

Mechanism of debismuthizing with calcium and magnesium

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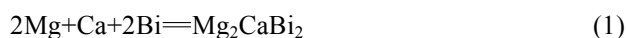
Abstract: In order to further understand the debismuthizing mechanism with calcium and magnesium, the influence of adding amount of calcium on the bismuth removal from lead was examined. A part of the debismuthizing dross samples were studied by electron probe microanalysis (EPMA). The results show that the calculated bismuthide governing debismuthizing process is $\text{Ca}_3\text{Mg}_7\text{Bi}_8$, which may be a mixture of Ca_3Bi_2 , CaBi , CaBi_3 and Mg_3Bi_2 . And the bismuthide formed during the debismuthizing process exists in two states: one is free bismuthide in the matrix of dross, and the other is symbiotic with Pb–Ca phase.

Key words: debismuthizing mechanism; Kroll–Betterton process; $\text{Ca}_3\text{Mg}_7\text{Bi}_8$; Pb–Ca phase; Bi–Ca–Mg phase

1 Introduction

Most of the alkali and alkaline earth metals can form intermetallic compound with bismuth, and this sort of reactions were often used for the research work on the debismuthizing of lead bullion [1–3]. The Kroll–Betterton (K–B) process with calcium and magnesium reagents is the only practical process in operation for pyrometallurgical bismuth removal [4,5]. There still have been arguments on the mechanism of debismuthizing, and the arguments mostly focused on the compounds which act on bismuth removal.

On the mechanism of bismuth removal from lead by the K–B process, BETTERTON and LEBEDEFF [6] suggested that it resulted from the formation of both Ca_3Bi_2 and Mg_3Bi_2 compounds according to the microscopic study of the debismuthizing dross. While EVERS [7] believed that it resulted from the formation of CaMg_2Bi_2 . The latter opinion has been accepted later by a majority of researchers [8–11]. According to this view, DAVEY [12] summarized the thermodynamic relationships that govern the removal of bismuth from lead by the K–B process. The removal of bismuth from lead is governed by the reaction equations (1) and (2):



$$K_{\text{sp}} = [\text{Mg}]^2[\text{Ca}][\text{Bi}]^2 \quad (2)$$

where K_{sp} is the solubility product of the magnesium, calcium and bismuth in lead bullion, and it should be

a constant at the same temperature. But the values of this solubility product obtained by many researchers changed in a very wide range [9–12]. The difference among solubility product values of CaMg_2Bi_2 obtained by different works indicates that there may be some unknown reasons affecting the debismuthizing results. Apart from these problems, the insufficiency of direct examination on the dross causes the debismuthizing mechanism lack of direct evidence to support.

This study focuses on ascertaining the mechanism governing debismuthizing with calcium and magnesium, especially on ascertaining the bismuthide and its occurrence in debismuthizing dross. In addition to revealing debismuthizing mechanism, this research can also play a significant role in understanding the influence of bismuth on the performance of Pb–Ca alloy, which is a very important material in the storage battery industry.

2 Experimental

By addition of bismuth (99.99% purity) into a steel pot containing about 15 kg molten lead (99.99% purity) at 450 °C, the lead–bismuth alloy (0.023% Bi) was obtained. Calcium was added as lead–calcium alloy (1.36% Ca) and magnesium (99.99% purity) as magnesium piece.

Five experiments were conducted in a sealed vertical tubular crucible electric furnace under the protection of a nitrogen atmosphere. For each test, 500 g of prepared Pb–Bi alloy was used, and the initial Mg

concentration was held at 0.155%, the initial Ca concentration varied between 0.040% and 0.135%. The temperature for bismuth removal was set at 330 °C, and the experimental procedure was the same as that in our previous work [13]. After the separation of lead bullion and dross, the alloys were weighed and sampled for ICP-AES analysis, and four of the dross samples were sent to electron microscopic and electron probe microanalysis. The results are shown in Table 1.

3 Results and discussion

The dross samples were taken from tests No. 2–5. The results show that all the samples are composed of matrix, Pb–Ca phase and Bi–Ca–Mg phase. The matrix and Pb–Ca phase account for about 60% and 30% of the dross, respectively. Bi–Ca–Mg phase is very little in the dross.

3.1 Analysis of matrix of dross

The composition of the matrix obtained by electron probe microanalysis is shown in Table 2. The backscattered electron image of the matrix and Pb–Ca phase is shown in Fig. 1, and the X-ray surface distribution images of Fe, Ca and Pb can be seen in Figs. 2(a–c), respectively.

Table 2 shows that the matrix is basically constituted by lead and iron. A large amount of iron in the matrix may come from the corrosion of stainless net by liquid lead alloy [14] during the separation of dross samples. Bi is enriched in matrix compared with the final lead (see Table 1). Through the average relative mass of Bi, Ca and Mg in matrix, the mass ratios of Ca and Mg to Bi were calculated as 0.243 and 0.234, respectively. They are all higher than 0.096 and 0.116, which are the mass ratios of Ca and Mg to Bi in CaMg_2Bi_2 compound, respectively. The surplus Ca and Mg may exist as $\text{Ca}_3\text{Mg}_4\text{Pb}_x$ [12].

In Fig. 1 it can be found that the distribution of Pb–Ca phase in the dross is uneven. This uneven distribution is strict in accordance with the surface distribution image of Ca (see Fig. 2(a)), which forms Pb–Ca phase. Pb–Ca phase has a relatively larger grain

size, generally larger than 20 μm , and takes the shape of round, strips or branch-like in the matrix. The boundary between the Pb–Ca phase and the matrix is smooth. Fe in the dross is also unevenly distributed (see Fig. 2(b), and is complementary with the distribution areas of Ca in the X-ray surface distribution images, which means that the Fe contaminated in the dross is corroded by lead bullion matrix, but not by Pb–Ca phase.

3.2 Analysis of Pb–Ca phase in dross

In contrast to the composition of matrix (see Table 2), the content of Ca in Pb–Ca phase (see Table 3) is well above that in the matrix. The mass ratio of Ca to Pb in Pb–Ca phase is about 5.71%, which is a little lower than that of compound CaPb_3 (6.45%). So, there must be a little lead left in Pb–Ca phase under the present dross separation conditions, and Pb–Ca phase can be taken as a solid solution of CaPb_3 and final lead alloy. Bi content in Pb–Ca phase is also higher than that in the matrix. But there is still some Bi in the matrix. This means that a part of bismuthide floats out of the lead before the formation of Pb–Ca phase during the falling of temperature. So, the compounds governing debismuthizing process consist of both free bismuthide and symbiotic bismuthide with Pb–Ca phase. Fe content in the Pb–Ca phase is well below that in the matrix. This also indicates that the stainless steel net is corroded by the final lead alloy, but not by Pb–Ca phase.

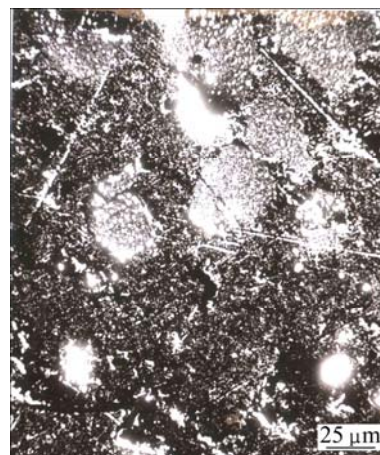


Fig. 1 Backscattered electron image of matrix and Pb–Ca phase (bright part)

Table 1 Initial conditions and analysis of final lead alloy in calcium dependent tests

No.	$w(\text{Bi})_{\text{Initial}}/\%$	$w(\text{Ca})_{\text{Initial}}/\%$	Dross ratio/%	$w(\text{Ca})_{\text{Final}}/\%$	$w(\text{Mg})_{\text{Final}}/\%$	$w(\text{Bi})_{\text{Final}}/\%$	K_{sp}
1	0.0233	0.040	4.05	0.036	0.124	0.011	6.70×10^{-8}
2	0.0219	0.065	5.09	0.061	0.126	0.010	9.68×10^{-8}
3	0.0215	0.089	6.88	0.070	0.132	0.007	5.98×10^{-8}
4	0.0211	0.112	8.02	0.076	0.134	0.008	8.73×10^{-8}
5	0.0207	0.135	9.02	0.077	0.134	0.005	3.46×10^{-8}

Table 2 Composition of matrix in debismuthizing dross samples

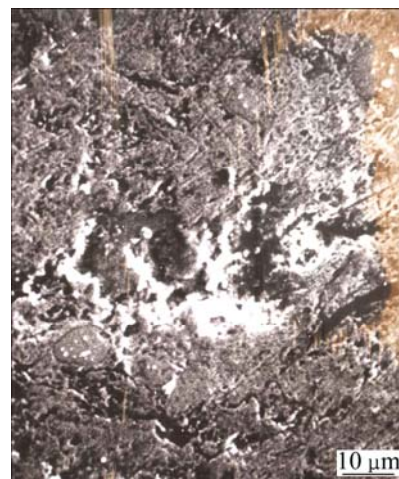
Sample No.	w(Pb)/%	w(Bi)/%	w(Mg)/%	w(Ca)/%	w(Fe)/%
2	91.083	0.239	0.066	0.092	4.826
3	92.123	0.377	0.085	0.089	4.297
4	90.842	0.401	0.090	0.098	4.375
5	92.630	0.240	0.075	0.050	4.220
Average	91.670	0.337	0.079	0.082	4.430

Table 3 Composition of Pb–Ca phase in dross samples

Sample No.	w(Pb)/%	w(Bi)/%	w(Mg)/%	w(Ca)/%	w(Fe)/%
2	92.838	0.343	0.034	5.374	Undetected
3	93.354	0.515	0.061	5.233	0.059
4	90.588	0.503	0.051	5.230	0.059
5	91.735	0.601	0.049	5.203	Undetected
Average	92.129	0.491	0.049	5.260	0.030

3.3 Analysis of Bi–Ca–Mg phase in dross

The Bi–Ca–Mg phase generally has a little grain size, the majority of which is about 10 μm , and only a little reaches to 20 μm (see Fig. 3). The X-ray surface distribution images of Ca, Mg and Bi are very similar (see Figs. 4(a–c), which means that elements Bi, Ca and Mg are really enriched in the dross to form Bi–Ca–Mg compounds.

**Fig. 2** X-ray surface distribution images of Ca (a), Fe (b) and Pb (c) in dross (bright part)**Fig. 3** Backscattered electron image of matrix and Bi–Ca–Mg phase

Apart from these mentioned above, it can be seen that this Bi–Ca–Mg phase is circulated by Pb–Ca phase (see Fig. 3). So, the Bi–Ca–Mg phase should be formed together with Pb–Ca phase. Then the reactivity of the Bi–Ca–Mg phase may decrease and the Bi content in final lead alloy also decreases.

We know that there is a peritectic point in Pb–Ca phase diagram. When the peritectic reaction occurs, a part of Pb–Ca phases (see Fig. 5) will be consumed and some Bi–Ca–Mg phases will be exposed to liquid lead. This will result in a bad debismuthizing effect due to the redissolution of some Bi–Ca–Mg phases. And it leads to the disturbance of Bi content in final lead according to the difference of Pb–Ca phase consumption (see Table 1). This disturbance will cause the change of the solubility product of the Bi–Ca–Mg compound.

The composition of Bi–Ca–Mg phase is determined as 63.312% Bi, 1.900% Pb, 6.580% Mg, 4.580% Ca,



Fig. 4 X-ray surface distribution images of Bi (a), Mg (b) and Ca (c) (bright part)

0.128% Fe, 23.280% O. A large amount of oxygen in this phase shows that the dross is significantly oxidized during the dross separation. If the contents of O, Pb and Fe are ignored, the compositions of the simplified Bi–Ca–Mg phase and CaMg_2Bi_2 compound can be compared (see Table 4).

Table 4 shows that the composition of Bi–Ca–Mg phase deviates from the stoichiometric coefficient of CaMg_2Bi_2 compound. Molecular formula of $\text{Ca}_{0.76}\text{Mg}_{1.79}\text{Bi}_2$ can be derived from the composition of

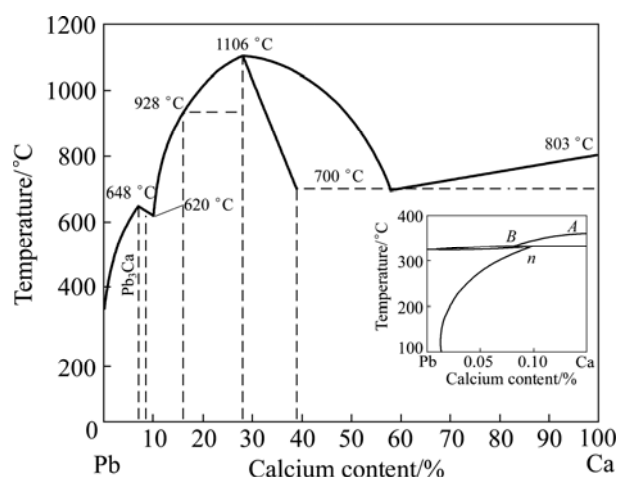


Fig. 5 Pb–Ca phase diagram and Pb-rich region [13]

Table 4 Compositions comparison between of Bi–Ca–Mg phase and CaMg_2Bi_2 compound

Item	w(Bi)/%	w(Ca)/%	w(Mg)/%
Bi–Ca–Mg phase	85.01	6.16	8.83
CaMg_2Bi_2	82.49	7.91	9.59
$\text{Ca}_{0.76}\text{Mg}_{1.79}\text{Bi}_2$	84.96	6.19	8.84

simplified Bi–Ca–Mg phase. When the mole number in $\text{Ca}_{0.76}\text{Mg}_{1.79}\text{Bi}_2$ is changed into round figure, $\text{Ca}_3\text{Mg}_7\text{Bi}_8$ can be obtained. The total amount of Ca and Mg in $\text{Ca}_3\text{Mg}_7\text{Bi}_8$ is not enough to maintain the ratio of Bi to Ca and Mg for both Ca_3Bi_2 and Mg_3Bi_2 . This demonstrates that the compound governing debismuthizing process is not produced by the union of Ca_3Bi_2 and Mg_3Bi_2 . So, we cannot conclude that CaMg_2Bi_2 forms during removing bismuth from lead with calcium and magnesium. If we intend to take $\text{Ca}_3\text{Mg}_7\text{Bi}_8$ taken apart into three CaMg_2Bi_2 , one MgBi_2 will be left aside. But there is no MgBi_2 compound in Bi–Mg system [15], so the Bi–Ca–Mg phase contains excessive Bi but lacks of Ca. Ca can form a series of compounds with Bi, such as Ca_3Bi_2 , CaBi and CaBi_3 [16]. This means that when the Ca content is not enough to form Ca_3Bi_2 , the other two compounds, CaBi and CaBi_3 may yield. So, we may view the calculated compound $\text{Ca}_3\text{Mg}_7\text{Bi}_8$ as the combination of Ca_3Bi_2 , CaBi and CaBi_3 with Mg_3Bi_2 . On the other hand, although there is only one compound in the Bi–Mg system, the phase diagram of Bi–Mg system shows that the composition of the compound has more Mg than Mg_3Bi_2 (see Fig. 6 [15]). It appears that the compound presents more like a solid solution of Mg_3Bi_2 and Mg. So, the calculated compound $\text{Ca}_3\text{Mg}_7\text{Bi}_8$ should not be taken as a compound with fixed compositions, and can be taken as a solid solution of Ca_3Bi_2 , CaBi , CaBi_3 , Mg_3Bi_2 and Mg, similar to $\text{Ca}_3\text{Mg}_4\text{Pb}_x$ in Pb–Ca–Mg system [12].

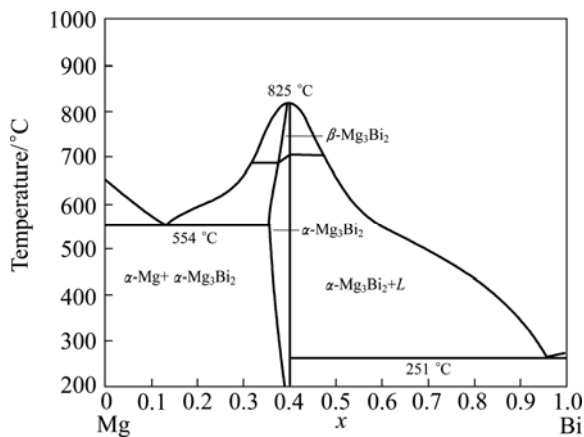


Fig. 6 Optimized phase diagram of Mg–Bi system [16]

4 Conclusions

1) The calculated bismuthide governing debismuthizing process is $\text{Ca}_3\text{Mg}_7\text{Bi}_8$, which can be taken as a solid solution of Ca_3Bi_2 , CaBi , CaBi_3 , Mg_3Bi_2 and Mg , similar to $\text{Ca}_3\text{Mg}_4\text{Pb}_x$ in Pb – Ca – Mg system.

2) The bismuthide formed during debismuthizing process exists in two states: one is free compound in the matrix of the dross, and the other is symbiotic bismuthide with the Pb – Ca phase.

3) When the peritectic reaction occurs, a part of the Pb – Ca phase will be consumed and a part of Bi – Ca – Mg phase dissolves into lead. This results in a bad debismuthizing effect and the disturbance of Bi content in final lead, according to the difference of Pb – Ca phase consumption.

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钙镁除铋的机理

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摘要: 为了深入了解钙镁除铋的机理, 研究了钙添加量对铅中铋脱除深度的影响。将除铋渣样进行电子探针分析(EPMA)。结果表明, 控制除铋过程的化合物是 $\text{Ca}_3\text{Mg}_7\text{Bi}_8$ 。与 Pb – Ca – Mg 体系中存在的 $\text{Ca}_3\text{Mg}_4\text{Pb}_x$ 化合物类似, $\text{Ca}_3\text{Mg}_7\text{Bi}_8$ 化合物可以看成是由 Ca_3Bi_2 、 CaBi 、 CaBi_3 和 Mg_3Bi_2 形成的固溶体。同时, 在除铋过程中所形成的 $\text{Ca}_3\text{Mg}_7\text{Bi}_8$ 化合物有两种赋存状态, 一种以自由铋化物状态存在于渣相的基体中, 另一种则与 Pb – Ca 共共生。

关键词: 除铋机理; 克罗尔–别特尔特顿法; $\text{Ca}_3\text{Mg}_7\text{Bi}_8$; Pb – Ca 相; Bi – Ca – Mg 相

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