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High efficient removal of tin from lead bullion based on the oxygen-controlling method under vacuum

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ABSTRACT

Conventional detinning process of lead bullion usually includes the following problems: the oxidizing refining process takes a long time to finish the oxidation of tin and products mass slag, while the basic refining process consumes large reagent, and the labor condition is poor. Therefore, a novel technique with oxygen controlled under vacuum condition for removing tin in crude lead was investigated, which shows characters such as, low-energy consumption, less metal wastage and environmental friendly. During this process, tin was removed from lead bullion by converting to tin oxide and concentrating in the dross. The experimental results showed that the residual Sn-concentration in detinned lead was about 2 ppm corresponding to the lead loss ratio about 2–3 wt% under the following experimental conditions: temperature of 750 °C, oxidation time of 80 min, agitation speed of 100 rpm and air flow rate of 60 mL/min corresponding to the residual gas pressure of 57 KPa.

1. Introduction

As one of the most common metals, lead is widely used in lead-acid batteries, ammunition, cables, lead tube and solder, etc. Crude lead is required to be refined to remove various impurities before its extensively application in various sectors. It is well known that tin is the most common impurity in crude lead. At present, there are various detinning methods, such as oxidizing refining, basic refining, and electrolytic refining, etc. The pyrometallurgical refining technique accounts for about 70% of the refined lead in the world. Until now, only some of countries, such as Canada, Peru, Japan and China utilize the electrolytic refining technique [1].

The pyrometallurgical refining technique of removing tin from crude lead is based on the principle that tin has a stronger affinity for oxygen than lead. In the process of oxidizing refining, tin in molten lead is oxidized by oxygen gas as oxidizing agent whereby the tin enters the slag, but this technique has following shortcomings such as a long time to finish the process of oxidizing refining, large loss of lead, poor working conditions, high fuel consumption, etc. The basic refining process that uses niter and caustic as oxidant to make tin be oxidized is shorter process, lower heating temperature and less metal wastage than the process of oxidizing refining. Therefore, the basic refining process is extensively applied. Nevertheless, this method also has some weaknesses, for example, large reagent consumption, poor work condition, complicated treatment process for basic refining slag [2–5]. In the electrolytic refining process, crude lead casting into the anode plate needs to be primary detinned to reduce tin-content and electro-refining process costs longer production period, which means more energy will be consumed. If the Sn-content of lead bullion is above 0.05 wt%, the electrolytic process is not suitable for the application of detinning [6,7]. Meanwhile this approach produces undesirable residue which is known as tin anode slime [1,8–10].

To solve above problems, a novel technique of treating lead bullion containing about 0.2 wt% of tin is investigated in this paper. In the new method, the reaction system was under vacuum and the oxygen content of the mixed gas introduced to system was controlled according to the need. Thus the detinning process was carried on with oxygen control under vacuum condition. We aim at obtaining a high-efficiency removal rate of tin (Sn-content less than 5 ppm), shorter production period, less lead loss ratio, economic and environment friendly method for detinning. That is significant for refining of lead bullion. As the latest car battery grids contain significant amounts of Sn, this issue is also of high importance for waste lead storage battery recycling plants.

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2. Experimental procedures

2.1. Materials

Because the average tin content in lead bullion is about 0.1–0.2 wt% in China according to the reference [11], raw material used in the experiments was crude lead bullion contented about 0.2 wt% by weight tin, which was self-prepared. When pure lead was smelted in melting furnace, pure tin (Sn-content 99.9%) metal was put into the molten lead to increase the tin content to about 0.2 wt%. The chemical composition of pure lead was shown in Table 1. This melting process maintained 3 h and was stirred by a graphite rod to ensure the alloy's homogeneous mixing, before the molten was casted to form cylindrically ingot (65 mm in diameter and 10 mm in height, Fig. 2(a)) to ensure the convenience for experiment operating. The homogenized samples of raw material were characterized by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry), which indicated the lead contained about 0.2 wt% Sn. The content of other impurities were very low, which basically has no effect on the experimental process and result.

2.2. Apparatus

The experiments were carried out on the self-made apparatus, which mainly consists of reactor, electric motor, resistance furnace, as shown in Fig. 1. The furnace temperature was controlled by a temperature controller connected with a thermocouple. The reactor was connected with a vacuum pump and pressure gage to maintain constant pressure of the reactor. The bottom of the reaction reactor was connected to gas-guide tube to make the air can enter the reactor. The stirring paddle was connected with electric motor to let itself stir the molten lead at a constant rotating speed. In the top of the reaction reactor was connected with water condenser to cool the plastic gland cover. The porcelain beads, which are less dense than molten lead, were put into the reactor and hinder slag powder by-product from blowing across. The vacuum pump model number was VP50, which was purchased from the company that named “LabTech” and its parameter was shown in Table 2.

2.3. Methods

The crude lead was primarily weighed, loaded in the stirring shaft and put into the reactor (Fig. 2(c)). Subsequently, the reactor was heated to certain temperature under vacuum. When the molten temperature reached the desired experiment temperature, the steel stirring paddle began to stir molten lead and the gas flowmeters were open to ensure that oxygen-enriched air was introduced into the molten from the bottom of the reactor (Fig. 3(a)), and then the timing of oxygen control by vacuum treatment process started. In order to mix the molten lead and oxygen of gas well, the diameter of the hole where gas entered is less than 1 mm. After the experiment, the plug-hole in the bottom of the reactor (5 mm in diameter) was opened to let the molten flow into the graphite crucible (Fig. 3(b)) and the dry oxide drosses left at the reactor poured out from the outlet (Fig. 3(c)). The cooled detinned lead and the dry oxide drosses were weighed, and sampled. The mass of the homogenized samples was about 25 g and the dry oxide drosses characterized by XRD (X-ray diffraction). The Sn-content (SC) of the detinning lead was determined by ICP-MS (Inductively coupled plasma mass spectrometry). The lead loss ratio (LR) was calculated by the following formulas:

$$\text{Lead loss ratio } (\%)\ L = \frac{m_1 - m_2}{m_1} \times 100\% \quad (1)$$

where m_1 is the mass of raw material (g) and m_2 is the mass of detinned lead.

Table 1
Chemical composition of pure lead.

Element	Content (wt%)
Pb	99.99524
Cu	0.00055
Bi	0.0028
Ag	0.00015
As	0.00026
Sb	0.0003
Sn	0.0002
Zn	0.0002
Fe	0.0003

2.4. Principle

The detinning process is on basis of tin of stronger oxidation activity than lead [7]. In the temperature range from 650 to 850 °C, the oxide of lead and tin were SnO_2 and PbO, respectively [12,13]. During the process, the basic oxidization reactions of this system are as follows:

$$Sn(l) + O_2(g) = SnO_2(s) \quad (2)$$

$$2Pb(l) + O_2(g) = 2PbO(s) \quad (3)$$

$$2PbO(s) + Sn(l) = 2Pb(l) + SnO_2(s) \quad (4)$$

The basic oxidization feasibility is determined based on the change of ΔG (Gibbs free energy). When ΔG is negative, the reaction is spontaneous under the constant pressure and constant temperature. Conversely, when ΔG is positive, the reaction is not spontaneous. The formula of ΔG is as follows:

$$\Delta G = \Delta G^0 + RT \ln Q \quad (5)$$

where ΔG^0 is the standard reaction Gibbs free energy, the change in the Gibbs free energy which accompanies the conversion of reactants in their standard states into products in their standard states; R is the universal gas constant; T is the temperature; Q is the reaction quotient. Fig. 4 shows the variation of ΔG^0 in the temperature range from 650 °C to 850 °C for reactions (2), (3) and (4) (HSC CHEMISTRY 5.1). According to Fig. 4, ΔG^0 of reactions (2), (3) and (4) are all negative as the system temperature increased and the ΔG^0 of reaction (2) is always more negative than that of reaction (3), which means the Sn is more easily oxidized than Pb in their standard states. However, the activity of Sn in molten lead is low and the activity of Pb is close to unity in practice. Because the amount of Pb is much larger than Sn in the molten. Therefore, the reaction (3) and (4) is dominant and the reaction (4) is the main reason for removing tin in lead bullion according to the reference [14,15].

3. Results and discussion

To investigate the detinning process of crude lead in more detail, the single-factor experiments were carried out and the experimental conditions including oxidation temperature, oxidation time, agitation speed of stirring paddle, the flow rate of oxygen-enriched air (air content 50%), and the percentage of air in oxygen-enriched air was investigated.