

PREPARATION OF Pb-Ca-Na MASTER ALLOY USING MOLTEN CHLORIDE SALT ELECTROLYSIS^①

Song Renying, Wang Xingjie, Luo Shumei, Jiang Chan, Tang Dingxiang
*Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022*

ABSTRACT An electrolysis technique for co-deposition of Ca^{2+} and Na^+ at the liquid lead cathode was put forward. The experiment was carried out at an electrolysis temperature below 650 °C and had a current efficiency of 98%, which are respectively 100~300 °C lower and 15%~30% higher than those reported both at home and abroad.

Key words Pb-Ca-Na master alloy molten chloride salt electrolysis preparation

1 INTRODUCTION

Pb-Ca and Pb-Ca-Na alloys are not only used in the metallurgy of bismuth free lead metal, but also the ideal materials for the manufacturing of cable shields. In recent years, Pb-Ca alloy has been used for the manufacturing of grids of maintenance free lead/acid batteries.

In the manufacture of Pb-Ca-Na alloy, either the metal mixing process or the metal thermoreduction process is inferior by comparison with the molten salt electrolysis process in the homogeneity of alloy composition, high calcium and sodium content in alloy, simplicity in technology, and continuous or semicontinuous manufacturing process.

However, the former molten salt electrolysis process was usually carried out at a temperature range of 750~800 °C and with a current efficiency lower than 80%^[1-4]. Furthermore, there was no report on the production of Pb-Ca-Na alloy by such process.

The improving of current efficiency and the lowering of electrolysis temperature have always been the targets of researchers working on molten salt electrolysis both at home and abroad. In order to achieve these aims we carried out the following investigations.

2 EXPERIMENTAL

(1) Raw Materials

The purity of lead was 99.9%, sodium chloride and calcium chloride were all of chemically pure grade.

(2) The contents of Ca, Na in alloy and the electrolyte composition were determined by means of SP1900 atomic absorption spectrophotometer.

(3) The initial crystallization temperatures of electrolyte and alloys were determined by means of 4.1 type differential thermal balance.

(4) Experimental Apparatus

The experimental arrangement is shown in Fig. 1. The graphite electrolytic cell was used as anode, the inner diameter and depth of this cell were 90 mm and 170 mm respectively. Ceramic crucible of 100 mL volume was used as alloy container. The cathodic conductor was molybdenum rod with a diameter of 10 mm. JWK-703 differential temperature regulator was used to control the furnace temperature which was heated from outside. Pt-PtRh thermocouple was used to control the furnace temperature. Pt-PtRh thermocouple was used to determine the temperature. A JWL-30 type 30 A/8 V supply of stabilized electricity was used for power supply of electrolysis.

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Fig. 1 Experimental arrangement

- 1 —SiC furnace;
- 2 —alloy container;
- 3 —graphite crucible as anode;
- 4 —cathode conductor;
- 5, 6 —thermocouple;
- 7 —thermocouple pyrometer;
- 8 —current rectifier

3 RESULTS AND DISCUSSION

3.1 Initial Crystallization Temperature of Pb-Ca Alloy

The initial crystallization temperatures of alloys with different Ca contents were determined; the results are shown in Table 1.

The data obtained are close to that reported in respective references^[1-4]. The eutectic composition of Pb-Ca is Ca 10%, Pb 90%; the eutectic temperature is 630 °C. When the Ca content is increased to 11%, the initial crystallization temperature is as high as 700 °C; when the Ca content reaches 12%, the initial crystallization temperature rises to 780 °C. The Pb-Ca master alloy used as a metallurgical additive is required to have properties similar to those of lead.

In consideration of the smelting of Pb-Ca grid applied alloy is usually carried out at temperatures lower than 600 °C; it can be seen from Table 1 that alloys with Ca content of 2% ~ 4% are more suitable for this purpose. They can successfully melt and diffuse, and do not cause deviating deposition.

3.2 Distribution of Calcium Element in the Alloy Ingot

Pb-Ca-Na alloy made by electrolysis process was drawn out and directly cast into ingot. The samples were taken from the upper and lower portions of the ingot, and the distribution of Ca element in the alloy was determined.

The data in Table 2 shows that there are serious deviating deposition of Ca in the upper and lower portions of the ingot made by the conventional electrolysis technique, while the present technique prominently improves the homogeneity in the distribution of Ca in the alloy. It also shows that with the same amount of current flow, the present technique brings about higher Ca contents, or in other words, higher current efficiency.

Table 1 Initial crystallization temperature of Pb-Ca alloys

Ca content in alloy/ %	1.0	1.7	2.0	3.0	4.0	5.4
Initial crystallization temperature/ °C	329	530	560	600	630	650
Ca content in alloy/ %	6.0	7.8	9.5	10	11	12
Initial crystallization temperature/ °C	660	650	652	630	700	780

3.3 Diffusion is the Main Control Step in the Electrode Process

During the manufacture of Pb-Ca-Na alloy with liquid state lead cathode, the diffusion of deposited calcium into lead is rather slow, and the electrolysis process is mainly controlled by the diffusion rates of calcium and sodium into lead. It is necessary to make the deposition rates of calcium and sodium match with the diffusion rates of calcium and sodium from the lead surface toward the inner portion of lead. Only in this condition can the normal electrolysis bring about.

The authors discovered that when electrolysis was carried out under conventional conditions, irrespective of the variations in the current density, there is always the phenomenon of Ca continuously floating over the surface and burning, with a current efficiency of only about 50%, and the deviating deposition of Ca in the

upper and lower portions of the alloy is very serious.

By controlling the diffusion rate of calcium into lead, the present technique has satisfactorily solved this serious problem. As shown in Table 3, 0.5 A/cm^2 is the suitable current density, which not only brings about homogeneous distribution of calcium in the alloy, but also the highest current efficiency.

Table 2 Distribution of calcium element in the alloy

Sample No.	Conventional technique Ca/ %		Present technique Ca/ %	
	Upper portion	Lower portion	Upper portion	Lower portion
1	0.44	0.28	0.38	0.38
2	0.60	0.54	1.55	1.55
3	0.76	0.70	5.80	5.80
4	0.60	0.08	7.50	7.80
5	0.99	0.02	10.60	10.60

3.4 Molten Salt System

The solution loss of metallic calcium in pure calcium chloride amounted to 17%. In order to decrease it, some other molten salt constituents, like LiCl, KCl, NaCl, BaCl₂, etc., were added to pure CaCl₂, thus decreased the melting point of the electrolyte. That CaCl₂-NaCl system was chosen is technically more reasonable and more economic on industrialization. The CaCl₂ content in the molten salt was controlled so as to make the initial crystallization temperature of the mixed salt lower than 550 °C. By using the

above chosen molten salt system as electrolyte, it is quite probable to prepare 2% ~ 4% Ca-Pb master alloy by electrolysis at a lower temperature as 600~ 650 °C. The electrolyte as chosen in this report had an initial crystallization temperature which can match with the initial crystallization temperature 560~ 630 °C of the 2% ~ 4% Ca-Pb master alloy, thus laid the foundation to carry out electrolysis at a lower temperature of 600~ 650 °C. Furthermore, the initial crystallization temperature of this alloy is close to the smelting temperature of Pb-Ca-Na grid applied alloy, thus providing favorable condition to use this master alloy to prepare applied alloy in an industrial scale.

3.5 Influence of Current Density

By adopting the CaCl₂-NaCl electrolyte system, current density experiments were carried out at 650 °C. As can be seen in Table 4, 0.5 A/cm^2 is the favorably suitable cathode current density. When the current density increases to 1.5 A/cm^2 , the current efficiency may attain 80%.

3.6 Influence of Electrolysis Temperature

One of the chief aim of the present technique is to reduce the electrolytic temperature, thus to improve current efficiency and metal recovery. It can be seen from Table 5 that 650 °C is the most suitable electrolysis temperature, which is 100~ 300 °C lower than those reported^[1-4] electrolysis temperature of 750 ~ 960 °C. It is important to carry out electrolysis at temperature lower than 700 °C, so as to

Table 3 Influence of current density on electrolysis

Operation	Cathode current density/ $\text{A} \cdot \text{cm}^{-2}$	Ca content in alloy/ %		Current efficiency / %
		Upper portion	Lower portion	
Conventional electrolysis	0.2	0.6	0.08	53
	0.5	0.99	0.02	52
	1.0	1.32	0.05	47
Present technique	0.2	0.38	0.38	88
	0.5	1.55	1.55	98
	1.0	3.66	3.58	91

Table 4 Influence of cathode current density on current efficiency

Current density / $\text{A} \cdot \text{cm}^{-2}$	Cathode lead/ g	Cell voltage/ V	Current efficiency / %
0.2	400 ± 5	4.1	83
0.5	400 ± 5	4.6	98
1.0	400 ± 5	5.3	83
1.5	400 ± 5	6.5	80

Table 5 Influence of electrolysis temperature on current efficiency

Electrolysis temperature/ $^{\circ}\text{C}$	Current efficiency/ %
600	94
650	98
700	96
750	93

reduce the secondary action of metal and the vaporization losses of the electrolyte, and to reduce the corrosion of the container too.

3.7 Influence of Electrolysis Time on Current Efficiency

In order to obtain electrolysis data operating for a longer time, continuous electrolysis experiments were separately carried out for 1~ 6h with 0.5 A/cm^2 current density at 650°C . Table 6 shows that current efficiency decreases with increase of electrolysis time, but after a continuous electrolysis of 6h, the current efficiency is still

Table 6 Relation of Ca and Na content in alloy with electrolysis time

Electrolysis time/ h	Ca content in alloy/ %	Na content in alloy/ %	Total current efficiency/ %
1	1.28	0.50	98
2	2.70	0.27	96
3	4.50	0.15	95
4	5.20	0.11	90
5	6.25	0.08	84
6	7.50	—	82

higher than 80%.

The increase of the electrolysis time not only increases the solution losses of calcium and sodium metals, but also brings about larger variations in the electrolyte composition owing to the deposition of calcium and sodium, which will lead to the decrease of the current efficiency. Therefore, it is necessary to continuously supply the lost constituent in the electrolyte so as to keep the original composition of the electrolyte.

4 CONCLUSIONS

(1) An electrolyte system suitable for electrolysis of Pb-Ca-Na master alloy at 650°C was put forward. The initial crystallization temperature of this system did not exceed 550°C .

(2) Eutectic composition of Pb-Ca alloy was 10% Ca-Pb, with an eutectic temperature of 630°C ; the initial crystallization temperature of 4% Ca-Pb alloy was lower than 630°C . Pb-2% ~ 4% Ca-Na alloy had a homogeneous composition suitable for master alloy.

(3) The initial crystallization temperature of the electrolyte with given composition and that of Pb-2% Ca-Na master alloy have been determined, which are close to the smelting temperature of Pb-Ca-Na grid applied alloy. These three temperatures can match with each other, which laid foundation for the electrolysis of Pb-Ca-Na alloy at a lower temperature of 650°C .

(4) The present technique can accelerate the diffusion rate of calcium and sodium atoms toward the liquid lead cathode, thus not only greatly raises the current efficiency, but also completely overcomes the deviating deposition of calcium in the alloy caused usually by the conventional electrolysis technique. No identical information concerning the present technique has been found in any other reports published at home or abroad.

(5) The electrolytic temperature of the present technique was $100 \sim 300^{\circ}\text{C}$ lower than those reported both at home or abroad^[1-4]. It saved energy and reduced the losses of electrolyte and electrolytic cell structural materials.

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Table 3 Chemical component of Ni powder(%)

Ni, %	Impurity elements, %				
	Co	Zn	Al	Si	
99.5	0.3	0.069	0.021	0.0068	
	Fe	Pb	Sb	Bi	Cd
	0.041	0.00063	0.001	0.0001	0.0003
	Mn	Mg	As	Sn	Cu
	0.0064	0.004	0.011	0.0005	0.0079

5 CONCLUSIONS

(1) With ammonium tartrate being complexing agent and NaOH adjusting pH value, the NiSO_4 bearing solution was reduced by hydrazine directly. Under the conditions of 29.35 g/L $[\text{Ni}^{2+}]$, 1:1 $[\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}]$, 60 g/L $[\text{NaOH}]$ and stirring at 80 °C for 1 h, ultrafine Ni powder

with an average particle size of 0.058 μm and purity larger than 99.5% was obtained.

(2) Orthogonal experimental results showed that the particle size of Ni powder was affected first by $[\text{NaOH}]$, second by $[\text{Ni}^{2+}]$, and then by $[\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}]$.

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(6) Under the optimum technical conditions, the highest current efficiency may reach 98%, which is 13% ~ 15% higher than those reported both at home and abroad^[1–4]. The current efficiency decreases with the extension of electrolysis time and the increase of calcium content in lead; after 6 h electrolysis, this current efficiency reaches 82%.

(7) The present electrolysis technique with co-deposition of Ca^{2+} and Na^+ at the liquid lead cathode was first put forward.

(8) A Pb-Ca-Na ternary master alloy at a lower electrolysis temperature was successfully

produced, thus providing a new material which was superior in quality to Pb-Ca alloy for manufacture of grid applied alloy used in the maintenance-free lead acid batteries.

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