td>
<td></td>
<td>0.24</td>
</tr>
<tr>
<td>D5</td>
<td>7%Si 5</td>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td>D6</td>
<td>7%Si 7</td>
<td></td>
<td>0.38</td>
</tr>
<tr>
<td>D7</td>
<td>7%Si 10</td>
<td>100ppm Na</td>
<td>0.20</td>
</tr>
<tr>
<td>D8</td>
<td>7%Si 7</td>
<td>250ppm Sr</td>
<td>0.28</td>
</tr>
<tr>
<td>Z1</td>
<td>4.5%Cu 0</td>
<td>3 minutes argon flushed</td>
<td>0.18</td>
</tr>
<tr>
<td>Z2</td>
<td>4.5%Cu 0</td>
<td>0.5% Al: H added</td>
<td>0.18</td>
</tr>
<tr>
<td>Z3</td>
<td>4.5%Cu 2</td>
<td>flushed with hydrogen</td>
<td>0.17</td>
</tr>
<tr>
<td>Z4</td>
<td>4.5%Cu 2</td>
<td>P =240mmHg</td>
<td>0.26</td>
</tr>
<tr>
<td>Z5</td>
<td>4.5%Cu 5</td>
<td></td>
<td>0.31</td>
</tr>
<tr>
<td>Z6</td>
<td>4.5%Cu 10</td>
<td>Hydrogen flame formed</td>
<td>0.32</td>
</tr>
<tr>
<td>Z7</td>
<td>4.5%Cu 20</td>
<td>Hydrogen flame formed</td>
<td>0.43</td>
</tr>
<tr>
<td>Z8</td>
<td>4.5%Cu 20</td>
<td>Hydrogen flame formed</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5% Al 0 powder added</td>
<td></td>
</tr>
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</table>
Figure 1. Schematic drawing of the melting and gas treatment apparatus.

Figure 2. Schematic drawing of mold
Figure 3. Variation of hydrogen content for Al-4.5%Cu.

Figure 4. Variation of hydrogen content for pure Al.

Figure 5. Variation of hydrogen content for Al-2%Si.
Figure 6. Variation of hydrogen content for Al-4%Si.

Figure 7. Variation of hydrogen content for Al-7%Si.
Figure 8. Variation of porosity in sample A1, pure Al.

Figure 9. Variation of porosity in sample A2, pure Al.

Figure 10. Variation of porosity in sample A3, pure Al.

Figure 11. Variation of porosity in sample A4, pure Al.
Figure 12. Variation of porosity in sample A5, pure Al.

Figure 13. Variation of porosity in sample A6, pure Al.
Figure 14. Variation of porosity in sample B1, 2%Si

Figure 15. Variation of porosity in sample B2, 2%Si

Figure 16. Variation of porosity in sample B3, 2%Si

Figure 17. Variation of porosity in sample B4, 2%Si
Figure 18. Variation of porosity in sample C1, 4%Si

Figure 19. Variation of porosity in sample C2, 4%Si

Figure 20. Variation of porosity in sample C3, 4%Si

Figure 21. Variation of porosity in sample C4, 4%Si
Figure 22. Variation of porosity in sample D1, 7%Si

Figure 23. Variation of porosity in sample D2, 7%Si

Figure 24. Variation of porosity in sample D3, 7%Si

Figure 25. Variation of porosity in sample D4, 7%Si
Figure 26. Variation of porosity in sample D5, 7%Si

Figure 27. Variation of porosity in sample D6, 7%Si

Figure 28. Variation of porosity in sample D7, 7%Si

Figure 29. Variation of porosity in sample D8, 7%Si
Figure 30. Variation of porosity in sample Z1, 4.5%Cu

Figure 31. Variation of porosity in sample Z2, 4.5%Cu

Figure 32. Variation of porosity in sample Z3, 4.5%Cu

Figure 33. Variation of porosity in sample Z4, 4.5%Cu
Figure 34. Variation of porosity in sample Z5, 4.5%Cu

Figure 35. Variation of porosity in sample Z6, 4.5%Cu

Figure 36. Variation of porosity in sample Z7, 4.5%Cu

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Figure 38. Sample B1.

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Figure 45. Enrichment of hydrogen in the melt during solidification.

Figure 46. Pressure drop due to shrinkage.
Figure 47. Calculated pore size (Eq. 19).
The effect of hydrogen on an iron based amorphous alloy

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ABSTRACT

In this investigation we have systematically studied the brittleness and the atomic structure in an Fe(SiBC) alloy. Different amounts of hydrogen have been dissolved in the alloy. It has then been studied at different cooling rates. Hydrogen gas of different partial pressures was dissolved into the melt. The alloy was then rapidly quenched by a chill block melt spinning method. The cooling rates were changed by changing the velocity on the chilling roll. The brittleness and the atomic structure were examined by bending tests and x-ray diffraction.

X-ray diffractions showed that the ribbons were amorphous when the cooling rate was sufficient. Amorphous ribbons without any hydrogen were ductile. Crystalline ribbons of this alloy were brittle. The ribbons with dissolved hydrogen and amorphous structure were brittle even at small amounts of hydrogen. At the highest cooling rates the ribbons with low hydrogen content were ductile. There seems to be a connection between the hydrogen content and the amorphous ribbons ductility. The hydrogen content only has a slight influence to amorphous structure.

INTRODUCTION

Hydrogen easily dissolves in liquid metals. The solubility decreases rapidly when the metal solidifies and with decreasing temperature. Many alloys become brittle even when a small amount of hydrogen is present. In this investigation we have dissolved different amounts of hydrogen in a Fe (Si₅B;₃C₄) liquid alloy. Ribbons were then directly cast from the melt by a chill-block melt-spinning method. Both amorphous and crystalline atomic structures were obtained by changing the velocity of the chilling substrate. The hydrogen content, the brittleness and the atomic structure were then examined on the ribbons.

EXPERIMENTAL

The ribbons were made by a single roller melt spinning equipment. The diameter of the copper roll was 159 mm. Three grams of the Fe (SiBC) alloy was used for each experiment and it was melted by a high frequency induction furnace. The crucible was made of quartz; in the crucible bottom there was a hole with a diameter of 0.5 mm. A gas mixture was blown for 30 seconds through a lance onto the top of the liquid alloy (Fig. 1). The gas mixture was a mixture of hydrogen and argon. The different amounts of hydrogen gas which were used in these experiments were 0, 5, 10, 50 and 100 volume %. The amount of gas was 200 liters per hour. The driving ejection pressure was 100 kPa; argon gas was used (Fig. 2). The distance between the crucible and the copper roll was 3 mm and the melt jet inclination was 90°. The substrate velocities were 4, 8, 13, 17, 21, 25, 29 and 33 m/s.
The atomic structure was determined by x-ray diffraction, using nickel filtered CuKα radiation. The amount of hydrogen in the specimens was measured by vacuum fusion with a Salzer analyzer EAH 220. Two grams of the sample were heated in graphite crucibles to 2000°C. This was done about one week after the ribbons were made.

Differential scanning calorimetry was carried out in a Mettler TA 2000 C. Samples of around 20 mg were heated in Pt cups with a rate of 5 K/min⁻¹ from 460°C beyond the crystallization temperature in inert atmosphere. The temperature axis and the peak area were calibrated from melting endotherms of pure indium, aluminium and gold.

RESULTS

Several different examinations were made on the ribbons to determine the effect of hydrogen on the samples.

The hydrogen content was determined by vacuum fusion. The results are shown in Fig. 3 and Fig. 4.

In Fig. 3 it is shown how the hydrogen content in the ribbons varies with the amount of hydrogen gas in the gas mixture. The substrate velocity was 29 m/s. Fig. 4 shows how the hydrogen content in the ribbons varies with the substrate velocity. The amount of hydrogen gas in the gas mixture was 50%.

The thickness of the ribbons was measured with a micrometer. No noticeable difference could be seen on ribbons with or without hydrogen. The average thickness as a function of the substrate velocity is shown in Fig. 5.

The x-ray diffraction examination showed that the structure was crystalline when the thickness was over 50 μm. No noticeable difference could be seen on ribbons with or without hydrogen.

The brittleness of the ribbons was investigated in a rather simple way by a bending test. The ribbon was bent 180°; if it breaks it is brittle and if not, it is ductile. In Fig. 6 these results are shown. There is a definite difference in brittleness of ribbons with different amounts of hydrogen in the gas mixture. The ribbons which were treated with pure hydrogen showed brittle behaviour for all substrate velocities. Ribbons without any hydrogen become brittle at substrate velocities lower than 20 m/s. At velocities lower than 13 m/s, ribbons were crystalline.
Fig. 3. The hydrogen content of the ribbons at different amounts of hydrogen gas in the gas mixture.

Fig. 4. The hydrogen content of the ribbons at different substrate velocities.

Fig. 5. The variation of thickness with substrate velocity.

Fig. 6. Ductility of the ribbons at different substrate velocities and different amounts of hydrogen gas in the gas mixture.

Different scanning calorimetry has been used to determine the crystallization temperature and heat of crystallization. Two series were determined, one in which the melt had been treated with 100 % H₂, and one in which 100 % Ar. Four representative DSC thermograms are shown in Fig. 7 and Fig. 8. All samples spun with between 33 and 13 m/s exhibit exothermic DSC peaks while no crystallization peaks could be observed for samples which were made at velocities lower than 13 m/s.
DISCUSSION

According to the x-ray diffraction evidence there was no noticeable difference in the atomic structure of the ribbons which were treated with or without hydrogen gas. It seems that hydrogen at these levels has no effect on the formation of the atomic structure for this alloy. This corresponds to the DSC thermograms. As can be seen in Figs. 7 and 8, the total crystallization peak seems to be composed of three overlapping peaks, indicating the kinetics of crystallization to consist of several processes. The total heat of crystallization has been found to be 1.34 kcal/mole, independent of the velocity and the hydrogen content. Our value is in good agreement with previous findings for Fe-P-C amorphous alloys (1). The shapes of the peaks of samples with the same velocity but different amounts of hydrogen were almost identical, but the shapes varied somewhat with the velocity as is to be seen in the figures.

It is known that amorphous alloys become brittle when certain amounts of hydrogen are present (2-6). The most common way of dissolving hydrogen used in these investigations was by cathodic polarization in an acid solution. The hydrogen content in the ribbons then becomes high and they cannot be bent 180° without breaking.

In this investigation the maximum content of dissolved hydrogen is limited by the solubility in the liquid phase which is about 25 ppm. At the highest cooling rates most of the hydrogen is left in the ribbons; thereafter the hydrogen content decreases with decreasing cooling rate. This can even be observed on ribbons made from melt treated with 100 % Ar. The amount of hydrogen is relatively high even though the melt has not been treated with hydrogen. This has also been reported by ref. (7).
Ribbons that are made at the highest substrate velocity, 33 m/s, become brittle when the hydrogen content is over about 20 ppm. The ribbons that are made at lower substrate velocity, 29 m/s, become brittle when the hydrogen content is over ca 15 ppm. It seems that the cooling rate on amorphous alloys has an effect on the sensitivity to hydrogen embrittlement.

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Thanks are due to Professor Hasse Fredriksson for many stimulating discussions.

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