

Fine debismuthizing with calcium, magnesium and antimony

LU Dian-kun¹, JIN Zhe-nan¹, JIANG Kai-xi²

1. School of Materials and Metallurgy, Northeastern University, Shenyang 110819, China;

2. Beijing General Research Institute of Mining and Metallurgy, Beijing 100044, China

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Abstract: In order to achieve fine debismuthizing of lead bullion, the effects of temperature, adding amount of calcium and magnesium and antimony on the bismuth removal from lead bullion were investigated. The mechanism of debismuthizing was also discussed. The results show that when adding amounts of calcium and magnesium reach 0.112% and 0.395%, respectively, bismuth level of 0.001% (mass fraction) in the final lead is achieved at 330 °C, without the need for antimony addition. Maintaining addition amount of magnesium at 0.155%, when calcium addition amount is less than 0.09%, the concentration of peritectic reaction point, the bismuth concentration can be easily decreased to 0.001% by the following antimony treatment. But the effect of antimony treatment on debismuthizing gets bad if the calcium addition exceeds 0.09%.

Key words: debismuthizing; Kroll-Betterton process; antimony treatment; peritectic reaction

1 Introduction

Most of the alkali and alkaline earth metals can form intermetallic compounds with bismuth, and the reactions are often used for the debismuthizing of lead bullion [1–3], but the Kroll-Betterton (K-B) process with calcium and magnesium reagents is the only practical process in operation for pyrometallurgical bismuth removal [4]. Historically, this was done by adding pure magnesium ingots and calcium crown or turnings. Lately, a new generation of debismuthizing reagent comprised of magnesium-calcium alloy was developed [5]. But the mechanism of debismuthizing retains unchanged. On the mechanism of bismuth removal from lead, 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 and calculation, while EVERS [7] believed that it resulted from the formation of CaMg_2Bi_2 . The latter opinion has been accepted by a majority of researchers [8–11]. 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 bullion is governed by the reaction, as shown in the following reaction:



The solubility relation near the freezing point of the lead can be approximately represented by:

$$\lg([\text{Mg}]^2[\text{Ca}][\text{Bi}]^2) = -7.37 \quad (2)$$

ILEY and WARD [9] obtained the solubility product of the magnesium, calcium and bismuth in lead bullion within 322–350 °C, as shown in Eq. (3). HANCOCK and HARRIS [10] got another relation, as shown in Eq. (4).

$$\lg([\text{Mg}]^2[\text{Ca}][\text{Bi}]^2) = 5.46 - 7560/T \quad (3)$$

$$\lg([\text{Mg}]^2[\text{Ca}][\text{Bi}]^2) = 12.007 - 11437/T \quad (4)$$

It can be seen apparently that the different results of solubility of CaMg_2Bi_2 in lead are obtained by different researchers. In addition, BETTERTON and LEBEDEFF [6] claimed that when using antimony treatment, it was possible to reduce bismuth to less than 0.001% [6], but DAVEY [8] doubted this result.

As to the mechanism of bismuth removal with antimony, BETTERTON and LEBEDEFF [6] suggested the formation of a quaternary Ca-Mg-Bi-Sb compound. DAVEY [8] suggested that calcium and magnesium antimonides precipitated to help floating out the residual small bismuthide crystals. ILEY and WARD [9] thought

that the formation of the insoluble antimonides causes the coprecipitation and/or post-precipitation of bismuthides.

As stated above, there is still great difference in the effects of calcium and magnesium addition and temperature on the level of bismuth removal, and there is still argument in the action of antimony treatment. In addition to these problems, most of the lead alloys used for previous research works are of relative high bismuth concentrations, i.e. bismuth content in primary lead above 0.1% (mass fraction), which is disadvantageous to the research on debismuthizing mechanism.

This study focuses on understanding the influence of calcium and magnesium addition and temperature on debismuthizing level from lead bullion, especially from the lead alloys with low bismuth concentration. The mechanism of antimony treatment following the K-B process on the fine bismuth removal is also investigated.

2 Experimental

Lead-bismuth alloy was prepared by the addition of bismuth with 99.99% purity into a steel pot containing about 15 kg molten lead with 99.99% purity at 450 °C, then a lead-bismuth alloy (Bi 0.023% in mass fraction) was obtained. Calcium was added as lead-calcium alloy (Ca 1.36%) and magnesium was added as magnesium piece with 99.99% purity.

All experiments were conducted in a sealed vertical tubular crucible electric furnace under the protection of nitrogen atmosphere. For each test, 500 g prepared Pb-Bi alloy was firstly melted in a ceramic crucible while Pb-Ca alloy and magnesium pieces were hung by steel wire in the furnace. When the temperature reached 400 °C, Pb-Ca alloy and magnesium were added with stirring into the molten alloy. The temperature was maintained at 400 °C for 10 min and then cooled at a rate of 5 °C/h to the destination temperature, 330 °C, except for temperature dependent tests. After keeping warm at final temperature for 4 h, the dross was fished out with a stainless steel net and hung over the crucible for 15 min to remove extra contaminated lead alloy. The separated alloys were weighed and sampled to ICP-AES analysis. A part of them were also treated with 0.07% (mass

fraction) of antimony.

3 Results and discussion

3.1 Effect of temperature on bismuth removal

All tests in this batch had the same initial concentrations of bismuth, magnesium and calcium, which were 0.0211%, 0.155% and 0.112%, respectively. The final cooling temperature was arranged between 330 °C to 363 °C, as shown in Table 1. The experiments results are also summarized in Table 1.

The data in Table 1 show that little CaMg_2Bi_2 formed above 352 °C under the present work conditions. The majority of the debismuthizing reaction occurred between 341 °C and 352 °C, only a little of extra bismuth was removed below 341 °C. The dross ratio is also in accordance with the debismuthizing level. There is a lot of dross produced at 363 °C, at which almost no bismuth is removed, while calcium in final lead reduces significantly. The dross at high temperature may be regarded as $\text{Ca}_3\text{Mg}_4\text{Pb}_x$, which is a mixture of CaPb_3 and Mg_2Pb , according to Pb-Ca-Mg-Bi phase diagram [12]. The calculated composition of the dross at 363 °C is $\text{Ca}_3\text{Mg}_{3.62}\text{Pb}_{49.08}$, in which the Pb content is well above the ratio of both CaPb_3 and Mg_2Pb . It means that the dross is a mixed solid solution of $\text{Ca}_3\text{Mg}_4\text{Pb}_x$ and final lead. This situation continues to the lower temperatures. The apparent solubility product of CaMg_2Bi_2 changes significantly with temperature from 341 °C to 352 °C, but the solubility product difference at 330 °C and 341 °C, as well as 352 °C and 363 °C, is relatively small. The apparent values of solubility product below 341 °C are about twice that calculated by DAVEY near the liquidus [11]. It means that the fine debismuthizing result can only be achieved near the liquidus, although the majority of bismuth has been already removed at about 341 °C.

3.2 Effect of magnesium addition on bismuth removal

During this batch of experiments, the initial calcium concentration was maintained at 0.112% and the final temperature was 330 °C. Others experimental conditions and the analysis results of final lead alloy are listed in Table 2.

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

No.	Temperature/°C	Dross ratio/%	Final mass fraction/%			[Ca][Mg] ² [Bi] ²
			Ca	Mg	Bi	
A1	330	12.83	0.076	0.134	0.008	8.73×10^{-8}
A2	341	12.22	0.073	0.126	0.009	9.39×10^{-8}
A3	352	10.32	0.104	0.136	0.019	6.94×10^{-7}
A4	363	6.41	0.093	0.146	0.021	8.74×10^{-7}

From Table 2 it can be seen that the final Bi content decreased continuously with the increase of magnesium addition. When the initial magnesium added come up to 0.395%, the bismuth content in lead alloy dropped to only 0.001%, much lower than 0.0025%, which is estimated from Pb-Ca-Mg-Bi phase diagram by DAVEY [8], and the concentration of magnesium left in lead is also well below 1%. The final magnesium concentration in lead always increased with the addition of magnesium, but calcium concentration in final alloy took a slow increasing trend and finally held at approximately 0.08%. The calculated apparent solubility of CaMg_2Bi_2 is smaller than that from Eqs. (2)–(4).

3.3 Effect of calcium addition on bismuth removal

All tests in this batch held an initial magnesium concentration of 0.155%. The other conditions and analysis of final lead alloy are listed in Table 3. The final

bismuth concentrations in Table 3 show a downward trend with the increase of initial calcium addition. But anomalous results occurred for No.C12 and C13. By carefully repeating the two tests, the result remains to be a same trend. These anomalous phenomena may have something to do with Pb-Ca phase diagram. Figure 1 shows the Pb-Ca phase diagram adopted by BETTERTON and LEBEDEFF [6]. In contrast with that provided by other references [13–14], there is a peritectic point *n* situated at approximate by 0.09% of calcium in the enlargement of the Pb-rich corner in Fig. 1.

The point *B* is situated at approximate 0.075% of calcium concentration. CaPb_3 will gradually separate out from lead along with the decrease of temperature when calcium content exceeds 0.075%, and the calcium left in lead approaches to 0.075% little by little along line *AB*. The separated CaPb_3 during cooling process will react with liquid lead to form solid solution near the freezing

Table 2 Initial conditions and analysis results of final lead alloy in magnesium dependent tests

No.	Initial mass fraction/%		Dross ratio/%	Final mass fraction/%			$[\text{Ca}][\text{Mg}]^2[\text{Bi}]^2$
	Bi	Mg		Ca	Mg	Bi	
B5	0.021 1	0.103	8.45	0.072	0.090	0.007	2.86×10^{-8}
B6	0.021 1	0.170	13.12	0.072	0.136	0.005	3.33×10^{-8}
B7	0.021 0	0.251	14.20	0.078	0.206	0.003	2.98×10^{-8}
B8	0.021 0	0.313	14.45	0.082	0.247	0.002	2.00×10^{-8}
B9	0.021 0	0.395	14.58	0.076	0.321	0.001	0.78×10^{-8}

Table 3 Initial conditions and analysis results of final lead alloy in calcium dependent tests

No.	Initial mass fraction/%		Dross ratio/%	Final mass fraction/%			$[\text{Ca}][\text{Mg}]^2[\text{Bi}]^2$
	Bi	Ca		Ca	Mg	Bi	
C10	0.0233	0.040	4.05	0.036	0.124	0.011	6.70×10^{-8}
C11	0.0219	0.065	5.09	0.061	0.126	0.010	9.68×10^{-8}
C12	0.0215	0.089	6.88	0.070	0.132	0.007	5.98×10^{-8}
C13	0.0211	0.112	8.02	0.076	0.134	0.008	8.73×10^{-8}
C14	0.0207	0.135	9.02	0.077	0.134	0.005	3.46×10^{-8}

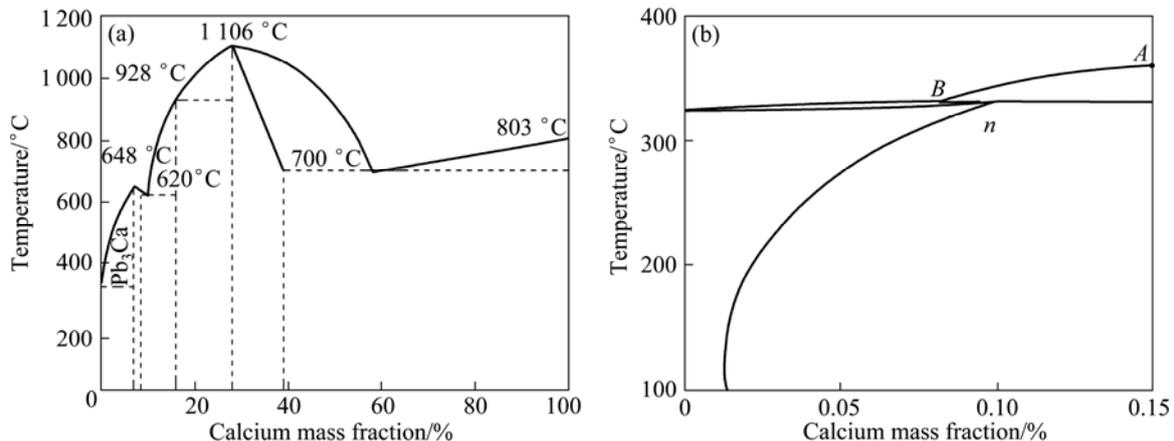


Fig. 1 Pb-Ca phase diagram (a) and Pb-rich region (b)

point. So when temperature decreases to about freezing point, part of the separated CaPb_3 will re-dissolve into lead.

Because CaMg_2Bi_2 separates out together with CaPb_3 during the last period of cooling process, the activity of CaMg_2Bi_2 in dross is reduced and debismuthizing effect gets reinforced. But when the peritectic reaction occurs, part of the separated CaPb_3 is consumed and the last dross touching with molten lead will be lack of CaPb_3 . This result, on a reverse turn, will increase the CaMg_2Bi_2 activity in dross. Thus the distribution balance of bismuth between dross and molten lead is broken, and part of the formerly separated CaMg_2Bi_2 re-dissolves into lead, resulting in a poor debismuthing effect. This situation occurred in all the last three experiments, Nos. C12, C13 and C14.

For No. C12, the initial calcium content is 0.089%, just a little above point *B*. Under this calcium content conditions, CaMg_2Bi_2 is separated out alone during the most time of cooling process, only a little of CaMg_2Bi_2 is separated out together with CaPb_3 in a very narrow temperature range in the last period. So the activity of CaMg_2Bi_2 in the latter part of dross gets small to reinforce debismuthizing level. When the peritectic reaction occurs, only a little of dross takes part in the reaction. So the re-dissolved CaMg_2Bi_2 is very little and the final bismuth in lead remains at a low level. But for No. C13, the initial calcium content is 0.112%, which is more above point *B*. So the alloy touches liquidus line at a relative high temperature. CaPb_3 is separated out together with CaMg_2Bi_2 at a relatively early time during cooling process. Therefore, a relatively large amount of CaMg_2Bi_2 and CaPb_3 coexist in the latter dross. When the peritectic reaction occurs, a larger amount of dross takes part in the reaction compared with No. C12, and more CaMg_2Bi_2 is formed before re-dissolving to lead. As a result, the final bismuth level in No. C13 is a little higher than that in No. C12. As to No. C14, the initial calcium concentration is 0.135%, which is also above point *B*. Like the No. C13, the molten alloy of No. C14 touches liquidus at a high temperature, and most of the CaMg_2Bi_2 is separated out together with CaPb_3 during the early time of cooling process. Although there is a large amount of dross taking part in the peritectic reaction during the end cooling process and part of the CaMg_2Bi_2 in dross re-dissolved into lead, there is adequate CaPb_3 still left in dross to lower the activity of CaMg_2Bi_2 to a relatively low level. So a satisfactory debismuthizing result can also be achieved.

3.4 Effect of antimony treatment on debismuthizing

In this batch of test, all final lead alloys obtained from previous calcium and temperature dependent tests were treated with 0.07% of antimony. Among these

antimony treatment tests, final lead alloys obtained from calcium dependent tests were treated at 330 °C; however, those from temperature dependent tests were treated at their original debismuthizing temperatures. The initial conditions and final results of the two group of tests are summarized into Table 4 and Table 5, respectively.

3.4.1 Effect of initial calcium concentration on antimony treatment

The data in Table 4 show that almost all the added antimony goes into dross. The initial calcium addition has a different effect on antimony treatment depending on whether it is above or below the calcium content of point *B*. When the initial calcium addition does not reach point *B*, the bismuth left in lead is lower than 0.001% after antimony treatment. However, when the initial calcium addition exceeds point *B*, debismuthizing effect gradually gets bad with the increase of initial calcium addition, and the bismuth content left in lead is high than 0.001%. When the initial calcium addition reaches 0.135%, antimony treatment has no effect on debismuthizing level. These results imply that the peritectic reaction has a remarkable inhibition effect on debismuthizing level by antimony treatment.

Calcium and magnesium can form both binary and ternary intermetallic compounds with antimony [15–17]. According to the report of ILEY and WARD [9], calcium and magnesium concentrations were reduced to their final levels shortly after the addition of antimony. But the bismuth concentration then continued to fall with additional stirring. These facts mean that the influence of antimony treatment on debismuthizing appears unlikely to act as the function of physical collection of residual CaMg_2Bi_2 in lead by Mg_3Sb_2 and CaMg_2Sb_2 . It can be hypothesized that all of the re-dissolved bismuth during peritectic reaction presents as the compound CaMg_2Bi_2 in final lead; however, for those tests in which no peritectic reaction occurs, most of bismuth in final lead are kept in bismuth atom. When a large amount of CaMg_2Sb_2 form and are floated rapidly up to the surface of lead batch, the antimony activity in lead drops to a very low value. So the residual free bismuth atom can substitute the antimony site and goes into dross during continued stirring. This hypothesis may give an interpretation of the results of antimony treatment on bismuth removal with different initial calcium content.

3.4.2 Effect of temperature on antimony treatment

From Table 5 it can be found that the antimony treatment can remove bismuth to a low level even at a relative high temperature. However, the bismuth concentration left in lead is lack of regularity. Almost all the added antimony goes into dross, resulting in a large amount of dross. The temperature of antimony treatment has no perceptible influence on the dross

Table 4 Test conditions and results of initial calcium concentration on antimony treatment

No.	Initial mass fraction/%		Dross ratio/%	Final mass fraction/%			
	Ca	Bi		Ca	Mg	Bi	Sb
D15	0.036	0.011	16.33	0.027	0.104	0.000 9	0.002
D16	0.061	0.010	16.83	0.051	0.103	0.000 9	0.002
D17	0.070	0.007	15.38	0.060	0.115	0.003	0.006
D18	0.076	0.008	17.57	0.064	0.113	0.004	0.002
D19	0.077	0.005	13.77	0.061	0.122	0.005	0.003

Table 5 Test conditions and results of temperature on antimony treatment

No.	Temperature/°C	Initial mass fraction/%		Dross ratio/%	Final mass fraction/%			
		Ca	Bi		Ca	Mg	Bi	Sb
E20	330	0.076	0.008	17.57	0.064	0.113	0.004	0.002
E21	341	0.073	0.009	17.39	0.059	0.100	0.001	0.004
E22	352	0.104	0.019	16.45	0.086	0.110	0.007	0.004
E23	363	0.093	0.021	17.71	0.078	0.116	0.006	0.003

production between 330 °C and 363 °C.

Because the initial calcium addition was fixed at 0.112% in preliminary debismuthizing tests (Table 1, No. A1 to A4), which is above the point *B*, all the alloys used in this batch tests had the chance to experience the peritectic reaction. But the extents of peritectic reaction differed at different end cooling temperatures. The alloy used in No. E20, which was cooled at 330 °C, would have experienced more peritectic reactions, resulting in more CaMg_2Bi_2 to re-dissolve into the final lead. This will lead to a poor bismuth removal result during the following antimony treatment. The bismuth level of No. 20 only dropped from 0.008% to 0.004% after antimony treatment at 330 °C. As for the test at 341 °C, a large amount of bismuth have been removed during debismuthizing by calcium and magnesium, and no peritectic reaction occurred before. So, most of the residual bismuth in lead may present as bismuth atom which is readily carried out by Mg_3Sb_2 and CaMg_2Sb_2 . The results of the No. E21 agree well with hypothesis, the bismuth concentration falls from 0.009% to 0.001% after antimony treatment. Compared with the alloy used in test at 341 °C, only little bismuth in alloy used at 352 °C has been removed by calcium and magnesium, and the solubility of CaMg_2Bi_2 is higher than that at 341 °C. Therefore, the bismuth level only decreased from 0.019% to 0.007% for the No. E22. To test at 363 °C, the original debismuthizing reaction with calcium and magnesium has been very limited, most of the bismuth in lead presented as bismuth atom and less CaMg_2Bi_2 formed. Therefore, the antimony treatment exhibited better result than that at 352 °C, and the bismuth level

fell from 0.021% to 0.006%.

4 Conclusions

1) The influence of calcium addition on debismuthizing is complicated due to the peritectic reaction. When the calcium addition is near the calcium concentration of peritectic reaction point, a little disturbance to the debismuthizing level can be expected.

2) Debismuthizing with calcium and magnesium alone can reach the level of 0.001% Bi in final lead at 330 °C, and the corresponding calcium and magnesium concentrations left in the final lead are 0.076% and 0.321%, respectively.

3) When the initial bismuth concentration in lead is 0.021%, majority of the debismuthizing reaction with calcium and magnesium occur below 352 °C; no bismuth can be removed above 363 °C.

4) When the calcium addition is less than the calcium concentration of peritectic reaction point, the bismuth concentration can be decreased to 0.001% easily by the following antimony treatment. A high amount of calcium added in the lead may has a negative effect on the antimony treatment for further debismuthizing.

5) Antimony treatment appears unlikely to act as a physical collection for CaMg_2Bi_2 . The probably mechanism is that the added antimony forms CaMg_2Sb_2 compound and the bismuth in the lead is further removed by partial substitution of Sb with Bi. So the antimony treatment can only remove free bismuth atoms but has little effect on the removal of CaMg_2Bi_2 .

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用钙、镁和铈深度除铋

路殿坤¹, 金哲男¹, 蒋开喜²

1. 东北大学 材料与冶金学院, 沈阳 110819;

2. 北京矿冶研究总院, 北京 100044

摘要: 为了实现铅的深度除铋, 对钙、镁添加量以及铈处理和温度对铅中除铋深度的影响进行研究, 并对除铋机理进行讨论。结果表明, 当钙、镁添加量分别达到 0.112% 和 0.395% 时, 在 330 °C 时不用添加铈就可以使产品的含铋量降低到 0.001%。维持镁加入量为 0.155%, 当钙添加量低于 0.09% (包晶反应点的浓度), 随后采用铈处理可以很容易使铋含量降到 0.001%; 但当钙添加量大于 0.09% 时, 铈处理对除铋的作用效果越来越差。

关键词: 除铋; 克罗尔-别特尔特法; 铈处理; 包晶反应

(Edited by YANG Hua)