

THERMOGRAVIMETRIC (TG) STUDIES OF THE REACTION OF LEAD OXIDE WITH LEAD SULPHIDE

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Preliminary Note – Prethodno priopćenje

In the paper, results of thermogravimetric study on reaction between lead oxide and lead sulphide, both loose and agglomerated samples. The research results showed that the reaction of lead sulphide with lead oxide is possible at temperatures exceeding 850 °C. Comparing the influence of the reaction temperature on the course of the TG curve and the percentage weight loss of the samples, it was found that the percentage weight loss of the samples increased with the increase of the temperature. This effect was observed both for samples introduced in loose form, as well as for the agglomerated one.

Keywords: pyrometallurgy, thermogravimetry, lead, lead oxide, lead sulfide

INTRODUCTION

Global lead production ranks fourth in the group of non-ferrous metals, after aluminum, copper and zinc. It is worth noting that in the case of this metal, the volume of production from secondary raw materials has for many years exceeded the production from primary sources [1]. Lead is primarily used in the production of car batteries. The most popular lead compounds are lead sulphide (PbS) and lead oxide (PbO). They are found, among others, in lead-bearing paste which constitutes about 50 % of the of used car battery mass. In pyrometallurgical processing of lead, including the processing of spent batteries, lead sulphide and lead oxide may react with each other, resulting of obtaining metallic lead [2-5]:



As part of the presented work, thermogravimetric tests (TG) of a mixture composed of lead sulphide and lead oxide in the temperature range of 900 - 1 000 °C were carried out.

METHODOLOGY

The experiments were carried out using the NETZSCH STA 449 F3 Jupiter analyzer. Each TG measurement started with placing the experimental mixture on an alumina plate in the thermo-analyzer. After closing the measuring chamber of the sample, an inert gas (argon) was introduced into the analyzer space and its flow was set at a level of 120 ml / min. The sam-

ple was heated to the desired temperature at the rate of 20 °C / min. The time of isothermal conditions step of sample was set to 30 minutes. After this time, the heating system was turned off and the sample was cooled to ambient temperature. During the entire experiment, the weight loss of the sample was recorded.

The experiments were carried out at the following temperatures: 900, 925, 950, 975 and 1 000 °C. The mixture of PbO and PbS used for all measurements was prepared in a stoichiometric ratio resulting from reaction 1. Measurements were carried out for both loose and agglomerated samples (which were prepared on a hydraulic press).

RESEARCH AND DISCUSSION

An exemplary TG curve obtained during the thermogravimetric analysis, with the addition of heating

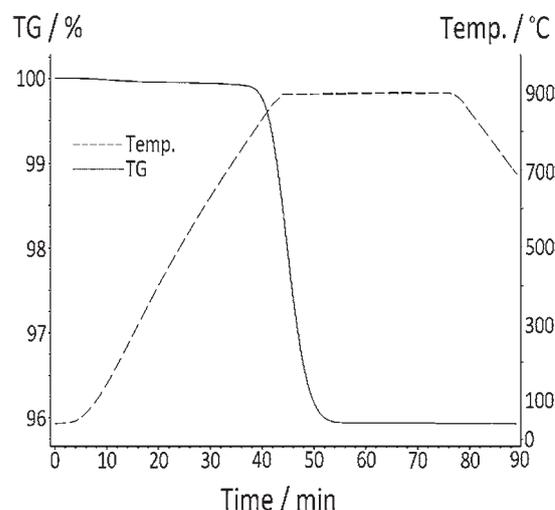


Figure 1 Thermogravimetric curve of PbS reaction with PbO at the temperature of 900 °C (loose sample)

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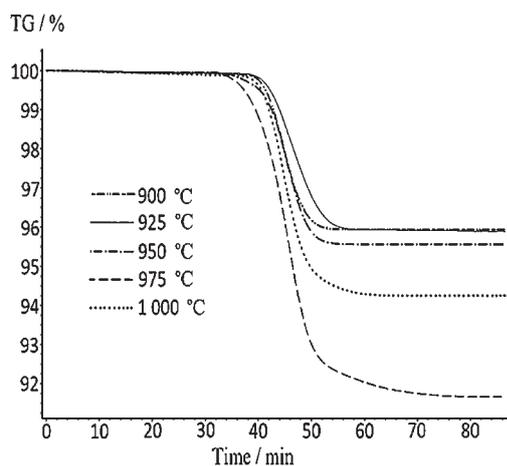


Figure 2 Summary of thermogravimetric curves of PbS-PbO reaction (in loose form)

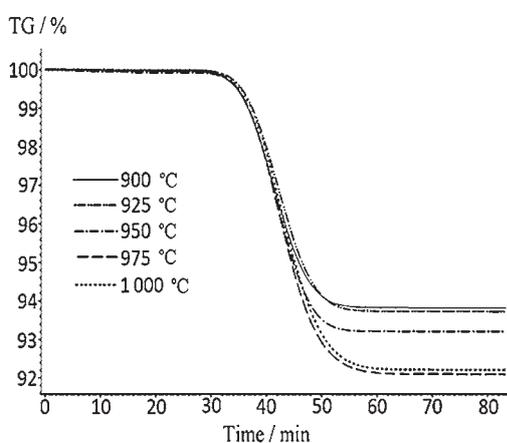


Figure 3 Summary of thermogravimetric curves of PbS-PbO reaction (in the form of an agglomerate)

curve, is shown in Figure 1. Figures 2 and 3 present all the TG curves obtained during the research for loose and agglomerated materials.

All the presented TG curves of the reaction between PbO and PbS follow a similar course. It was found that practically up to about 35 minutes of the process (temperature about 840 °C) there was no visible change in the mass of the samples. This proves that this reaction does not take place at low temperatures. In order to confirm this observation, the Gibbs free energy (ΔG) was determined for the considered reaction. Gibbs free enthalpy was determined with HSC Chemistry software. The curve of the Gibbs free enthalpy change as a function of temperature is shown in Figure 4. It can be seen that for the considered reaction ΔG assumes values less than zero above the temperature of 850 °C, which confirms the observed lack of reaction in the sample below this temperature value. Based on the additional differential thermal analysis (DTA) of the sample (Figure 5), it was also found that the reaction under consideration was exothermic. The appearance of exothermic effects is indicated by the developed surface area under the DTA curve and the presence of distinct extremes on it.

Based on reaction 1, the theoretical weight loss of the sample was determined, which was used to calculate

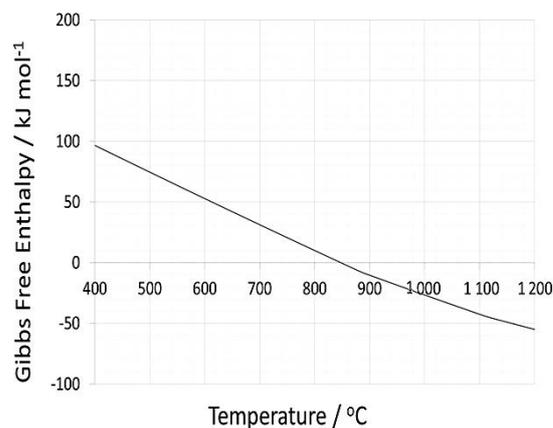


Figure 4 Gibbs free enthalpy change for reaction 1

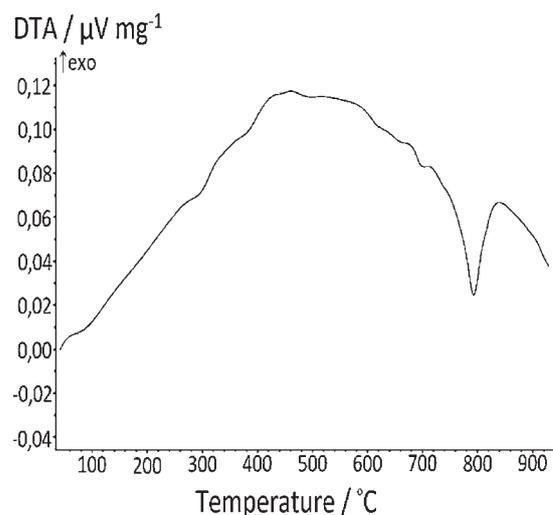


Figure 5 DTA curve of PbO reaction with PbS

the efficiency of individual processes. The results of the calculations, together with the weight losses recorded during the measurements, are presented in Table 1.

Comparing the influence of the reaction temperature on the course of the TG curve and the percentage weight loss of the samples, it was found that the percentage weight loss of the samples increased with the increase of the temperature. As a result, the speed and intensity of the tested reaction is increased. The effect was observed both for samples introduced in loose form, as

Table 1 List of registered weight losses of samples and determined reaction efficiency

The form of the material	Temp. / °C	Registered percentage weight loss of the sample / % mass.	Efficiency of the reaction / %
Loose material	900	4,07	43,48
	925	4,12	44,01
	950	4,45	47,54
	975	5,76	61,53
	1 000	8,35	89,20
Agglomerate	900	6,18	66,02
	925	6,27	66,98
	950	6,79	72,53
	975	7,79	83,21
	1 000	7,91	84,50

well as for the agglomerated one. The increase of the process temperature to 1 000 °C for the loose mixture resulted in an increase of the reaction efficiency by over 40 %, compared to the lowest temperature. In the case of the agglomerated samples, an increase in the process efficiency was also found with the temperature increase, but it was lower than in the case of loose samples and amounted to about 18 %. On the basis of the obtained results, it can be concluded that the agglomeration process has a significant impact on the course and efficiency of the tested process only in the lower temperature range. The use of agglomerate material in the lower temperature range resulted in an increase in process efficiency of up to about 25 %. This is mainly due to the increased contact surface of the mixture components, and thus the mass exchange, which significantly improves the initiation and course of the reaction at lower temperatures. The slower increase in process efficiency at higher temperatures for agglomerated samples is most likely due to the obstructed removal of the gas (SO₂) evolved from the reaction, which slows down the reaction.

SUMMARY

Based on the conducted thermogravimetric tests, it was found that the course of the reaction of lead sulphide with lead oxide is possible at temperatures exceeding 850 °C. The TG curves of the considered reaction for the charge materials in the form of loose and agglomerate have a similar course. In all cases, an increase in temperature results in an increase in weight loss. In the temperature range of 900 - 1 000 °C, the

efficiency of the reaction for the reagents in the loose form varies from 43,48 to 89,20 %. On the other hand, when the samples were agglomerated, the reaction efficiency varied from 66,02 to 84,50 %.

Due to the course of the analyzed reaction of lead sulphide with lead oxide, in the pyrometallurgical processes of lead production, the demand for technological additives in the form of fuels and reducing agents necessary for the proper course of the process is reduced.

Acknowledgments

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REFERENCES

- [1] Smaniotto A., Antunes A., Filho I. N., Venquiaruto L. D.: Qualitative lead extraction from recycled lead-acid batteries slag, *Journal of Hazardous Materials* 172 (2009), 1677–1680
- [2] Quirijnen L.: How to implement efficient local lead-acid battery recycling, *Journal of Power Sources* 78 (1999), 267–269
- [3] Bourson J.: Recycling of lead/acid batteries in a small plant, *Journal of Power Sources* 57 (1995), 81–83
- [4] Gomes G. M., Mendes T. F., Wada K.: Reduction in toxicity and generation of slag in secondary lead process, *Journal of Cleaner Production* 19 (2011), 1096–1103
- [5] Ellis T. W., Mirza A. H.: The refining of secondary lead for use in advanced lead-acid batteries, *Journal of Power Sources* 195 (2010), 4525–4529

Note: Nowak P. is responsible for English language, Katowice, Poland