ELSEVIER

Thermochimica Acta 322 (1998) 69–75

thermochimica acta

DTA and TG study of $PbSO_4$ dissociation in the presence of solid fuels

B. Boyanov[a,*], R. Dimitrov[b]

[a] Department of Inorganic Chemical Technology, University of Plovdiv, 24 Tsar Assen Street, Plovdiv, Bulgaria
[b] Fundamentals of Chemical Technology, University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd, Sofia, Bulgaria

Received 12 December 1997; accepted 30 June 1998

Abstract

Various semi-finished products, containing $PbSO_4$, can be processed in lead production. $PbSO_4$ dissociation is investigated in order to estimate the effect of temperature, time and presence of various solid fuels as reducing agents on the degree and mechanism of dissociation. It is shown that the presence of coal considerably decreases the dissociation temperature and increases the degree of $PbSO_4$ dissociation.

A mechanism of the studied process is proposed. The results obtained, and their industrial applicability, are confirmed by thermal-treatment study of lead cake and coal mixtures and a modeling of the agglomeration process. © 1998 Elsevier Science B.V.

Keywords: $PbSO_4$; DTA; TGA; Dissociation; Solid fuels; Mechanism

1. Introduction

In zinc production, when using the hydrometallurgical method of wealz and fuming oxide leaching, an insoluble residue remains, namely lead cake. Although it is a waste product of zinc production, it can be used as a raw material for the production of lead [1,2].

A main shortcoming of lead cake appears to be the fact that a major lead-containing phase is $PbSO_4$. The mixing of this by-product with the used lead sulfide concentrates results in the formation of metallic lead at the time when agglomeration is carried out. This worsens the process indexes and the quality of the obtained agglomerate.

A number of studies have been devoted to the dissociation of various metal sulfates [3–11], but so far less attention has been paid to $PbSO_4$. The dissociation of $ZnSO_4$, which is also present in the lead cake, has been studied thoroughly [7,12].

The thermal treatment of different raw materials containing $PbSO_4$ at a temperature of 1000–1050°C decreases the content of sulfur sulfate but the degree of dissociation achieved is low. A greater degree of dissociation is achieved when their processing takes place in a reducing medium [13–15].

The lead cake contains mainly Pb, Zn, Cu and some other non-ferrous metals [1]. It is a valuable and cheap raw material; therefore, from an economical point of view, it is expedient to increase its part in the initial lead mixture.

The purpose of the present study is to investigate the influence of different fuels on the dissociation of $PbSO_4$ by using DTA and TG.

---

*Corresponding author. Tel.: +359-3226-15361; fax.: +359-322-35049.

PII: S0040-6031(98)00480-8

Table 1
Chemical and phase composition of lead cake

Content, mass %							
Pb	Zn	S	S_{SO_4}	Cu	Fe	SiO_2	CaO
41.85	8.44	11.55	10.92	0.44	2.69	1.10	1.00
Cl	Pb_{SO_4}	Pb_{met}	Pb_{ox}	Pb_s	ZN_{SO_4}	Zn_s	Zn_{ox}
0.82	26.80	0.03	5.36	0.19	6.53	0.08	0.34

Table 2
Chemical composition of the used solid fuels

No.	Fuel	Content, mass%					
		C	H	S	S_{SO_4}	SiO_2	CaO
1	Coke	75.33	2.78	1.90	0.37	2.34	—
2	Coal 1	41.83	6.23	1.96	0.46	3.74	1.05
3	Coal 2	25.00	3.02	6.00	0.25	13.26	1.22
4	Coal 3	36.40	5.19	2.03	0.57	7.00	0.30

2. Experimental

DTA and TG experiments (Q Derivatograph, MOM, Hungary) were carried out under the following conditions: sensitivity of DTA – 0.5 mV; DTG – 1 mV; TG – 200 mg; heating rate, 10 K min^{-1}; sample mass – 200 mg. A ceramic crucible (diameter 14 mm and height 17 mm) was used. The size of sample particles was −0.2 mm. All the studies were performed in air medium.

X-ray diffraction analysis of the solid phases was carried out with a TUR-M62 apparatus (Dresden, Germany) using CoK_α radiation and an iron target.

The chemical and phase compositions of the lead cake in relation to lead and zinc are presented in Table 1 and those of the studied fuels – in Table 2.

The experimental studies were performed at different ratios of $PbSO_4$ and C (1 : 5; 1 : 3; 1 : 1).

3. Results and discussion

The TG and DTA studies of the fuels show a considerable difference in the initial and final temperatures of the combustion process, the intensities of exothermal effects, moisture contents, and the loss of sample mass in the course of combustion and at 1000°C. The most important results of TG and

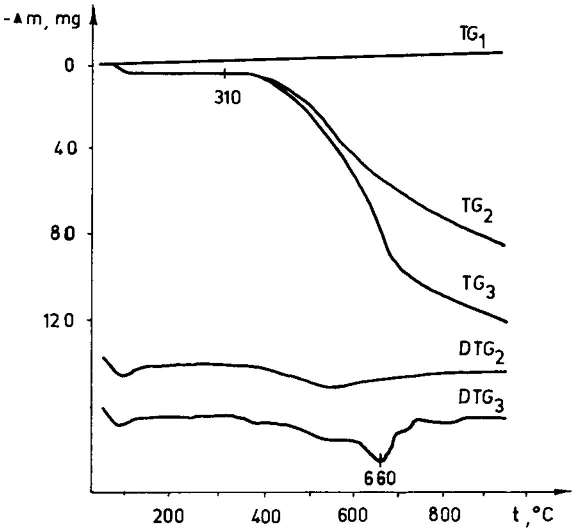


Fig. 1. TG and DTG curves of: 1 – $PbSO_4$; 2 – coal 1; 3 – $PbSO_4$+coal 1 ($PbSO_4$: C=1 : 5).

Table 3
Results from DTA and TGA of the fuels

No.	Fuel	Exothermal effects/°C	t_{beg}/°C	t_{end}/°C	Mass loss −Δm/% (1000°C)
1	Coke	695	520	915	85.0
2	Coal 1	550	330	670	46.0
3	Coal 2	655	525	800	22.0
4	Coal 3	325 410 485 [a]	200	555	75.0

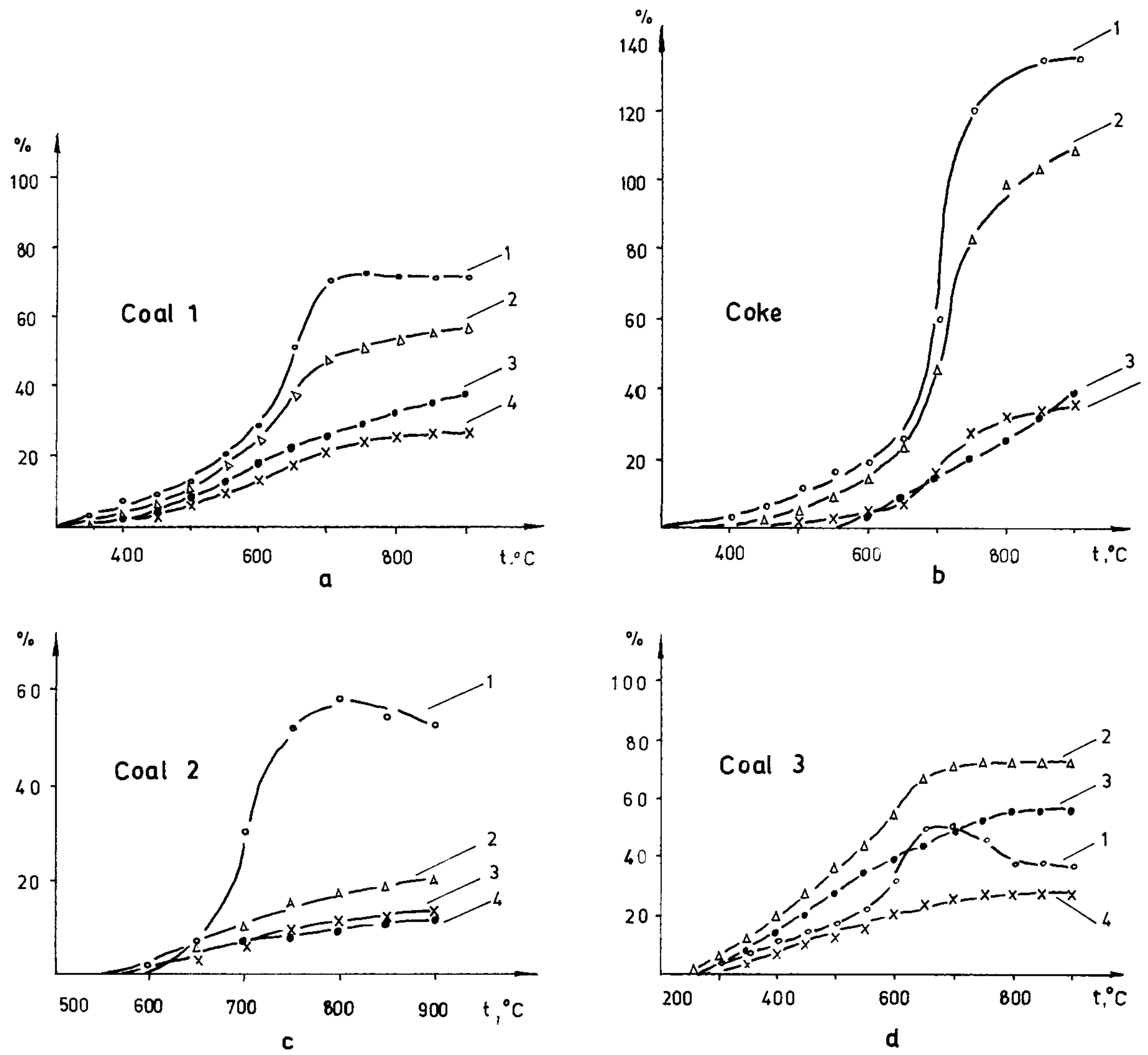
[a] The most intense exothermal effect.

DTA of the fuels (temperatures of the exoeffect maximums, the initial, t_{beg}, and final, t_{end}, temperatures of mass loss, loss of mass, Δm, at 1000°C) are presented in Table 3.

The dissociation of $PbSO_4$, alone and in mixture with solid fuels, was studied. The results obtained with coal 1 are shown in Fig. 1. The degree of dissociation of $PbSO_4$ is calculated on the basis of the obtained TG curves.

The TG_1 curve shows that, in the studied temperature interval, the individual $PbSO_4$ undergoes a very small increase in its mass. The TG_2 curve shows that the mass of coal begins to decrease above 350°C.

On comparing the TG curves, the considerable difference in the change of sample mass is quite apparent when the sample contains both $PbSO_4$ and coal 1. The experiments of the remaining fuels show



a

b

c

d

Fig. 2. (1) Degree of 'decomposition' of $PbSO_4$ in the presence of solid fuel (curves 1); (2) change of fuel mass in the presence of $PbSO_4$; (3) change of fuel mass; and (4) change of the samples mass of fuel and $PbSO_4$ ($PbSO_4$: C=1 : 5).

similar results. This difference in the change of sample mass is mostly due to the chemical interaction between $PbSO_4$ and the products of fuel combustion, as a result of which the temperature of sulfate decomposition decreases considerably. It is quite possible that the presence of $PbSO_4$ results in intensifying the combustion process of the coal used.

In order to find out the reasons for the higher mass losses, Fig. 2 presents curves based on the experiment and on the calculations. Curve 1 shows the degree of dissociation (α) of $PbSO_4$ (in %) on the assumption that the difference in the change of sample mass is completely due to the dissociation of $PbSO_4$. Curve 2 depicts the change of fuel mass if assumed that the change of sample mass is due to the intensification of coal combustion. Curve 3 presents the change of mass of fuel alone, and curve 4 represents the change of sample mass related to the total mass of the mixture $PbSO_4$+fuel.

From Table 3, it is obvious that the maximum loss of mass in the coal 1 combustion, up to a temperature of 1000°C, can be 46%. At the same time, from curve 2 (Fig. 2(a)) it is seen that the loss of mass is 58.8%, which can only be due to a higher degree of dissociation of the $PbSO_4$ present in the mixture.

On comparing Fig. 2(a) with the results obtained when using other fuels (Fig. 2) certain considerable differences are noticed.

According to curve 1 in Fig. 2(b) the $PbSO_4$ present 'decomposes' more than 100%, which is impossible. Therefore, apart from the higher degree of dissociation of $PbSO_4$, another probable explanation of the greater sample mass loss is that it is also due to intensified coke combustion and the reduced process-performing temperature.

The change in the rate of combustion process in the presence of $PbSO_4$ is also confirmed by curve 1 in Fig. 2(c). Accordingly, the dissociation of $PbSO_4$ increases up to ca. 800°C, beyond which it decreases. That is impossible and the probable explanation is in the different combustion rate of coal when combustion takes place in the presence of $PbSO_4$. A similar shape of curve 1 is also noticed when coal 3 is used (Fig. 2(d)).

The results obtained show that the maximum 'decomposition' of $PbSO_4$ takes place at different temperatures in the different samples. In case of coke and coal 2, this process takes place at ca. 750°C, while in the other two fuels this temperature is ca. 100°C lower.

According to the achieved 'degrees of decomposition' of $PbSO_4$ when using different fuels, they can be arranged in the following descending order: coke, coal 1 (α ca. 70%), coal 3 (α ca. 65%) and coal 2 (α ca. 55%).

The main conclusion which can be drawn is that the presence of fuel considerably decreases the dissociation temperature of $PbSO_4$. The TG and DTA showed that $PbSO_4$ decomposition begins at 910°C. At the same time, a considerable part of

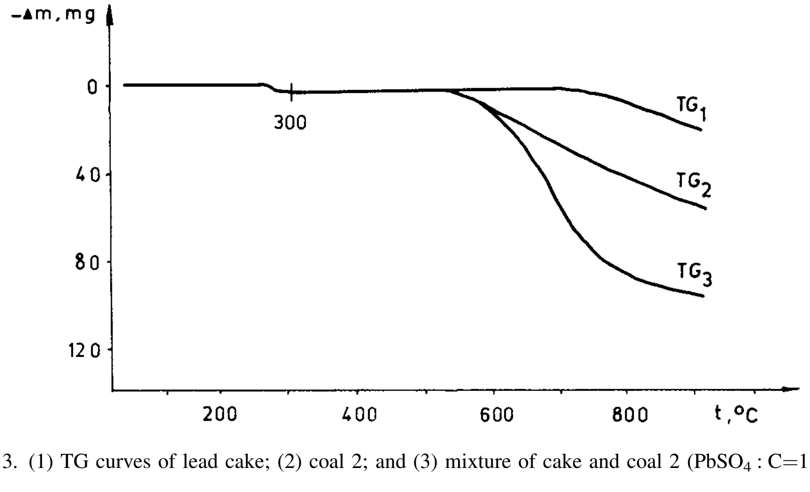


Fig. 3. (1) TG curves of lead cake; (2) coal 2; and (3) mixture of cake and coal 2 ($PbSO_4$: C=1 : 5).

$PbSO_4$ decomposes up to 900°C when a solid fuel is present.

Studies of $PbSO_4$ dissociation are made under conditions of reduced carbon content ($PbSO_4$: C= 1 : 3; 1 : 1). Under these conditions, $PbSO_4$ dissociation may also begin at a lower temperature, but the degree of dissociation decreases.

The results obtained lead to the assumption that the greater part of the decrease in the mass of $PbSO_4$+C mixture is both, due to the higher degree of $PbSO_4$

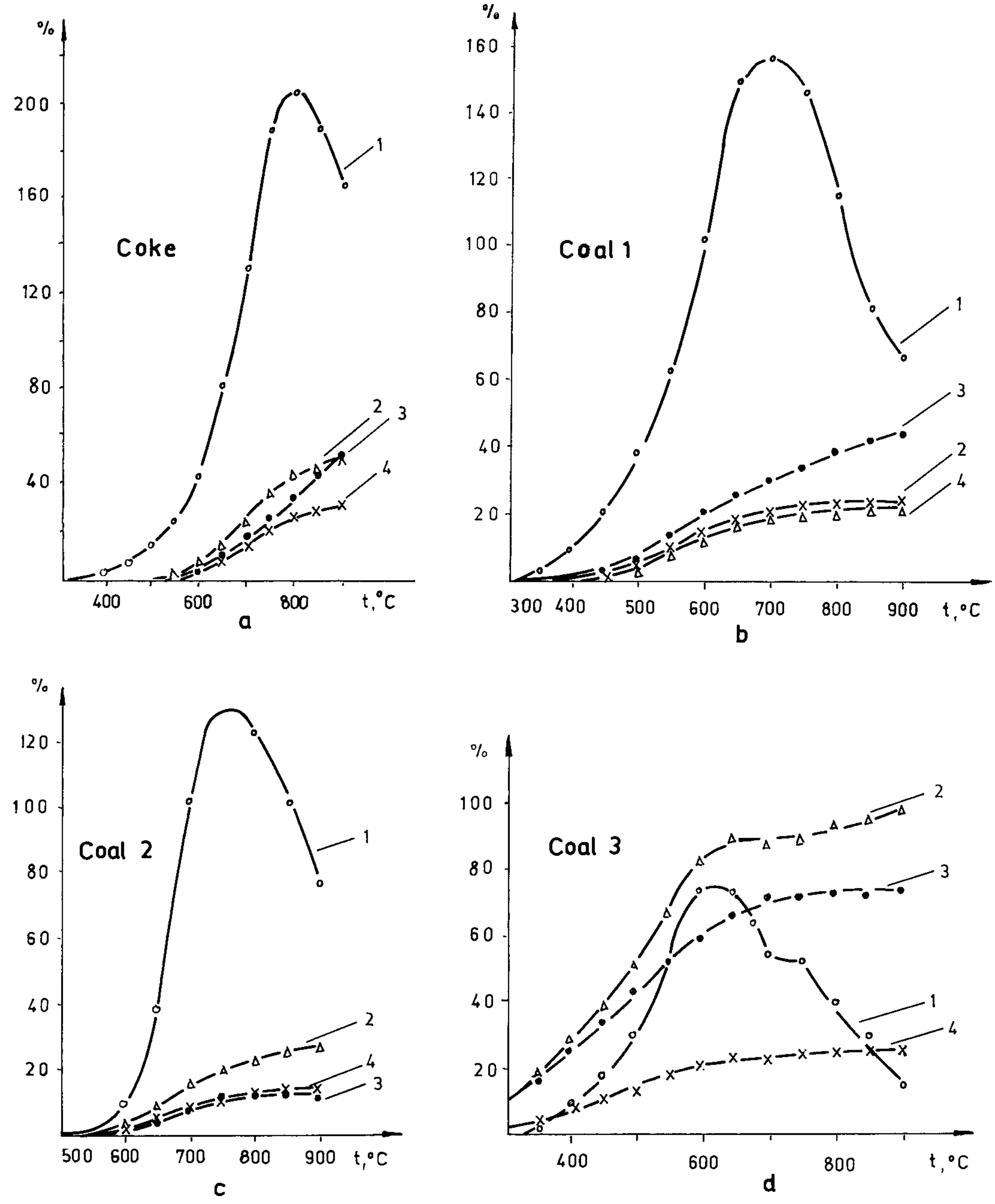


Fig. 4. (1) Degree of 'decomposition' of cake sulfates in the presence of solid fuel (curves 1); (2) change of fuel mass in the presence of cake; (3) change of fuel mass; and (4) change of the samples mass of fuel and cake ($PbSO_4$: C=1 : 5).

dissociation and to the intensification of the combustion process.

Most probably, in the thermal treatment of $PbSO_4$ in the presence of solid fuel the following reactions take place:

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$C + CO_2 \rightarrow 2CO \quad (2)$$

$$PbSO_4 + CO \rightarrow PbO + SO_2 + CO_2 \quad (3)$$

$$PbSO_4 \rightarrow PbO + SO_3 \quad (4)$$

$$SO_3 \rightarrow SO_2 + 1/2O_2 \quad (5)$$

$$C + 1/2O_2 \rightarrow CO \quad (6)$$

$$PbSO_4 + 4CO \rightarrow PbS + 4CO_2 \quad (7)$$

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \quad (8)$$

$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2 \quad (9)$$

The results from TG and DTA confirm the possibility of the intensification of $PbSO_4$ dissociation when using a solid fuel. The final products of thermal treatment in a reducing atmosphere are PbO, SO_2, CO_2 and H_2O.

By means of X-ray diffraction analysis, the following lead-containing phases were found in the cake: $PbSO_4$, PbO and PbS. Calculations, based on the chemical composition of the lead cake and the fuels, are made for different $PbSO_4 : C$ ratios in the tested samples.

Fig. 3 presents the TG curves of lead cake, coal 2, and of the mixture cake+coal 2. It shows a considerable difference between the changes of cake mass with, and without, the participation of solid fuel in the thermal treatment. The greater loss of sample mass is due to the more intense dissociation of the sulfates.

Fig. 4 presents the curves obtained after calculating the results from the derivatograms of the fuels, cake and their mixture ($PbSO_4 : C=1 : 5$). The results show that, in the presence of fuel, the dissociation of sulfates (curve 1) goes through a maximum. This, once more, confirms the complex mechanism of the process taking place. This is probably once again due to the higher degree of sulfate dissociation and the intensification of fuel combustion as a result of the availability of atomic oxygen. With the decrease of the quantity of carbon in the mixture, the intensification of the dissociation processes is lower.

The obtained results were the basis for increasing, in industrial conditions, the quantity of $PbSO_4$-containing by-products for agglomeration in the mixture. For this purpose, the fuel that was used gave a high enough degree of sulfate dissociation at the lowest possible price. This resulted in an improvement of the economic indexes of the process of agglomeration mainly due to the use of waste lead-containing materials. The developed technology has also a certain ecological effect, resulting from having created the possibility for processing by-products of other metallurgical processes.

4. Conclusions

1. The dissociation of $PbSO_4$ in the presence of solid fuel (coke and three types of coal) takes place to a much higher degree, compared to the process carried out without fuel, which is mainly due to a decrease in the dissociation temperature.
2. The intensification of the sulfates decomposition (mainly $PbSO_4$), present in the lead cake, results in an acceleration of the release of oxygen which improves fuel combustion.
3. On the basis of the obtained experimental data, a mechanism of the processes is proposed.
4. The obtained results were used in industrial production of lead for processing of additional quantities of lead cake and favorable technical and economical results have been achieved.

References

[1] V. Karoleva, Metallurgy of Non-ferrous Metals, Tekhnika, vol. 2, Sofia, 1986, p. 299.
[2] W. Volke, H. Kunibert, Erzmetall 30 (1977) 135.
[3] H. Tanaka, M. Kawano, N. Koga, Thermochim. Acta 182 (1991) 281.
[4] H. Tagawa, K. Kawabe, Thermochim. Acta 158 (1990) 293.
[5] H. Tagawa, Thermochim. Acta 80 (1984) 23.
[6] H. Tagawa, H. Saijo, Thermochim. Acta 91 (1985) 67.
[7] M. Brown, D. Dollimore, A. Galwey, Solid State Reactions, Mir, Moscow, 1983, p. 260.
[8] Y. Pelovski, V. Petkova, I. Dombalov, I. Gruncharov, J. Therm. Analysis 36 (1990) 1727.
[9] Y. Pelovski, Ictac News, year 27(2) (1994) 95.
[10] V. Jordanovska, R. Trojko, B. Boyanov, Thermochim. Acta 275 (1996) 301.

[11] B. Boyanov, Thermochim. Acta 240 (1994) 225.
[12] B. Boyanov, R. Dimitrov, Thermochim. Acta 93 (1985) 733.
[13] P.N. Pestunova, V.A. Lysenko, V.F. Larin, Non-Ferrous Metals (in Russian) 8 (1976) 30.
[14] P.N. Pestunova, Yu.G. Ognev, V.F. Larin, Non-Ferrous Metals (in Russian) 12 (1980) 42.
[15] D. Hadjistavrev, R. Dimitrov, S. Chalkov, N. Aleksandrov G. Georgiev, Khr. Paleshnikov, Z. Dragov, Report presented at the VI National Conference on New Technologies and Materials in Non-Ferrous Metallurgy, Plovdiv, Bulgaria, 25–27 February, 1988.