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BRIEF COMMUNICATIONS

Interaction of Aluminum with Admixtures Dissolved in Liquid Lead

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Abstract—The behavior of antimony, tin, copper, bismuth, and arsenic admixtures during refining black lead with aluminum application was considered.

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One of possible methods of considerable reducing antimony content in lead obtained by processing secondary lead-containing raw material, first of all scraps of lead batteries, is the insertion of aluminum in molten metal with the subsequent formation of the AlSb compound in the form of a solid phase. The melting point of AlSb is 1058 ± 10°C, and density, about 4.2 g cm^{-3} [1]. The method is known for a long time [2], but its thermodynamic substantiation, including temperature process conditions, and also an experimental verification of the fulfilled calculations were carried out rather recently [3, 4].

It was found that refining secondary lead antimonide (the initial antimony content about 2–3 wt %) with aluminum is effective under the following operating conditions: the temperature of aluminum input 690–720°C and the duration of intermixing at this temperature up to 30 min, therewith the aluminum consumption can vary over a wide range, but should be no less than 40% of the weight of removed antimony [3]. The recommended subsequent rate of cooling up to the final temperature of 350°C is 5–6 deg min^{-1}. The antimony content in lead can be reduced up to 0.005 wt %. Experimental studies completely confirmed the thermodynamic analysis [3].

It is of interest to consider behavior of some possible admixtures in secondary lead, namely, tin, copper, bismuth, and arsenic during this process. The phase diagram of the lead–aluminum–tin system at 650, 730, and 800°C was studied by Davies rather explicitly [5]. This ternary system was also studied in other works [6, 7]. The systems Al–Sn and Pb–Sn belong to eutectic systems, and the ternary system Pb–Al–Sn includes an extensive phase separation area adjacent to the Al–Pb side and somewhat decreasing as temperature increases.

Data on the distribution of tin small amounts between aluminum and lead phases in liquid state are given in the work of Pleva et al. [8]. Unlike antimony removal by adding aluminum, which belongs to intermetallic refining processes, in the case of tin the extracting separation of metals takes place. It was shown in [8] that in the temperature range of 700–900°C the coefficient K_x of tin distribution between aluminum and lead, expressed as the ratio of mole fractions in coexisting aluminum (I) and lead (II) liquid phases, is

$$\frac{x_{\mathrm{Sn(Al)}}}{x_{\mathrm{Sn(Pb)}}} = \frac{x^{\mathrm{I}}_{\mathrm{Sn}}}{x^{\mathrm{II}}_{\mathrm{Sn}}} = 0.32 \pm 0.04.$$

The same authors [8] noted that at a phase equilibrium the mole fraction of lead in the aluminum layer $x_{\mathrm{Pb(Al)}}$ does not exceed 0.005, and the lead layer practically does not contain aluminum.

In the other work [7] the distribution of components between two not mixing phases in the system Pb–Al–Sn was studied at higher tin contents in the temperature range 800–1020°C. Depending on the total tin content in the ternary system its distribution coefficient between phases I and II at 800°C expressed in terms of tin mole fractions lays within the limits of 0.381–0.424.

At equilibrium tin activity in coexisting phases is the same, $\alpha^{\mathrm{I}}_{\mathrm{Sn}} = \alpha^{\mathrm{II}}_{\mathrm{Sn}}$ and $\alpha^{\mathrm{I}}_{\mathrm{Sn}}\,\gamma^{\mathrm{I}}_{\mathrm{Sn}} = \alpha^{\mathrm{II}}_{\mathrm{Sn}}\,\gamma^{\mathrm{II}}_{\mathrm{Sn}}$, where γ_{Sn} is the

tin activity coefficient in a corresponding phase. This implies

$$\frac{x_{Sn}^{I}}{x_{Sn}^{II}} = \frac{(\gamma_{Sn})^{II}}{(\gamma_{Sn})^{I}}. \quad (1)$$

If tin concentrations are low, as it usually takes place in processes of lead refining, equation (1) can take the following form:

$$\frac{x_{Sn}^{I}}{x_{Sn}^{II}} = \frac{(\gamma_{Sn}^{\infty})^{II}}{(\gamma_{Sn}^{\infty})^{I}}. \quad (2)$$

In this expression γ_{Sn}^{∞} represents the tin activity coefficient at infinite dilution $x_{Sn} \rightarrow 0$. The range of tin concentrations, where the distribution coefficient K_x retains a constant value at a specified temperature, is connected with the ranges where Henry's law for tin in alloys with lead and aluminum is obeyed [9]. Equation (2) implies that at the considered concentrations of the component (tin) distributed between phases I and II Henry's law is obeyed in the both phases and the dependences $\alpha_{Sn}^{I} = f(x_{Sn})$ and $\alpha_{Sn}^{II} = f(x_{Sn})$ $\alpha_{Sn}^{I} = \alpha_{Sn}^{II}$ are linear.

According to [10], at 800°C the activity coefficient of tin in liquid alloys with lead at the infinite dilution is 1.84 and its limiting value in liquid alloys with aluminum is 5.79. According to equation (2), the value of K_x appears to be 0.30, which is close to its average value in the temperature range 700–900°C. Such distribution coefficient of tin in the lead-aluminum system does not allow us to expect appreciable reduction of the tin content in liquid lead at refining with aluminum application.

In the lead-copper system an area of layering is observed, its expansion at the monotectic temperature (954.8°C) being within the limits $0.18 \leq x_{Pb} \leq 0.57$ [11]. The upper critical temperature is 1006°C. Liquid alloys of lead with copper are characterized by positive deviations from an ideal behavior, the maximal value of mixing enthalpy being 6.8 kJ mol^{-1} at 1200°C [11]. In the aluminum-copper system a number of ordered phases are formed in the copper-rich region of compositions, which results in rather noticeable negative deviations of activity isotherms of the components from Raoult's law. The enthalpy of mixing is negative, and its maximal value reaches –19.0 kJ mol^{-1} [12, 13].

According to Tanaka et al. [10], $\gamma_{Cu(Pb)}^{\infty}$ at 800°C is 8.44. In [11] the temperature dependence of the limiting activity coefficient of copper dissolved in liquid lead (T, K) is given:

$$\ln \gamma_{Cu(Pb)}^{\infty} = -1.43 + 3913T^{-1}.$$

Correspondingly, at 800°C $\ln \gamma_{Cu(Pb)}^{\infty} = 2.217$ and $\gamma_{Cu(Pb)}^{\infty} = 9.18$.

The calculation of the limiting activity coefficient of copper in a liquid alloy with aluminum at 800°C by the data recommended in [10] gives the value 0.068. In [14] $\gamma_{Cu(Al)}^{\infty} = 0.043$ at a higher temperature (1100°C). In the handbook [12] the following values of $\gamma_{Cu(Al)}^{\infty}$ are given: 0.045 (1100°C) and 0.047 (1200°C). Anyway, according to equation (2), the distribution coefficient is very high (120–130°), which points to a possibility to reduce copper admixture content in liquid lead by a refining operation with aluminum application.

Aluminum and bismuth are partially soluble in a liquid state, appreciable positive deviations from an ideal behavior [12] are observed in the system. A layering area in the ternary system lead–bismuth–aluminum occupies a greater part of the concentration triangle at 900°C. All this suggests that bismuth content in liquid lead would not decrease on its refining with aluminum.

In the aluminum–arsenic system a single compound AlAs melting congruently is formed (mp about 1760°C), which is characteristic for $A^{III}B^{V}$ systems. Eutectic points in the subsystems Al–AlAs and AlAs–As are located in the vicinity of the pure components [16]. We failed to find information on the thermodynamic properties of AlAs. The aluminum–arsenic system belongs to eutectic systems, and thermodynamic properties of its liquid alloys were studied repeatedly by various methods [17–19]. According to [19], the activity coefficient of arsenic in its dilute solutions in liquid lead at 527°C does not exceed 1.4. In the studied range of compositions of the Pb–As system ($x_{Pb} < 0.7$) only slight positive-negative deviations from an ideal behavior are observed. When aluminum is inserted into liquid lead containing an arsenic admixture, we can expect a certain intermetallic refining effect in connection with the formation of the AlAs compound.

In the patent [4] a two-stage refining of black lead is provided. The considered interaction of admixtures with liquid aluminum forms the first stage of the refining process. The second stage consists in the anode polarization of lead in molten sodium hydroxide at 350–380°C for the further decreasing the antimony

Contents of admixtures in desulfated active mass (oxide-carbonate cake), in black lead, and in lead after refining

Material	Content of admixtures, wt %				
	Sb	Sn	Cu	Bi	As
Initial desulfated active mass	1.5	0.007	0.007	0.003	0.005
Lead after reducing melting (black lead)	2.1	0.010	0.010	<0.004	0.007
Lead after the first refining stage	0.004	0.010	4.00×10^{-4}	<0.004	0.005
Lead after the second refining stage	0.0013	1.6×10^{-5}	4.0×10^{-4}	0.004	0.001

content and the removal of excess aluminum and some admixtures according to their electrochemical behavior [20–22]. The results of the two-stage refining of black lead obtained by processing real active masses of a lead battery are given in the table. According to the accepted technology, active masses of positive and negative plates were treated by a sodium carbonate solution for obtaining an oxide-carbonate cake, which was exposed to reducing melting. Black lead was analyzed by the method of atomic-and-absorption analysis with the use of a 4100-Z "Perkin-Elmer" spectrophotometer.

It is seen from the table that even after the first refining stage lead corresponds to the C2 grade according to GOST 3778-98 on the antimony content. As it was shown earlier [21], the anode polarization mode with low current densities makes it possible to obtain lead containing less than 0.001% of antimony that corresponds to C1-grade lead. By the tin content lead corresponds to the C0 grade after the second refining stage. By the copper content even after the first refining stage correspondence to the C0 grade is reached. As it was already pointed out, bismuth admixtures are not characteristic for black lead obtained by processing battery scraps, its initial content does not vary during the two-stage refining. The arsenic content corresponds to the C2 grade. The absence of information on the thermodynamic properties of the AlAs compound does not allow us to make a corresponding estimate of the refining process possibilities.

CONCLUSIONS

(1) The black lead refining with application of aluminum results in a stable decrease in the contents of antimony up to 0.005 and copper, up to 0.0005 wt %. There is no decrease in the tin and bismuth contents.

(2) Additional refining with application of anode polarization of lead in a hydroxide melt makes it possible to decrease the contents of antimony up to 0.001, tin, up to 1.6×10^{-5}, and arsenic, up to 0.001 wt %.

(3) The described method of two-stage refining does not change the bismuth admixture content.

REFERENCES

1. Glazov, V.M., Chizhevskaya, S.N., and Glagoleva, N.N., *Zhidkie poluprovodniki* (Liquid semiconductors), Moscow: Nauka, 1967.
2. Tsyganov, A.S., *Proizvodstvo vtorichnykh tsvetnykh metallov i splavov* (Production of Secondary Non-ferrous Metals and Alloys), Moscow: Metallurgizdat, 1961.
3. Morachevskii, A.G., Vaisgant, Z.I., Khabachev, M.N., and Mal'tsev, V.I., *Zh. Prikl. Khim*., 2000, vol. 73, no. 1, pp. 3–7.
4. RF Patent 2219265.
5. Davies, M.H., *J. Inst. Metals*, 1953, vol. 81, April, pp. 415–416.
6. Campbell, A.N. and Kartzmark, R., *Canad. J. Chem*., 1956, vol. 34, no. 10, pp. 1428–1439.
7. Shim, J.-H., Lee, H.N., Ha, H.P., et al., *J. Alloys a. Comp*., 2001, vol. 327, pp. 270–274.
8. Pleva, J., Woznik, J., Sliwa, A., and Wotala, J.K., *Metallurgia i Oldenictwo*, 1986, vol. 12, no. 1, pp. 53–69.
9. Morachevskii, A.G. and Kokhatskaya, M.S., *Prikladnaya khimicheskaya termodinamika* (Applied Chemical Thermodynamics), St. Petersburg: Izd. Politekhn. universiteta, 2008.
10. Tanaka, T., Gokcen, N.A., Neuschutz, D., et al., *Steel Research*., 1991, no. 9, pp. 385–389.
11. Teppo, O., Niemela, J., and Taskinen, P., *Thermochim. Acta*, 1991, vol. 185, pp. 155–169.
12. Batalin, G.I., Beloborodova, E.A., and Kazimirov, V.P., *Termodinamika i stroenie zhidkikh splavov na osnove alyuminiya* (Thermodynamics and Structure of Liquid Alloys on the Basis of Aluminum), Moscow: Metallurgiya, 1983.
13. Belousov, A.A., Bakhvalov, S.G., Aleshina, S.N., et al.,

Fiziko-khimichskie svoistva zhidkoi medi i ee splavov: Spravochnik (Physicochemical Properties of Liquid Copper and its Alloys: Handbook), Ekaterinburg: Institut metallurgii UrO RAN, 1997.

14. Wilder, T.C., *Trans. Met. Soc. AIME*, 1965, vol. 233, July, pp. 1202–1208.
15. Wilder, T.C. and Elliott, J.F., *J. Electrochem. Soc*., 1964, vol. 111, no. 3, pp. 352–362.
16. McAlister, A.J., *Bull. Alloy Phase Diagr*., 1984, vol. 5, no. 6, pp. 577–579.
17. Zaleska, E., *Roczn. Chem*., 1974, vol. 48, no. 2, pp. 195–200.
18. Schlesinger, M.E. and Lynch, D.C., *Met. Trans. B*, 1985, vol. 17B, March, pp. 235–238.
19. Onderka, B. and Wypartowicz, J., *Z. Metallkunde*, 1990, vol. 81, no. 5, pp. 345–348.
20. Morachevskii, A.G., Vaisgant, Z.I., Klebanov, E.B., and Kal'ko, O.A., *Zh. Prikl. Khim*., 1996, vol. 69, no. 1, pp. 66–68.
21. Morachevskii, A.G., Vaisgant Z.I., and Mal'tsev V.I., *Zh. Prikl. Khim*., 1999, vol. 72, no. 4, pp. 692–693.
22. Morachevskii, A.G., Vaisgant Z.I., and Demidov, A.I., *Elektrokhimiya svintsa v ionnykh rasplavakh* (Electrochemistry of Lead in Ionic Melts), St. Petersburg: Khimiya, 1994.