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Resistivity Quantitative Measurement Model and Accuracy Analysis of Hydrogen Content in Pure Aluminum

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Abstract: Hydrogen content in pure aluminum melting was increased through inserting fresh branches and measured by decompression solidification method and density method. Resistivity of pure aluminum casting was measured by means of the electrical resistance method, and physical model of resistivity measuring method was established. Combined with experimental data, the mathematical relationship between resistivity of pure aluminum casting and hydrogen content was derived. To further verify the feasibility of resistivity measurement model on the hydrogen content in aluminum melting, this paper also has carried on the hydrogen evolution experiment.

Keywords: Pure Aluminum, Physical Model, Hydrogen Content, Resistivity

1. Introduction

With the development of science and technology, the application of aluminum alloy is more and more widely, and control of the quality of aluminum alloy castings also will be more stringent. When aluminum melting reacts with water vapor in the atmosphere at high temperature, hydrogen will be generated, which dissolve in molten and produce porosity. The porosity split matrix material, which limit the performance of aluminum alloy in the very great degree. Therefore, how to determine hydrogen content accurately and removal of hydrogen in aluminum melt timely in the process of smelt is the comparison of the scholars pay close attention to the problems [1-2]. Nowadays, the determination of hydrogen methods mainly consist of the Straube-Pfeiffer method, the Dardel method, the CHAPEL method, the Telegas method and the Concentration cell method, which perfect with the development of technology [3]. But good hydrogen measuring instruments mainly from Switzerland FMA company and ABB company, Japan NOTORP KYHS -A2 and British seven technology company, These products' price is expensive, product maintenance is not convenient, not widely used in the enterprise [4]. In this paper, a physical model of resistivity is established, which connect the hydrogen content of pure aluminum with resistivity, thus the model can reflect the hydrogen content in aluminum alloys through sensitive resistivity.

2. Experimental Materials and Procedure

In the experiment, experimental equipment are mainly consist of crucible resistance furnace (SX-5-10), decompression coagulation instrument and resistance Instruments. Experimental materials are pure aluminum and fresh branches, the component of pure aluminum as shown in Table 1. Pure aluminum was melted at 800ºC for 30 mins, and the fresh branch was inserted into the molten aluminum in order to increase supersaturated hydrogen and then aluminum melt was casted in the low pressure (0.01MPa) and normal pressure (0.1MPa) respectively. Continuing to insert the branches and casting aluminum melt, we get 7 groups experiments whose hydrogen content are different were carried out in this paper. The hydrogen content of the pure aluminum was measured by decompression solidification method and density method. Resistance samples were taken from the 7 groups of sample with is the size of 50×5×2mm. In the resistance test, when the sample was loaded the current with 0.1A, the resistivity can be obtained through measuring the voltage of resistance sample.

3. Experiment Results and Discussion

3.1. Determination of Hydrogen Content and Resistivity

According to decompression solidification method and density method, the hydrogen content in the melt can be determined by the formula (1) and (2).

$$C_H = 100\frac{P_2}{P_1}\left(\frac{1}{\rho}-\frac{1}{\rho_0}\right) \quad (1)$$

$$\rho = \frac{m_a}{m_a - m_w} \quad (2)$$

Where, C_H is the hydrogen content, ml/100gAl. ρ is the density of samples after decompression and solidification, g/cm^3. ρ_0 is the pressure solidification sample density, 2.7g/cm^3. P_2 is the low pressure, 0.01MPa. P_1 is the atmospheric pressure, 0.1MPa.m_a is the quality of the sample in air, g. m_w is the quality of the water sample, g. m_a and m_w can be measured by the suspension weighing function of 1/10000 electronic balance of the model FA2104N.

The resistivity of pure aluminum samples can be obtained by the formula (3).

$$\rho = \frac{R \cdot A}{L} \quad (3)$$

Where, L is the sample length which has a fixed value 34mm, measurement area A is calculated from different samples' width and thickness. ρ is known as resistivity, which is a geometry-independent numerical value. Thus, the conductive of metal is usually measured with ρ.

3.2. The Result of the Experiment and Analysis

Table 1 shows the calculation results of hydrogen content and resistivity of pure aluminum. As can be seen from table 1, the hydrogen content and the resistivity increase gradually with the increasing of fresh branches. The resistivity of the sample in Seven groups are higher than the theoretical resistivity of pure aluminum (2.8249x10^{-8}Ω•m) [5]. The calculation result shows that there is small amount of gas in the first group which did not insert branch, because the aluminum melting surface contacts with water vapor in the air and react with it, which leads to a little hydrogen dissolving into melting aluminum in the smelting process.

Table 1. *Relationship between saturated hydrogen content and resistivity of pure aluminum sample.*

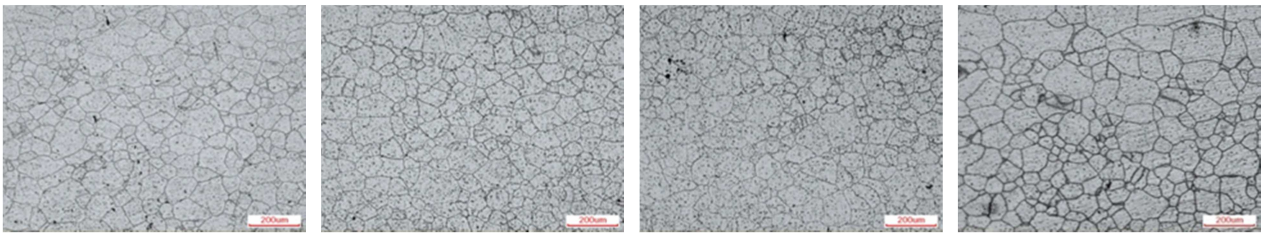
NO.	C_H (ml/100g Al)	ρ (×10^{-8}Ω·m)
1#	0.015	2.8919
2#	0.082	2.9034
3#	0.215	2.9365
4#	0.314	2.9477
5#	0.400	2.9548
6#	0.420	2.9572
7#	0.650	2.9664

3.3. Quantitative Model of Calculating Hydrogen Content

According to Matthiessen law [6], the resistivity of pure aluminum casting mainly consists of pure aluminum matrix, matrix supersaturated solid solubility, second phase, grain size, porosity and inclusions, which are listed in the formula (4).

$$\rho = \rho_{(pure)} + \sum \rho_i C_i + \rho_p + \rho_{gz} + \rho_{gas} + \rho_{mix} \quad (4)$$

$\rho_{(pure)}$ is the resistivity of pure aluminum. C_i refers to the content of substance i (where i is common element of aluminum liquid, such as silicon etc). ρ_i is the resistivity of the alloy element i. ρ_p is the resistivity of second phase. ρ_{gz} is the effect of grain size on the resistivity. ρ_{gas} is the effect of porosity on the resistivity. ρ_{mix} is effect of inclusion on the resistivity.



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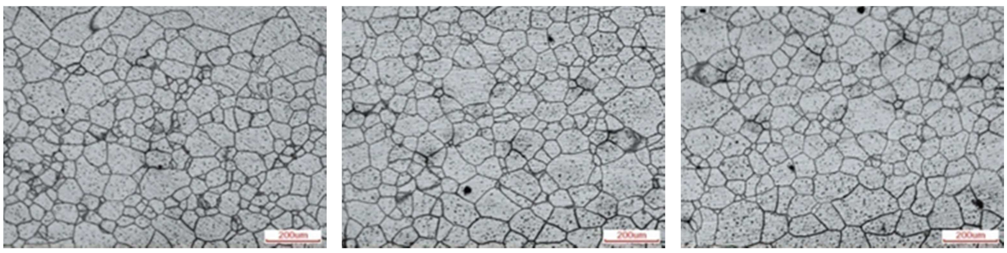

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Fig. 1. *Grain size of samples.*

In this experiment, the experimental material is pure aluminum which have no supersaturated solid solution and second phase, so $\rho_i C_i=0$, $\rho_p=0$. Furthermore, there is no difference among the casting process in each group, and the grain size and inclusions also keep the same, so $\rho_{gz}=0$, $\rho_{mix}=0$, which is shown in Fig. (1).

Therefore, the resistivity of pure aluminum in this paper is only influenced by $\rho_{(pure)}$ and ρ_{gas}, which are listed in the formula (5):

$$\rho = \rho_{(pure)} + \rho_{gas} \tag{5}$$

$\rho_{(pure)}$ is the resistivity of aluminum. ρ_{gas} is the effect of porosity, that is hydrogen content on the resistivity.

According to the formula (5), the theoretical resistivity of pure aluminum is constant, the hydrogen content is the only dependent variables. Therefore, relationship between hydrogen content and resistivity can be deduced with following physical model.

The physical model of resistivity is shown in Fig. 2. In order to simplify the calculation, one porosity with the radius r represent all the hydrogen in the pure aluminum, therefore, the volume of the porosity is equal to the hydrogen content in pure aluminum castings. Assuming the sample's length, width and thickness are a, b, c respectively, when the current passes through the X-axis direction, it will flow to the porosity and bypass because the porosity is not conductive. Therefore, the material's resistance consists of two parts, i.e. R_1, which is the resistance of porosity and R_2, which is the resistance of aluminum matrix. Thus the total resistance is the sum of R_1 and R_2. The black arrow indicates the direction of the electron motion in the Fig. 2.

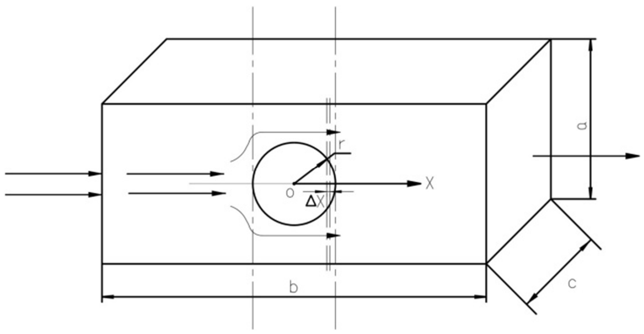

Fig. 2. The resistivity model of pure aluminum.

Cutting out a cross-section whose thickness is Δx in the dotted line, its resistance can be described as,

$$\Delta R = \rho_{Al} \cdot \frac{\Delta x}{a \cdot c - \pi(r^2 - x^2)} \left(x \in (0 \sim r)\right) \tag{6}$$

$$R_1 = \rho_{Al} \cdot \int_0^r \frac{1}{a \cdot c - \pi(r^2 - x^2)} dx \tag{7}$$

$$R_1 = \frac{\rho_{Al}}{\pi} \cdot \frac{1}{\sqrt{\frac{ac}{\pi} - r^2}} \arctan \frac{r}{\sqrt{\frac{ac}{\pi} - r^2}} \tag{8}$$

$$R_2 = \rho_{Al} \frac{b - 2r}{ac} \tag{9}$$

$$R_{total} = R_1 + R_2 = \frac{\rho_{Al}}{\pi} \cdot \frac{1}{\sqrt{\frac{ac}{\pi} - r^2}} \arctan \frac{r}{\sqrt{\frac{ac}{\pi} - r^2}} + \rho_{Al} \frac{b - 2r}{ac} \tag{10}$$

$$R_{total} = \rho_{total} \cdot \frac{b}{ac} \tag{11}$$

According to (6)-(10), ρ_{total} can be obtained

$$\rho_{total} = \frac{ac}{\pi} \cdot \frac{\rho_{Al}}{b} \cdot \frac{1}{\sqrt{\frac{ac}{\pi} - r^2}} \arctan \frac{r}{\sqrt{\frac{ac}{\pi} - r^2}} - \frac{\rho_{Al}}{b} \cdot 2r + \rho_{Al} \tag{12}$$

C_H is hydrogen content listed in the formula (13), if a=b=c, formula (13) can be converted into formula (14).

$$C_H = \frac{4\pi r^3}{3abc} \tag{13}$$

$$\frac{r}{a} = \left(\frac{3C_H}{4\pi}\right)^{\frac{1}{3}} \tag{14}$$

The relationship between resistivity and hydrogen content can be inferred though formula (12) and (14) (D, E, F are constants):

$$\rho_{total} = D \cdot \frac{1}{\sqrt{\frac{1}{\pi} - \left(\frac{3C_H}{4\pi}\right)^{\frac{2}{3}}}} \arctan \frac{\left(\frac{3C_H}{4\pi}\right)^{\frac{1}{3}}}{\sqrt{\frac{1}{\pi} - \left(\frac{3C_H}{4\pi}\right)^{\frac{2}{3}}}} + E \cdot \left(\frac{3C_H}{4\pi}\right)^{\frac{2}{3}} + F \tag{15}$$

According to the formula (15) and the experimental data, the relationship between resistivity and hydrogen content can be obtained through Origin software, which is listed in the formula (16). The result shows that the $R^2=0.96165$ (R^2 tends to 1, which demonstrates the fitting is credible) [7], and the fitting results are believable.

$$\rho_{total} = -0.00114 \cdot \frac{1}{\sqrt{\frac{1}{\pi} - \left(\frac{3C_H}{4\pi}\right)^{\frac{2}{3}}}} \arctan \frac{\left(\frac{3C_H}{4\pi}\right)^{\frac{1}{3}}}{\sqrt{\frac{1}{\pi} - \left(\frac{3C_H}{4\pi}\right)^{\frac{2}{3}}}} + 0.22976 \cdot \left(\frac{3C_H}{4\pi}\right)^{\frac{2}{3}} + 2.85207 \tag{16}$$

3.4. The Validation of the Resistivity Measurement Model

In order to further verify the feasibility of the model of measuring the hydrogen content in pure aluminum, the hydrogen evolution experiment of pure aluminum melting was carried out at 800ºC. And the fresh branches which can generate supersaturation hydrogen were inserted into it to increase hydrogen, then the sample was casted after different times. During this process, the hydrogen gas in the aluminum melting will slowly release until the equilibrium state is reached. The hydrogen content was measured by decompression solidification method and density method, and the resistivity was obtained by resistivity method.

The relevant results are shown in Table 2, the theory of hydrogen content C_L can be gained by taking the measured resistivity ρ_S into formula (16). As shown in Table 2, 5 groups of samples show that the measured hydrogen content is smaller than the theoretical result.

Fig. 3 shows the effect of melting time on hydrogen content, the hydrogen gas escapes intensely at the beginning, after about 20mins, the hydrogen content reaches equilibrium whose concentration is about 0.22 ml / 100g Al.

Table 2. *Hydrogen content and resistivity of pure aluminum casting with different melting time.*

NO.	Melting time (t/min)	Measured hydrogen content C_S (ml/100g Al)	Actual resistivity ρs ($\times 10^{-8}\Omega\cdot m$)	Theoretical hydrogen content C_L (ml/100g Al)	$\frac{\lvert C_S - C_L \rvert}{C_L} \times 100\%$
1	0	0.428	2.9561	0.430	0.465%
2	10	0.344	2.9495	0.348	1.149%
3	20	0.224	2.9370	0.227	1.322%
4	40	0.213	2.9362	0.220	3.182%
5	80	0.218	2.9367	0.224	2.679%

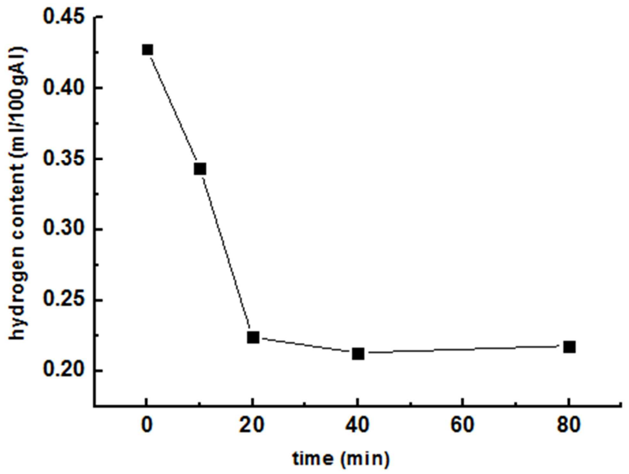

Fig. 3. *Effect of melting time on hydrogen content.*

1) Equilibrium concentration

In order to further verify the accuracy of the experiment and data, the final equilibrium concentration and precipitation time are discussed in the following. According to Sievert's law, the relationship between the concentration of hydrogen in the aluminum liquid C_H and the partial pressure of the hydrogen in the gas phase can be described as:

$$\lg C_H = -\frac{A}{T} + B + \frac{1}{2}\lg P_{H_2} \quad (17)$$

Where, T refers to melting temperature, K. A and B value are constants which related with the composition of the melts, the A value is 2550, and the B value is 2.62 in pure aluminum [8].

The partial pressure of the hydrogen in the gas phase can be obtained by combining the formula (18), (19) and (20).

$$P_W = 611.2\exp\left(\frac{17.62t}{243.12+t}\right) \quad (18)$$

$$U = P_{H_2O}/P_W \quad (19)$$

$$k = P_{H_2}/P_{H_2O} \quad (20)$$

t represents atmospheric temperature, ºC. P_W refers to saturated water vapor partial pressure, Pa. U is relative humidity, %. P_{H2} is the equilibrium pressure of hydrogen above the surface of aluminum liquid, Pa. P_{H2O} is the equilibrium pressure of water vapor above the surface of aluminum liquid, Pa. k refers to the ratio of partial pressure of hydrogen gas and water vapor pressure on the surface of aluminum liquid, whose value is related to temperature [9-10], according to the literatures [11-12], the value of the calculation is 1.65 x 10^{-5} at 1073K.

The saturated water vapor partial pressure P_W can be calculated which is 3160Pa by the formula (18) under the conditions of the atmospheric pressure and atmospheric temperature 25ºC, then the water vapor partial pressure P_{H2O} is 948Pa under the atmospheric relative humidity 30%. In the formula (20), (17), it is known that the hydrogen content in the molten aluminum is decreased to 0.219ml/100gAl when achieve the dynamic equilibrium under the melting temperature 1073K. The equilibrium hydrogen content is 0.22 ml/100gAl in the experiment, which is closed to the theoretical equilibrium concentration.

2) Precipitation time

Hydrogen precipitated from molten aluminum has two manners: atomic diffusion and the formation of bubbles escape. According to the literatures [13], it is known that bubble zone is 18cm deep from formula calculation, but the crucible is high 50cm. so hydrogen atom can only rely on the form of diffusion to precipitate at the bottom of the aluminum melting. Therefore, hydrogen diffusion path is 32cm, and the floating path of bubble is 18cm. The diffusion time of hydrogen in the melt can be determined by formula (21) [14], and the diffusion coefficient of hydrogen can be calculated by formula (22) [15].

$$L = \sqrt{2Dt} \quad (21)$$

$$D = 3.8 \times \exp\left(-\frac{2315}{T}\right)\ cm^2/s \quad (22)$$

L refers to the diffusion distance of hydrogen, L=32cm. D is hydrogen diffusion coefficient, D=0.439cm^2/s. t is diffusion time, s. T is temperature, T=1073K. So we can calculated hydrogen diffusion time t_l=19.44min.

The rising velocity of hydrogen bubble can be calculated by Stokes formula (formula 23) [16].

$$v = \frac{2R_H^2(\rho_{Al}-\rho_H)}{9\eta} g \quad (23)$$

V is the rising velocity of hydrogen bubble. R_H is bubble radius, according to the literature [17] $R_H=10^{-3}$m. ρ_{Al} is the density of liquid aluminum alloy, ρ_{Al}=2.31×10^3kg/m^3. ρ_H is the density of hydrogen, which can be neglected. η is the viscosity of aluminum liquid, according to empirical formula [18], η=1.908×10^{-3} pa·s. g is the acceleration of gravity, g=9.8m/s^2.

We can calculate the bubble rising velocity v=2.637m/s by the formula (23), so the hydrogen bubble rise time t_2=4.10min. The total time of hydrogen evolution from aluminum liquid is 23.53min, and the equilibrium time was about 20min in the experiment, which was close to the equilibrium time obtained by theoretical calculation.

It is found that the theoretical values which are equilibrium hydrogen content and equilibrium time through theoretical derivation and formula calculation are close to the experimental results. It indicates that the hydrogen evolution experiment is more objective and reliable. The theoretical hydrogen content calculated by formula (18) has a little difference from the actual hydrogen content measured in the hydrogen evolution experiment, which verifies the feasibility of the resistivity measurement method for the hydrogen content in pure aluminum.

4. Conclusion

1) The resistivity can reflect the hydrogen content of aluminum casting, the higher the hydrogen content, the higher the resistivity.

2) The relationship between resistivity and hydrogen content in pure aluminum castings can be described as,

$$\rho_{total} = -0.00114 \cdot \frac{1}{\sqrt{\frac{1}{\pi} - \left(\frac{3C_H}{4\pi}\right)^{\frac{2}{3}}}} \arctan \frac{\left(\frac{3C_H}{4\pi}\right)^{\frac{1}{3}}}{\sqrt{\frac{1}{\pi} - \left(\frac{3C_H}{4\pi}\right)^{\frac{2}{3}}}}$$

$$+0.22976 \cdot \left(\frac{3C_H}{4\pi}\right)^{\frac{2}{3}} + 2.85207$$

3) The hydrogen content reaches the equilibrium concentration (0.224Alml/100g) in the smelting of pure aluminum about 20min under the melting temperature 800ºCand relative humidity 30%. The data coincide with the theoretical equilibrium time 23.53min and theoretical equilibrium concentration (0.219ml/100g), indicating that the hydrogen evolution experiment of objective and reliable, verify the feasibility of hydrogen content in pure aluminum resistivity measurement model.

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