

Kinetics of absorbing hydrogen of Al melt^①

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Abstract: The kinetics process of absorbing hydrogen of Al melt was analyzed and it was considered that the concentration of hydrogen in Al melt was determined by the concentration of water vapor in the interface of the oxide layer and Al melt. The change of the alloying composition will result in the change of compactability of oxide layer and affect the process of the water vapor gas penetrating the oxide layer and entering the interface of Al melt and oxide layer. Based on the above analysis, the kinetics equation of Al melt absorbing hydrogen was established, and compared with the test result. The results of calculation were elementally coincident with the test result. The curve of hydrogen concentration varying with reaction time in Al melt can be obtained from this equation. And scientific basis could be provided to select melting technology parameter properly and control the concentration of hydrogen in Al melt.

Key words: Al melt; absorbing hydrogen; kinetics

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1 INTRODUCTION

Hydrogen in Al melt mainly comes from water vapor^[1]. It is the water vapor absorbed between the oxide layer and the Al melt, but not the gaseous water vapor that reacts with the liquid metal, because there is always a thin oxide layer on the surface of the Al melt. Following is their chemical equation:



where $\text{H}_2\text{O}_{\text{G-L}}$ is water vapor between the oxide layer and the Al melt, $[\text{H}]_\text{L}$ is hydrogen dissolved in the Al melt, Me is element that has the maximum affinity with the oxygen, and m , n are parameters that relate to the metal melt.

The reaction equilibrium constant of Reaction (1) is^[2]

$$K = \left[\frac{c_{\text{H}}^{\text{G-L}}}{c_{\text{H}_2\text{O}}^{\text{G-L}}} \right]^2 \quad (2)$$

where $c_{\text{H}}^{\text{G-L}}$ is the hydrogen concentration on the interface, $c_{\text{H}_2\text{O}}^{\text{G-L}}$ is the concentration of the water vapor adsorbed on the interface.

The restriction factor of Reaction (1) is hydrogen's transmitting process in metal melt^[3,4]. The reaction speed depends on the hydrogen concentration gradient and its orientation in the melt. The above reaction process may be either absorbing or eliminating hydrogen which will be determined by the relationship of the hydrogen concentration in the interface and that in the melt. When the hydrogen concentration on the interface is higher than that in the melt, it will absorb hydrogen. Else, it will eliminate hydrogen. The kinetic process of absorbing hydrogen was

analyzed emphatically as below.

2 KINETICS OF AL MELT ABSORBING HYDROGEN

The speed of the melt absorbing hydrogen may be expressed by the following equation^[2]:

$$v = \frac{dc_{\text{H}}^{\text{L}}}{dt} = k_1(c_{\text{H}}^{\text{G-L}} - c_{\text{H}}^{\text{L}}) \quad (3)$$

where c_{H}^{L} is the concentration of hydrogen dissolved in the melt, k_1 is the transmitting coefficient of hydrogen in the melt.

Suppose when reaction time $t = 0$, $c_{\text{H}}^{\text{L}} \rightarrow c_{\text{H},0}^{\text{L}}$ ($c_{\text{H},0}^{\text{L}}$ is the original concentration of hydrogen in the melt), we can get Eqn. (4) through resolving Eqn. (3):

$$c_{\text{H}}^{\text{L}} = c_{\text{H}}^{\text{G-L}} - (c_{\text{H}}^{\text{G-L}} - c_{\text{H},0}^{\text{L}})e^{-k_1 t} \quad (4)$$

From Eqn. (4), we can conclude that when $t \rightarrow \infty$, $c_{\text{H}}^{\text{L}} \rightarrow c_{\text{H}}^{\text{G-L}}$. The kinetics curve is showed in Fig. 1^[5].

In a multi-element system, the change of element composition will cause the change of $c_{\text{H}_2\text{O}}^{\text{G-L}}$, which will appear in two kind of situation:

- 1) $c_{\text{H}}^{\text{G-L}}$ is decreased with time expanded;
- 2) $c_{\text{H}}^{\text{G-L}}$ is increased with time expanded.

The two situations will be discussed respectively hereunder.

2.1 $c_{\text{H}}^{\text{G-L}}$ decreased with time expanded

Now that the change of the alloy element composition can cause the decrease of $c_{\text{H}_2\text{O}}^{\text{G-L}}$, the concentration of water vapor adsorbed in the interface of the

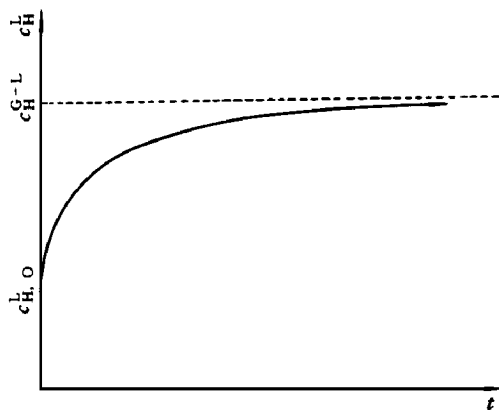


Fig.1 Relationship between concentration of hydrogen in melt and reaction time

oxide and the melt, the $c_{H,0}^{G-L}$ will also decrease, which may be expressed by below formula:

$$c_{H,0}^{G-L} = c_{H,0}^{G-L} - a(1 - e^{-k_2 t}) \quad (5)$$

where $c_{H,0}^{G-L}$ is the original concentration of hydrogen in the interface; a , k_2 is constant.

From Eqn.(5), we can see that, when $t \rightarrow \infty$, $c_{H,0}^{G-L} \rightarrow c_{H,0}^{G-L} - a$, which is the final concentration of hydrogen ($c_{H,\infty}^L$) in the melt. We can conclude that the physical meaning of a is the difference between the original concentration of hydrogen in the interface ($c_{H,0}^{G-L}$) and the final concentration of hydrogen in the melt ($c_{H,\infty}^L$) after keeping the temperature for a long time.

Substituting Eqn.(3) into Eqn.(5), we can get the equation as below:

$$\frac{dc_H^L}{dt} = k_1(c_{H,0}^{G-L} - a + ae^{-k_2 t}) - k_1 c_H^L \quad (6)$$

From Eqn.(6), we know that the function $c_H^L = f(t)$ has an extreme value. Because it is the process of absorbing hydrogen that is studied, the extreme value should be the maximum value. t_{\max} can be resolved from Eqn.(6), which is

$$t_{\max} = \left(\frac{1}{k_2}\right) \ln \left[\frac{a}{c_{H,\max}^L - c_{H,\infty}^L} \right] \quad (7)$$

where t_{\max} , $c_{H,\max}^L$ are time and hydrogen concentration in the function $c_H^L = f(t)$ corresponding to the extreme point.

Eqn.(6) is a first-order linear differential equation. Its general form is $y' + P(x)y = Q(x)$, where $P(x) = k_1$, $Q(x) = k_1(c_{H,0}^{G-L} - a + ae^{-k_2 t})$. So according to the form of general solution of the differential equation, which is

$$y = e^{-\int P(x)dx} \left[\int Q(x)e^{\int P(x)dx} dx + \text{Const} \right]$$

and noticing that $c_{H,0}^{G-L} - a = c_{H,\infty}^L$, we can get the solution of Eqn.(6), which is

$$c_H^L = c_{H,\infty}^L + \frac{k_1 a}{k_1 - k_2} e^{-k_2 t} + \text{Const} \times e^{-k_1 t}$$

Using the boundary condition $t = 0$, $c_H^L = c_{H,0}^L$, we can get that

$$\text{Const} = c_{H,0}^L - c_{H,\infty}^L - \frac{k_1 a}{k_1 - k_2}$$

So the function $c_H^L = f(t)$ has such form as

$$c_H^L = c_{H,\infty}^L + \frac{k_1 a}{k_1 - k_2} e^{-k_2 t} + \left[c_{H,0}^L - c_{H,\infty}^L - \frac{k_1 a}{k_1 - k_2} \right] e^{-k_1 t} \quad (8)$$

Supposed that the boundary condition is $t = 0$, $c_H^L = c_{H,0}^L$; $t \rightarrow \infty$, $c_H^L \rightarrow c_{H,\infty}^L$ we can get a 's expression from Eqns.(7) and (8) when $t = t_{\max}$.

$$a = \frac{c_{H,0}^L - c_{H,\infty}^L - \frac{k_1 a}{k_1 - k_2} e^{-k_1 t_{\max}} (c_{H,\infty}^L - c_{H,\max}^L) + c_{H,0}^L - c_{H,\infty}^L}{k_1 t_{\max}} \times \ln \frac{a}{c_{H,\max}^L - c_{H,\infty}^L} \quad (9)$$

If t_{\max} , $c_{H,\max}^L$, $c_{H,0}^L$, $c_{H,\infty}^L$ and k_1 can be got by test, then the value of a can be calculated, and $c_{H,0}^{G-L} = c_{H,0}^{G-L} + a$ can be calculated further. Eqn.(9) can be solved by iterative and graphic method^[6]. Then k_2 can be got from Eqn.(7) after a is calculated.

2.2 $c_{H,0}^{G-L}$ increased with time expanded

When the concentration of the water vapor absorbed on the interface increases for the change of the alloy element, $c_{H,0}^{G-L}$ will increase too. Similar to Eqn.(5), we can get

$$c_{H,0}^{G-L} = c_{H,0}^{G-L} + a(1 - e^{-k_2 t}) \quad (10)$$

Substituting Eqn.(3) into Eqn.(10), we can get

$$\frac{dc_H^L}{dt} = k_1[c_{H,0}^{G-L} - a - a \exp(-k_2 t)] - k_1 c_H^L \quad (11)$$

Same as $c_{H,0}^{G-L} = c_{H,\infty}^L + a$, we can get the expression of t_{\max} :

$$t_{\max} = \left(\frac{1}{k_2}\right) \ln \left[\frac{a}{c_{H,\infty}^L - c_{H,\max}^L} \right] \quad (12)$$

From Eqn.(12), we can see that $c_{H,\max}^L$ can not be greater than $c_{H,\infty}^L$. Therefore, the function $c_H^L = f(t)$ hasn't extreme value, whose kinetics curve is showed in Fig.1. The resolution of Eqn.(11) is

$$c_H^L = c_{H,\infty}^L - \frac{k_1 a}{k_1 - k_2} e^{-k_2 t} + \left[c_{H,0}^L - c_{H,\infty}^L + \frac{k_1 a}{k_1 - k_2} \right] e^{-k_1 t} \quad (13)$$

3 ANALYSIS OF RESULT OF CALCULATION AND TEST

A group of test was designed in order to verify the mathematics model above according to references [7~10]. Two kinds of alloy Al-12%Si and Al-7%

Si-0.3 % Mg were selected. They were melted and held at the temperature of 720 °C, the initial concentration $c_{H, O}$, $c_{H, \infty}^L$ at the time of t and $c_{H, \max}^L$ were measured. Then the figure about $\ln(c_{H, \infty}^L / c_{H, O}^L)$ and t was made. Finally a line was obtained by connecting every point in the figure, and the transmitting coefficient k_1 could be calculated from the slope of the line. Substituting the data above into Eqn.(9), we can get the value of a . And we can get k_2 by substituting them into Eqn.(7). The parameters obtained were listed in the Table 1.

Table 1 State parameter of alloy melt

State parameter	Al-12 %Si	Al-7 %Si-0.3 % Mg
$c_{H, O}^L / (mL \cdot kg^{-1})$	6.27	7.52
$k_1 / 10^{-4} s^{-1}$	3.428	3.761
$k_2 / 10^{-4} s^{-1}$	3.408	3.740
$a / (mL \cdot kg^{-1})$	12.868	16.074
$c_{H, \infty}^L / (mL \cdot kg^{-1})$	14.275	16.930

The kinetics equation of melt absorbing hydrogen was obtained after the data in Table 1 were substituted into Eqn.(8).

For alloy Al-12 %Si:

$$c_{H, O}^L = 1.43 + 220.55 e^{-3.408 \times 10^{-4} t} - 221.35 e^{-3.428 \times 10^{-4} t} \quad (14)$$

For alloy Al-7 %Si-0.3 % Mg:

$$c_{H, O}^L = 1.69 + 302.27 e^{-3.74 \times 10^{-4} t} - 303.21 e^{-3.76 \times 10^{-4} t} \quad (15)$$

The concentration of hydrogen in the melt obtained from test at different time and the curves obtained from the equations above were shown in Fig.2.

From Fig.2, we can see that the calculation result is the same as the test result basically. So we can draw a conclusion that Eqn.(8) expressed accurately the relationship of the amount of hydrogen and the time on the condition that the concentration of hydrogen in the interface of the oxide and the melt decreased with increasing time.

In the same way, we can verify Eqn.(13), and describe the relationship of the amount of hydrogen and time on the condition that the concentration of hydrogen in the melt increases with increasing time.

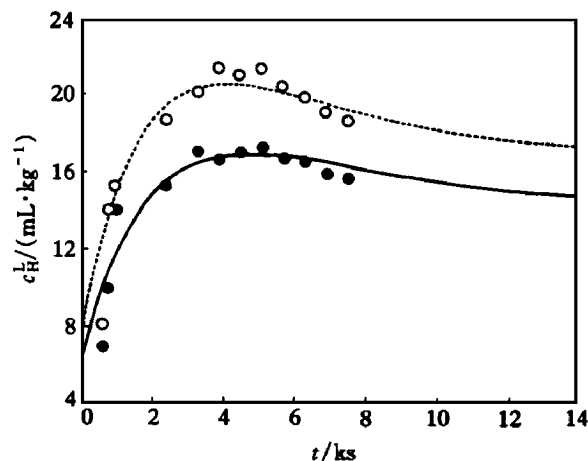


Fig.2 Relationship between amount of hydrogen and reaction time
● — Al-12 %Si; ○ — Al-7 %Si-0.3 % Mg

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