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Influence of element Cu on hydrogen content in superheated aluminum melt①

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[Abstract] The hydrogen content in molten Al-Cu alloy increases remarkably when the temperature of the melt rises to about 780 ℃. The effects of alloying element are theoretically analyzed in terms of Wagner interaction parameter. Furthermore, analyses indicate that the alloy element Cu plays an important role in the hydrogen content in superheated Al-Cu alloy melt below about 780 ℃. The conclusion is drawn that the degree of gassing in molten Al-Cu alloy is bound up with the properties of oxide film of Al alloy melts. The results make it clear that the hydrogen content in the molten aluminum reduces with increasing element Cu dissolved in aluminum melts at the same temperature.

[Key words] element Cu; hydrogen; interaction parameter; oxide film
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1 INTRODUCTION

Hydrogen is the main gas appreciably soluble in aluminum and its alloys. The difference in solubility between liquid and solid aluminum often leads to the rejection of almost all of the dissolved hydrogen on the solidification of liquid aluminum and results in the formation of hydrogen bubbles which ultimately cause porosity in castings and ingots and blisters on sheets and plate. Gas porosity has a negative effect, not only on the mechanical properties but on the machinability and the surface properties of aluminum castings[1~3]. For many years, the hydrogen in aluminum alloy melts have been investigated and analyzed. But it is the serious problem to the foundryman of aluminum alloys because the hydrogen content in aluminum alloy melts was influenced by many factors such as alloying elements[4], temperature[5], holding time. The hydrogen content in aluminum alloy melts needs to be discussed further.

So far, the reports have only been about the qualitative analysis that superheated temperature has an effect on hydrogen content, namely, it is considered that the hydrogen solubility rises straightly with increasing temperature above melting point of metals popularly[6]. Furthermore, the earlier research considered that the hydrogen solubility in the molten aluminum varies up and down with increasing temperature[7], but this viewpoint was short of powerful experimental evidence. Few people studied superheated aluminum melts which have a positive effect on inherent quality of products[7], so it is of important practical significance to study the hydrogen content in superheated aluminum melts. The influence of the element Cu on the hydrogen content in molten aluminum is studied both from theoretical aspect and experimental aspect in this paper.

2 EXPERIMENTAL

The ingot materials for this experiment are Al-4% Cu alloy, Al-6% Cu alloy, Al-8% Cu alloy, and Al-12% Cu alloy. Melting equipment adopted is a resistance furnace with a crucible made from graphite clay.

A RPT method (Reduced Pressure Test) is used to determine the hydrogen in aluminum melts. The instrument used in our work is HYSCAN Ⅱ made by SEVERN SCIENCE LTD., UK. Measurement accuracy is 10^{-4} mL/g and measurement range is 0~0.019 9 mL/g. Each measurement needs about five minutes.

The testing procedure is: a constant mass of the melt (approximately 100 g) is placed in a chamber and the pressure is reduced to a predetermined value (10 Pa) by a vacuum pump. The chamber and associated vacuum system is then isolated from the pump and the sample is 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. The hydrogen content value of the melt is displayed and printed after about five minutes. The hydrogen content in every alloy respectively is tested from 660 ℃ to 900 ℃ at an interval of 40 ℃ with the same holding time.

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3 RESULTS AND DISCUSSION

Fig. 1 shows that the hydrogen content in molten Al-Cu alloys retains constant below about 780 ℃, but it rises straightly above this temperature. Fig. 2 shows that the hydrogen content in the molten aluminum reduces with increasing element Cu dissolved in aluminum melts at the same temperature.

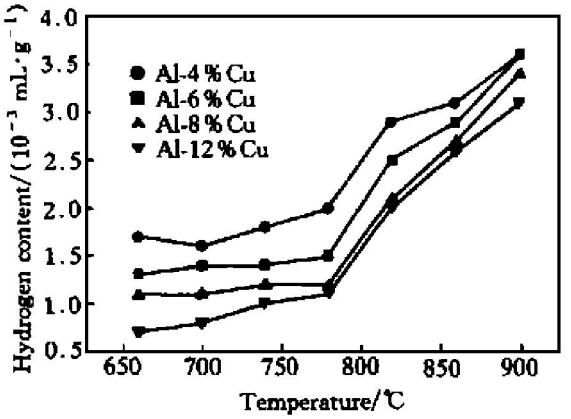

Fig. 1 Variation of hydrogen content in Al-Cu alloy melts with temperature

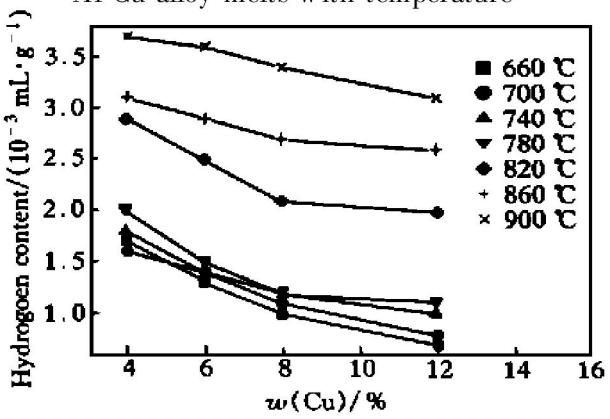

Fig. 2 Variation of hydrogen content in Al-Cu alloy melts with copper content at different temperatures

From one viewpoint, the reason for our gas problem lies in the chemical and physicochemical properties of aluminum. The partial pressure of hydrogen in the air is about 5×10^{-6} Pa, which is lower than that in aluminum alloy melts. So it is learned that the hydrogen in aluminum alloy melts does not come from the hydrogen in the air. From the practical point of view, aluminum is highly relative and easily decomposes the oxide of hydrogen by

$$2Al(l) + 3H_2O(g) \rightarrow \gamma\text{-}Al_2O_3(s) + 6[H] \quad (1)$$

This means that it is easy to aid gas to our metal by bringing steam or water vapor (present in the air as humidity) in contact with the melt. In the range from 934 to 1 123 K, the standard free energy $\Delta G^{\ominus}$ can be computed by the following equation:

$$\Delta G^{\ominus} = -67\,624 - 19.39T \quad (2)$$

This reaction continues even if the partial pressure of water vapor in the dry air is 2.59×10^{-20} MPa at 1 000 K. At 18 ℃, 63% of relative humidity and 1.3 kPa partial pressure of water vapor in the air, the partial pressure on the surface of aluminum alloy melts is up to 9.02×10^{9} MPa. Note that hydrogen content is proportional to the square root of $p(H_2)$, which means that $p(H_2)$ increases rapidly as hydrogen increases. In fact, the partial pressure of hydrogen is far lower than the above one because of the Al_2O_3 oxide film on the aluminum alloy melts.

From above, the critical factor of aluminum alloy melts gassing is the partial pressure of water vapor in the air and also bears on the smelting temperature. As the aluminum alloy melts, the critical factor of aluminum alloy melts gassing is the properties of oxide film on the surface which has something with the alloy elements[8]. The alloy elements in aluminum alloy are divided into two groups in terms of their properties. One is non-surface active elements such as Cu, Fe and Si. The other is surface active elements such as Li and Mg (not discussed). The reason of the addition of Cu reducing hydrogen content is that the oxide film of Al atoms with Cu, Fe and Si has the same crystal lattice of γ-Al_2O_3 whose structure is compact. Fig. 1 shows that the reason of the hydrogen content above about 780 ℃ increasing abruptly is that the allotropic conversion of Al_2O_3 happens by

$$\gamma\text{-}Al_2O_3 \xrightarrow{750\sim 900\ ℃} \alpha\text{-}Al_2O_3 \quad (3)$$

The inner surface of γ-Al_2O_3 is compact, but the outer surface is loose, having many small holes(d 50~100 Å). Vapor and hydrogen are absorbed in those holes. When γ-Al_2O_3 turns into α-Al_2O_3, the oxide film losing vapor and hydrogen cause the hydrogen content to increase sharply in liquid aluminum alloy.

From the other viewpoint, one is that their addition to liquid Al decreases the affinity of the melt for hydrogen such as Cu, Fe and Si. As shown graphically in Fig. 3 by some of the most reliably reported values[5, 9], alloying elements have a strong (and varying) influence on hydrogen solubility in liquid aluminum. The Taylor series expansion formalism first proposed by Wagner and Chipman for describing the functional relationship between logarithm of activity coefficient and composition of a dilute constituent in an alloy system consisting of three or more components can be applied to quantify the effects of alloying elements on the thermodynamic behavior of hydrogen in aluminum. Lupis and Elliott extended the treatment of Wagner to include the higher orders which are required for higher concentrations of alloying elements. Thus, for an Al-H-Cu system, the functional relationship between $\lg f_H$ and the concentration of alloying elements in mass fraction can be described by

$$\lg f_H = \lg f_H^{o} + e_H^{H} w(H) + \sum_{x=2}^{n} r_H^{Cu} [w(H)]^2 + \sum_{x=2}^{n} e_H^{Cu} w(Cu) + \text{higher order terms} \quad (4)$$

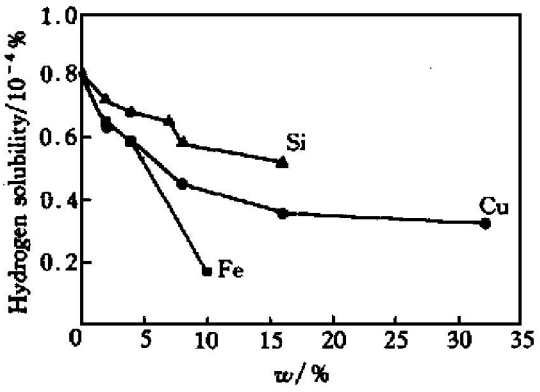

Fig. 3 Reported effects of alloying elements on hydrogen solubility in liquid aluminum at 973 K and 101.3 kPa partial pressure of hydrogen

Since the standard and reference states are based on an infinitely dilute solution of hydrogen (1% H) in liquid aluminum, $f^{o}_{H}=1$; the self-interaction parameter of hydrogen in liquid aluminum, e^{H}_{H}, is zero since hydrogen solution obeys Sievert's law over the reported temperature ranges of interest. Other interaction parameters are defined as follows:

$$e^{Cu}_{H}=\left[\frac{\partial(\lg f^{Cu}_{H})}{\partial w(Cu)}\right]_{T,\ p(H_2)}$$

$$r^{Cu}_{H}=\left[\frac{1}{2}\frac{\partial^2(\lg f^{Cu}_{H})}{\partial[w(Cu)]^2}[w(Cu)]^2\right]_{T,\ p(H_2)} \quad (5)$$

where e^{Cu}_{H} and r^{Cu}_{H} are referred to as the first and second order interaction parameters respectively[4].

The values of the first order interaction parameter are obtained from the slopes of the linear portions of the plots of $\lg f^{Cu}_{H}$ versus w(Cu) (Fig. 4). With relatively dilute solutions and low concentrations of the alloying elements, the behavior of hydrogen usually can be expressed satisfactorily by the use of the first order term, e^{Cu}_{H}, only. However as apparent in Fig. 4, there is a considerable curvature in the $\lg f^{Cu}_{H}$ versus w(Cu) plots for Cu. Thus, the second order

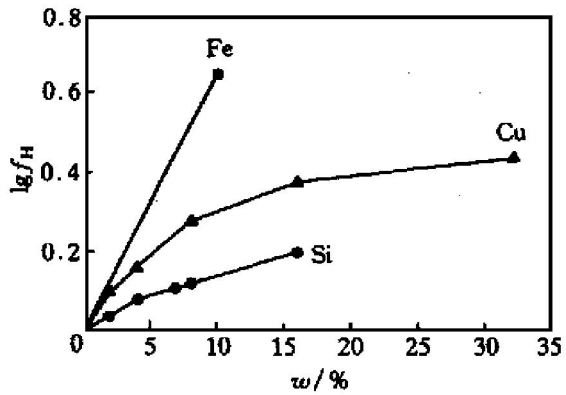

Fig. 4 Logarithm of activity coefficient of hydrogen versus mass fraction of alloying elements in liquid aluminum at 973 K and 101.3 kPa partial pressure of hydrogen

coefficients, r^{Cu}_{H} was calculated, by curvilinear regression analyses. The analyses yielded coefficients that were statistically significant. It is noteworthy that all of the calculations and analyses were limited to the reported alloying element composition and temperature ranges. The interaction parameters obtained from the analyses are given in Table 1 in a range of temperature.

Table 1 Calculated first order (e^{Cu}_{H}) and second order (r^{Cu}_{H}) interaction parameters for hydrogen solution in Al-H-Cu alloy at $p(H_2)=101.3$ kPa[5]

Interaction parameters	973 K	1 023 K	1 073 K	1 123 K
e^{Cu}_{H}	0.033 4	0.031	0.028	0.026 6
r^{Cu}_{H}	−0.000 65	−0.000 58	−0.000 52	−0.000 46

The other is that their addition to liquid Al increases the affinity of the melt for hydrogen. This is not entirely surprising since these elements have high affinity for hydrogen.

The properties of oxide film which can prevent Al melt from absorbing hydrogen change owing to the influence of Cu in Al melt below 780 ℃. The more the Cu content is, the lower the hydrogen content will be. Above 780 ℃, the conversion of crystal lattice of Al_2O_3 will happen and lots of the oxide inclusion will form with increasing temperature. Consequently, the hydrogen content of the melt increases sharply with temperature.

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