Degassing of Pure Copper Melt by Ultrasonic Cavitation

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Abstract. The effect of high intensity ultrasonic vibration (UV) on degassing of pure copper has been studied in this paper. The methods of reduced pressure test (RPT) and direct hydrogen and oxygen measurements are used for the evaluation of degassing efficiency on hydrogen and oxygen concentrations. The results showed that high intensity UV had a significant degassing effect for the commercially pure copper (CP-Cu) melt. With UV, the density index Di was reduced from 11.94 to 1.13%, and the product of hydrogen-oxygen concentration ([%H] [%O]) in the liquid Cu was decreased to 1.44×10⁻⁵ from 6.62×10⁻⁵. It was also found that electric power and ultrasonic treatment time could influence the degassing efficiency.

1. Introduction

Usually, in copper foundries, several degassing techniques have been developed for the analysis of hydrogen in pure Cu [1]. These techniques can be divided into three categories: Vacuum Degassing is capital intensive, limited by the vacuum pressure that can be created over the melt, and can lead to the loss of desirable elements. In some cases, Argon or Nitrogen is used in a lance application for degassing. The purge gas collects hydrogen, and to a certain extent, precipitated oxide phases from the melt. In the case of Chemical Degassing, some of the reagent metals (Rare earths, Li and Ca) can be expensive, and the compounds of the undesirable elements may remain as inclusions in the metal. Therefore, there exists a need for a commercially viable, energy efficient, and environmentally sound molten metal degassing technique which overcomes the aforementioned disadvantages.

Ultrasonic degassing (USD), an environmentally clean and cheap technique, uses high intensity ultrasonic vibrations (UVs) to generate oscillating pressures in liquid metal, which is a possible way to overtake such drawbacks and to improve hydrogen removal [2]. USD is common in molten Al [3], but this method is not as of yet utilized in pure copper or copper alloy foundries to any great extent.

In this work, an experimental device has been built in Dalian Jiao Tong University for the degassing of commercially pure copper (CP-Cu) using UV at a frequency of 20 kHz and vibration intensities up to 3000 W. Parametric studies have been carried out to investigate the efficacy of the USD of molten pure Cu under reduced pressure. This article mainly focuses on the effect of UV on hydrogen and oxygen concentrations and porosity formation for CP-Cu.

2. Experimental

2.1. Raw materials and USD Apparatus
The copper of 500 g was held in a graphite crucible with a 50 mm diameter and 75 mm height, then melted in a standard silicon carbide resistance furnace. Melt temperature was controlled with a PID temperature controller. When the copper were completely melted, it was stood 30 min for homogenization. Afterward, the crucible with the pure Cu melt was took out rapidly by crucible tongs from the furnace. Immediately USD was carried out under the various processing conditions, which included the electric power, degassing time, temperature of melt, and ambient humidity. The electric power was 1000, 2000 and 3000 W. The degassing time was 5, 10 and 15 s. The humidity was varied from 46, 56 to 66%. Four melt temperatures, 1210, 1230, and 1250 °C were tested, respectively.

In addition, USD combined with chemically degassing was also carried out in air. Chemical degassing was conducted by using dry nontoxic degasser tablets (NDT) containing nitrate and active carbon (1.0 wt. % of the molten Cu). For comparison, the single NDT and without USD were first carried out in the Cu melt. The experimental processing is shown in Figure 1.

2.2. Reduced pressure test
A Reduced Pressure Test (RPT) [4] was used to evaluate porosity levels in the pure Cu. Molten Cu (~200 g) was poured into a preheated clay-graphite cup and allowed to solidify under a reduced pressure of 73 mbar. At the same time, atmospherically solidified cup sample was also prepared from the same melts for comparison (see Figure 1).

The gases content (mainly H₂ and H₂O [1]) was then assessed by calculating the density index \( D_i \) [5] from the measured densities using a MP61001J balance:

\[
D_i = \frac{D_a - D_v}{D_a}
\]

where, \( D_i \) is the density index, \( D_a \) is the density of the sample solidified in air and \( D_v \) is the density of the sample solidified under partial vacuum. \( D_i \) can be used as a measure of the gases content. The smaller the \( D_i \) value, the lower the content of hydrogen and oxygen. After measuring the density, the RPT specimens were sectioned in the middle vertically and were polished to reveal the extent of the gas porosity.

2.3. Direct measurement of hydrogen, oxygen concentration
According to the Ostrom’s studies [6], the molten copper mainly evolve water vapour with some hydrogen. Therefore, both the elements of hydrogen and oxygen were selected to test. To confirm the RPT results, the hydrogen and oxygen concentrations of samples solidified in air were melted in a high purity graphite crucible (the inner diameter of 12.7 mm and height of 24 mm) and directly measured using the LECO-TCH600 analyzer. The test precision is 0.001 ppm. For comparison, the hydrogen and oxygen concentrations in the non-treated melt were also directly measured at the same conditions.

3. Results

3.1. Samples solidified at atmospheric pressure and partial vacuum without UV

Figure 2 shows the porosity levels in the specimens without melt degassed in air (Figure 2a) and under partial vacuum (Figure 2b). The top surface of the sample solidified in air is a little of convex. There is a flat porosity about 10 mm in length near the top of the sample, and a round pores about 1 mm in diameter inside the sample (seen in Figure 2a). Such porosities are formed due to gaseous evolution during the final stage of solidification.

Under partial vacuum, the gases content is high. The sample has a convex top surface, the morphology of porosities look like a honeycomb with size in order of centimetre, and is full of big and small cavities (Figure 2b). They are formed in liquid state during or shortly after columnar crystals coherency bridging. When shrinkage occurs, there is a negative pressure in the sample, more pores will be formed because of higher gases level, which can offset the solidification shrinkage. Therefore, there is an obvious convex top surface, as shown in Figure 2b. The measured densities \( D_a \) and \( D_v \) were 8.2953 and 7.3051 g cm\(^{-3}\), respectively. The calculated density index \( D_i \) was 11.94\%, which implies the gases level is high.

3.2. Degassing by UV

In the same conditions as the non-treated one, the pure Cu melt was treated by UV at 1210 °C and 3000 W for 15 s. The measured densities \( D_a \) and \( D_v \) were 8.5849 and 8.4875 g cm\(^{-3}\), respectively; moreover, the calculated density index \( D_i \) was 1.13\%, which indicates the gases level for the treated Cu melt is low. The comparison of the densities and the density indices between treated and non-treated samples is shown in Figure 3, which shows that the \( D_i \) value from 11.94\% (without UV) to 1.13\% (with UV). The result indicates that UV has a significant degassing effect on the CP-Cu.

Figure 4 shows the vertical cross-section of the treated samples solidified in air (Figure 4a) and under partial vacuum (Figure 4b). For the treated sample solidified in air, due to the lower gases level, it is more difficult to form porosity during solidification, and shrinkage cannot be so easily offset by gases porosity. Therefore, the concave top surface was formed, as shown in Figure 4a. Although USD can degas the pure Cu melt, there is still some hydrogen and oxygen in the molten Cu. Because there
is less offsetting by the formation of pores, there will be more shrinkage. Consequently, more shrinkage porosity was formed. For the treated sample solidified under partial vacuum (Figure 4b), the pores are smaller and much less number, the top surface is more convex than the non-treated sample (Figure 2b). This is due to the reduction in hydrogen and oxygen concentrations by USD.

In order to confirm the degassing effect by USD, the hydrogen and oxygen concentrations in the Cu samples solidified in air before and after USD was also directly measured using the LECO analyzer. The results are shown in Figure 5. After USD, the hydrogen and oxygen concentration product $[\%H][\%O]$ was reduced from $6.624 \times 10^{-5}$ to $1.440 \times 10^{-5}$, which supports the results of RPT. Due to the difficulties of direct hydrogen and oxygen measurement on a laboratory scale, based on the coincidence of the results between the RPT and the direct hydrogen, oxygen measurement, therefore, only the RPT was used to evaluate the gases level in the melts processed under different conditions.

**Figure 3.** Comparison of densities and density indices of CP-Cu with and without USD.

**Figure 4.** Sectioned CP-Cu samples solidified after UV 15 s.

**Figure 5.** $[\%H][\%O]$ product in CP-Cu melt with and without USD.

### 3.3. Evaluation of USD for processing parameters

It is necessary to study the effect of processing parameters on the degassing efficiency and to optimise the processing conditions. In the present work, ultrasonic electric power and ultrasonic treatment time were studied.

To evaluate the effect of ultrasonic electric power, the molten Cu was treated at 1210 °C for ultrasonic electric power of 0 (i.e. without USD), 1000, 2000 and 3000 W for 15 s. The values for $D_a$, $D_v$ and $D_i$ are shown in Figure 6. With the increase of electric power, $D_i$ decreases rapidly from 11.94, 8.08, 3.34 and 1.13 %, respectively. It seems that the USD efficiency is electric power dependent, and that this has an evident influence on both the gases level and the Cu ingot density.
The effect of degassing time on degassing effect was investigated by USD the CP-Cu melt at 1210 °C for 5, 10 and 15 s. During degassing the ultrasonic electric power was kept at 3000 W and the ambient humidity was 56%. The results are shown in Figure 7. With increased USD time, $D_i$ does not change much within the first 5 s and then rapidly reaches a minimum level, indicating that USD time has a significant degassing effect on CP-Cu, and the optimal degassing time is 15 s in this work.

**Figure 6.** Variation in densities and $D_i$ of CP-Cu as function of ultrasonic power.

**Figure 7.** Variation in densities and $D_i$ of CP-Cu as function of ultrasonic time.

4. Discussion

4.1. Degassing and Deoxidation by Ultrasonic Cavitation

Figure 5 illustrates the hydrogen and oxygen concentration in molten Cu by USD above liquidus. It seems, USD not only can degas the hydrogen but also can deoxidize the copper melt. The mechanism of ultrasonic degassing is closely related to the phenomenon of cavitation in the molten Cu. Figure 8 presents the schematic diagram of the degassing and deoxidation mechanism by ultrasonic cavitation. Generally, the mechanism of degassing and deoxidation above liquidus can be divided into four stages:

**Figure 8.** Schematic diagram of degassing and deoxidation mechanism by ultrasonic cavitation.
(1) Nucleation of cavitation bubbles on nuclei (usually nonwettable oxide particles containing cavities) and growth of the bubbles due to the diffusion of hydrogen atoms from the surrounding Cu melt to the bubbles. i.e., for the elementary reaction can be expressed as [7]:

$$2H \text{(melt)} = H_2 \text{(g)}$$  \hspace{1cm} (2)

(2) In the present case of deoxidation of molten Cu, the reaction in equilibrium at the gas/melt interface is represented by [7]:

$$H_2 \text{(g)} + Cu_2O \text{(melt)} = 2Cu \text{(melt)} + H_2O \text{(g)}$$ \hspace{1cm} (3)

As a result, the reaction formed vapor, which act as nucleating sites further promote the formation of cavitation bubbles in liquid Cu and create a large number of cavitation bubbles which accumulate hydrogen, because vapor does not dissolve in molten Cu.

(3) Coalescence of bubbles to form large bubbles [3, 8].

(4) Float of large bubbles to the surface of the molten Cu and escape of the bubbles at the top melt surface [3].

5. Conclusions

High-intensity UV was introduced in the molten pure Cu. Both RPT and direct hydrogen and oxygen measurement were carried out to study the effect of UV on hydrogen, oxygen concentration and porosity formation. Based on the experimental results, the following conclusions can be drawn:

(1) USD has a significant degassing effect on molten pure Cu, which can reduce the hydrogen and oxygen concentration product [%H]-[%O] in pure Cu from $6.624 \times 10^{-5}$ to $1.440 \times 10^{-5}$ and the density index $D_i$ from 11.94 to 1.13%.

(2) With the increase of ultrasonic electric power and ultrasonic treatment time, the density index $D_i$ decreases rapidly and then reaches a minimum value. On the contrary, with the increase of melt temperature and ambient humidity, the density index $D_i$ increases gradually and then reaches to a maximum value.

(3) The USD not only can degas the hydrogen but also can deoxidize the Cu melt.

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