

EXPERIMENTAL STUDY ON HYDROGEN DIFFUSION IN MOLTEN ALUMINUM

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Abstract. An innovative method which determines the equivalent diffusion coefficient of the hydrogen in molten aluminum is presented in this paper. The molten aluminum is placed in a permeable porous crucible and is maintained at a predetermined temperature. The vacuum is created outside of the crucible and the hydrogen in the molten aluminum will diffuse through the porous crucible wall out due to the hydrogen concentration difference at the aluminum melt/crucible interface. The hydrogen contents in the molten aluminum decrease as the vacuuming time extends. The relationship between equivalent diffusion coefficient and average hydrogen contents can be determined by solving Fick's diffusion equation at polar coordinate under certain initial and boundary conditions. Experiments were carried out to test the hydrogen contents in molten aluminum foundry alloy at different times. The equivalent diffusion coefficients of the hydrogen in molten A357 alloy have been obtained by combination of the testing data and computation. The values of $(9.4-10.2) \times 10^{-3} \text{ cm}^2/\text{s}$ are estimated for the equivalent diffusion coefficient between the temperature of 700 and 730 °C.

1. INTRODUCTION

Hydrogen is the most harmful element in aluminum alloys. The hydrogen solubility decreases with the decreasing of temperatures in molten aluminum, which results in the formation of porosity in castings, and has negative effects on the mechanical, physical properties and appearance of castings. The current technologies of degassing mainly depend on the mechanism of transfer of hydrogen in aluminum melt, such as hydrogen transfers into gas bubbles and hydrogen transfers from molten aluminum to flux, and so on. The diffusion coefficient of hydrogen in molten aluminum is an important parameter that is used to describe the transfer behavior of hydrogen in molten aluminum. The calculation of diffusion coefficient of hydrogen in molten aluminum has been given in the previous literatures [1,2], but so far, few researches on determining of the diffusion

coefficients by experiment have been reported. In this paper an innovative method, which is based on the Fick's diffusion principle, has been proposed to determine equivalent diffusion coefficient of hydrogen in molten aluminum.

2. THE PRINCIPLES

The hydrogen diffusion in molten aluminum can be described by the Fick's law [3]:

$$\frac{\partial C}{\partial t} = \text{div} (D \cdot \text{grad} C), \quad (1)$$

where C and D are concentration and diffusion coefficient of hydrogen in molten aluminum, respectively.

Suppose diffusion coefficient of hydrogen D is a constant, on the cylindrical coordinate, Eq. (1) can be written as:

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$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial R^2} + \frac{1}{R} \cdot \frac{\partial C}{\partial R} \right). \quad (2)$$

where t is time, R is the polar coordinate.

A liquid cylindrical of R in radius is taken for consideration. The porous gas permeable material is used for the crucible. However, the molten aluminum can't penetrate into the crucible when the space around the crucible is vacuumized. During the process of vacuum, the hydrogen which dissolved in molten aluminum will diffuse out through the porous gas permeable crucible. The average concentration of hydrogen in the crucible can be expressed by Eq. (3):

$$\frac{\bar{C} - C_s}{C_i - C_s} = \sum_{n=1}^{\infty} \frac{4}{\xi_n^2} \exp \left(\frac{-\xi_n^2 \times D \times t}{R^2} \right), \quad (3)$$

where \bar{C} is the average concentration of hydrogen at time t ($\text{cm}^3/100 \text{ gAl}$); C_s is the hydrogen concentration of at the interface between inner wall of crucible and molten aluminum ($\text{cm}^3/100 \text{ gAl}$); C_i is initial hydrogen concentration ($\text{cm}^3/100 \text{ gAl}$); D is diffusion coefficient of the hydrogen in molten aluminum (cm^2/s); R is the radius of crucible (cm); ξ_n is the root of equation $J_0(x) = 0$, which is the Bessel function of zero order.

When $n=1, 2, 3, 4, 5$, $\xi_n = 2.405, 5.52, 8.654, 11.792, 14.931$, respectively.

Substituting the approximate calculation of first-order series into Eq. (3), it has:

$$\frac{\bar{C} - c_s}{c_i - c_s} = \frac{4}{\xi_n^2} \exp \left(\frac{-\xi_n^2 \cdot D \cdot t}{R^2} \right). \quad (4)$$

Furthermore, Eq. (4) can be changed to:

$$D = \frac{-R \ln \left(\frac{\bar{C} - c_s}{c_i - c_s} \times \frac{\xi_n^2}{4} \right)}{\xi_n^2 \times t}. \quad (5)$$

based on the assumption that the hydrogen concentration at the interface between inner wall of crucible and molten aluminum instantly reduces to zero when vacuuming starts. Thus Eq. (5) can be written as:

$$D = \frac{-R^2 \ln \left(\frac{\bar{C}}{c_i} \times \frac{\xi_n^2}{4} \right)}{\xi_n^2 \times t}. \quad (6)$$

From Eq. (6), it can be concluded that the hydrogen diffusion coefficient can be calculated by measuring the average concentration of hydrogen (\bar{C}).

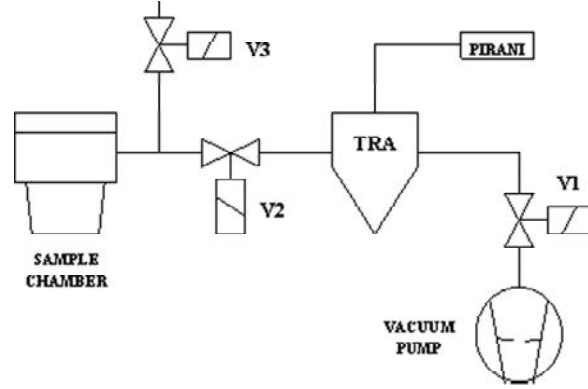


Fig. 1. Schematic of hydrogen content tester.

3. EXPERIMENTS

3.1. Experimental material

A357 alloy is used for experimental material. The chemical composition is 7.6 wt.% Si, 0.52 wt.% Mg, 0.10 wt.% Ti, 0.06 wt.% Be and balance being aluminum. The charge was melted at an electric resistance furnace. The hydrogen contents in the molten aluminum were tested at 700, 715, and 730 °C, respectively.

3.2. Experimental apparatus

Determination of hydrogen contents was carried out based on reduced pressure technique (RPT). The instrument, which is manufactured by Severn Science Company of Britain, measures the hydrogen in molten aluminum using RPT, as the Fig. 1 shows. A constant mass of the melt (approximately 100 g) is placed in a chamber and the pressure reduced rapidly to a predetermined value by a vacuum pump. Shut off electromagnetic valve V1, the chamber and associated vacuum system are then isolated from the pump and the sample allowed to solidify. As the melt cools hydrogen is released and its partial pressure is measured by a calibrated Pirani gauge whose output is converted continuously to a digital display of hydrogen content. It will take about 5 minutes to finish one whole testing procedure.

The experimental apparatus for determination of diffusion coefficient is shown in Fig. 2. In Fig. 2, A is a vacuum pump; B is the heat shield; C is the heater; D is porous gas permeable crucible; E is thermal couples; F is aluminum melts; G is stainless steel plate; H is vacuum gauge; I is sealed container and V1 and V2 are solenoid valves, respectively.

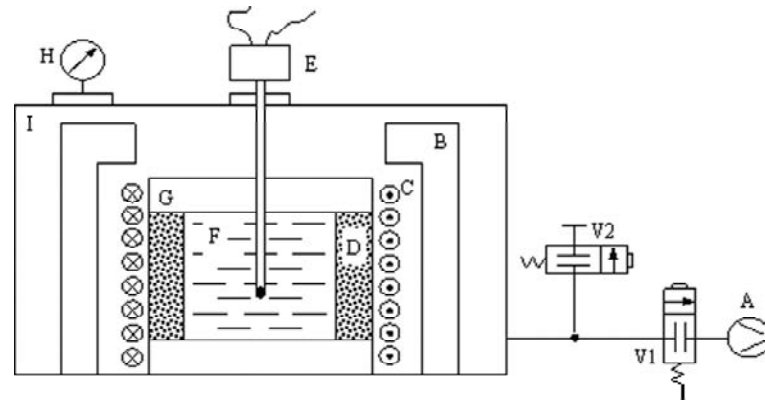


Fig. 2. Schematic of instrument of hydrogen diffusion coefficient.

3.3. Experimental procedure

A357 alloy was melted in a resistance furnace. The charges of 10 kg include 80 wt.% of new material and 20 wt.% of cutting scraps with same compositions. After melting, molten aluminum was maintained for one hour at 700, 715, and 730 °C, respectively with a water-soaked porous firebrick covering the crucible in order to increase the hydrogen concentration, due to the chemical reactivity of molten aluminum and water vapor to form hydrogen and alumina. Hydrogen contents of the molten aluminum were then measured by hydrogen tester as shown in Fig. 1. After that, the molten aluminum was poured into the crucible and was sealed in it. As soon as the temperature of molten aluminum got to a predetermined value, vacuum was started and time was recorded at the same time. After reaching the setting time, the chamber automatically switched to connect with the atmosphere, and then, hydrogen content in the melt could be measured once again.

4. RESULTS AND ANALYSIS

During the process of the vacuum pumping, the hydrogen content was measured at 710, 715, and 730 °C for 100, 200, 300, 400, 500, and 600 s, respectively. The experimental results are shown in Fig. 3.

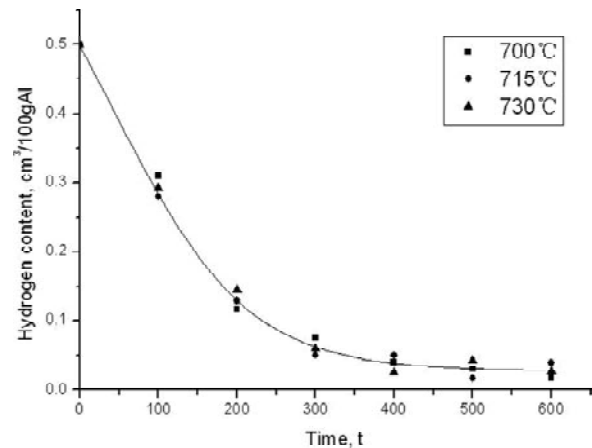


Fig. 3. Hydrogen content vs. vacuum time.

It can be seen from Fig. 3, as the vacuum time increases, hydrogen content initially exhibits a sharp drop and then decreases slowly. The hydrogen contents tend to be unchanged after the time beyond 300 s. Therefore, the measured data before 300 s can be used to calculate D by Eq. (6). The calculated results are given in Table 1.

Obviously, this proposed method does not consider the influence of thermal convection on hydrogen diffusion. In fact, the diffusion of hydrogen is dependant upon not only the concentration gradient but also many other factors, such as convection, chemical composition of the alloys, inclusion contents, *etc.* For that reason, the diffusion coefficient we measured, strictly speaking, is not “physi-

Table 1. Diffusion coefficient of hydrogen in molten aluminum for different vacuum pumping time.

Time [s]	\bar{c} [cm³/100gAl]	Average Value[cm³/100 gAl]	D [cm²/s]
100	0.28, 0.30, 0.30	0.293	9.4×10^{-3}
200	0.12, 0.12, 0.13	0.123	10.2×10^{-3}
300	0.06, 0.06, 0.06	0.060	9.8×10^{-3}

cal" but "engineered". Even so, it is significant in engineering.

5. SUMMARY

An new method which determines the equivalent diffusion coefficient of the hydrogen in molten aluminum has been put forward in this paper. The relationship between equivalent diffusion coefficient and average hydrogen contents can be determined by solving Fick's diffusion equation at polar coordinate under certain initial and boundary conditions. Experiments were done for molten A357 alloy to test the hydrogen contents at different times. The values of $(9.4\text{--}10.2)\times 10^{-3}\text{ cm}^2/\text{s}$ are estimated for the equivalent diffusion coefficient between the temperature of 700 and 730 °C.

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