Thermochimica Acta, 230 (1993) 65–75
Elsevier Science Publishers B.V., Amsterdam
SSDI 0040-6031(93)01145-S

Thermodynamic analysis of the quasi-binary section A–Pb in the ternary system Pb–Bi–Mg. Part 1. Thermodynamic analysis of the quasi-binary section A–Pb in the ternary system Pb–Bi–Mg by the Oelsen Calorimetric method

Dragana Živković [a], Živan Živković [a] and Jaroslav Šesták [b,*]

[a] *Technical Faculty, University of Belgrade, JNA 12, Yu-19210 Bor (Minor Yugoslavia)*
[b] *Institute for Physics, Czech Academy of Sciences, 18040 Prague (Czech Republic)*

(Received 22 February 1993; accepted 9 March 1993)

Abstract

The results of Oelsen calorimetric measurements in the quasi-binary section A–Pb of the ternary system Pb–Bi–Mg are given in this paper, and include the phase diagram of this section, partial molar quantities, activities, and activity coefficients for lead at different temperatures. The results of X-ray analyses and the metallography used for phase analysis of the investigated section are also presented in this paper.

INTRODUCTION

Magnesium can be used in the refining of lead from bismuth in the extractive metallurgy of lead [1], during which many processes take place in the ternary system Pb–Bi–Mg. Therefore, the determination of the thermodynamic properties of this system is important from the scientific and practical point of view.

Thermodynamic data for the binary systems Pb–Bi, Bi–Mg, and Mg–Pb are available in the literature [2–6], but there are only a few articles dealing with the thermodynamic behavior of the ternary system Pb–Bi–Mg [7, 8].

The ternary system Pb–Bi–Mg is presented in Fig. 1 which also indicates the investigated section A–Pb.

The quasi-binary section A–Pb was chosen because it passes through the ternary eutectic point, the composition of which is [9] (in wt.%) Pb, 62%; Bi, 8%; Mg, 30%. Also, this section describes the thermodynamics the lead

* Corresponding author.

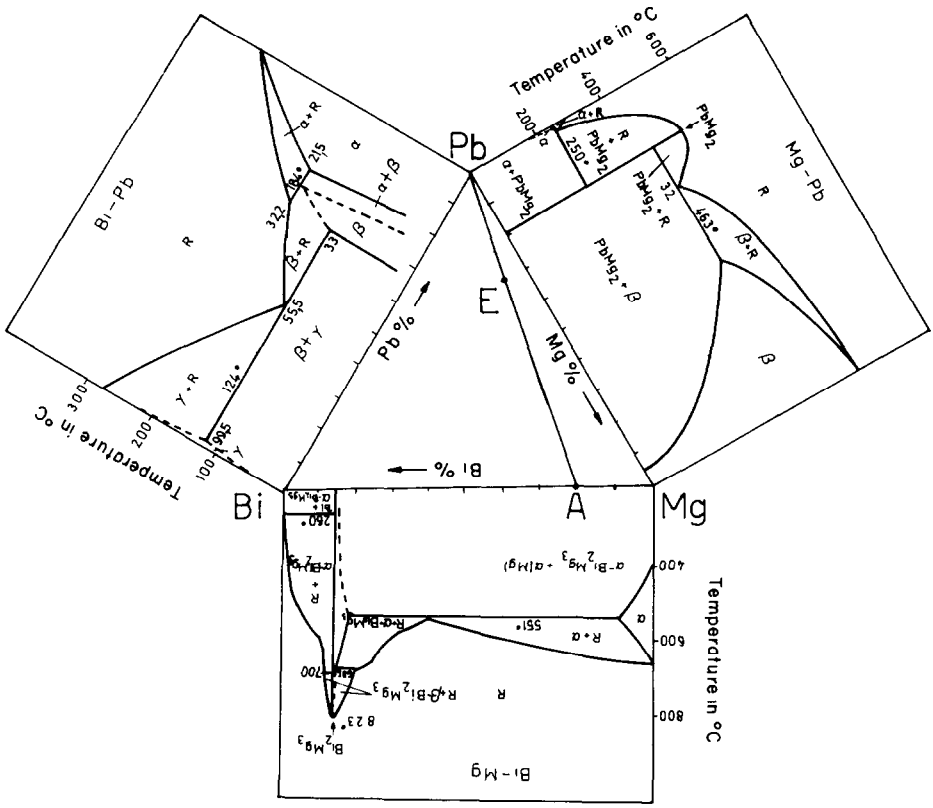

Fig. 1. The ternary system Pb–Bi–Mg.

corner of the ternary system Pb–Bi–Mg, which is important in the refinement of lead from bismuth using magnesium.

EXPERIMENTAL

Oelsen calorimetry was used for the thermodynamic analysis of the quasi-binary section A–Pb in the ternary system Pb–Bi–Mg. Descriptions of this experimental technique are reported in refs. 10–12. All the metals used were of analytical grade.

Eleven samples were chosen for further experimental investigation; their composition is given in Table 1. In addition, the water equivalent was determined by a standard method using dissolved Na_2CO_3; for the calorimeter used, it has a value of 3560 $J\,K^{-1}$.

The phase structure was examined using a Reichert MeF2 optical microscope.

X-ray diffraction analysis was performed on equipment produced by Siemens AG. The recording was made with a Cu anti-cathode and a Ni filter at a voltage of 40 kV and a current of 18 mA.

TABLE 1

Composition of the investigated samples

No	Composition/ wt.%			Molar content			m/g			$m\Sigma$/g
	Pb	Bi	Mg	x_{Pb}	x_{Bi}	x_{Mg}	Pb	Bi	Mg	
A1	100	0	0	1	0	0	11.400	–	–	11.400
A2	98	1	1	0.919	0.009	0.072	10.572	0.108	0.108	10.788
A3	96	1	3	0.787	0.008	0.205	10.323	0.107	0.323	10.753
A4	90	2	8	0.566	0.013	0.421	7.092	0.158	0.630	7.880
A5	78	5	17	0.347	0.022	0.631	4.556	0.292	0.993	5.841
A6	70	6	24	0.246	0.021	0.733	3.406	0.292	1.168	4.866
A7	62	8	30	0.188	0.024	0.788	2.639	0.341	1.277	4.257
A8	40	13	47	0.087	0.028	0.885	1.256	0.408	1.476	3.140
A9	8	19	73	0.012	0.029	0.959	0.179	0.426	1.637	2.242
A10	3	21	76	0.004	0.031	0.965	0.065	0.456	1.649	2.170
A11	0	21	79	0	0.030	0.970	0	0.442	1.661	2.103

RESULTS AND DISCUSSION

Based on the cooling curves obtained by Oelsen calorimetry, the phase diagram of the investigated quasi-binary section A–Pb in the ternary system Pb–Bi–Mg was obtained and is shown in Fig. 2. The experimental data show good agreement with literature data [9]. Two eutectic points appear in the quasi-binary section A–Pb: the first, at a temperature of 217°C, of composition (wt.%) Pb, 96%; Bi, 1%; Mg, 3%; the second is a ternary eutectic point at 429°C, of composition (wt.%) Pb, 62%; Bi, 8%; Mg, 30%. Also, there is an intermetallic compound at 78% Pb, 5% Bi, 17% Mg, which has a melting temperature of 523°C.

According to limiting factors of the method used, the basic equation used in Oelsen thermodynamic analyses [10–12]

$$-G_i^M/T = \int_{1/T_0}^{1/T} H_{x,T}\, d(1/T) = -R \ln a_i \qquad (1)$$

where G_i^M is the partial Gibbs energy for component i, T_0 is the starting temperature, T the finite temperature, $H_{x,T}$ the enthalpy value measured in the Oelsen calorimeter for the temperature change from T_0 to T, R the gas constant and a_i the activity of the component i, is not valid for conditions under which an intermetallic compound is formed. Therefore, thermodynamic analyses of this system cannot be made for samples over $x_{Pb} = 0.347$ (sample A5), because an intermetallic compound exists at that composition (see Fig. 2).

The first step in the Oelsen thermodynamic analysis is the construction

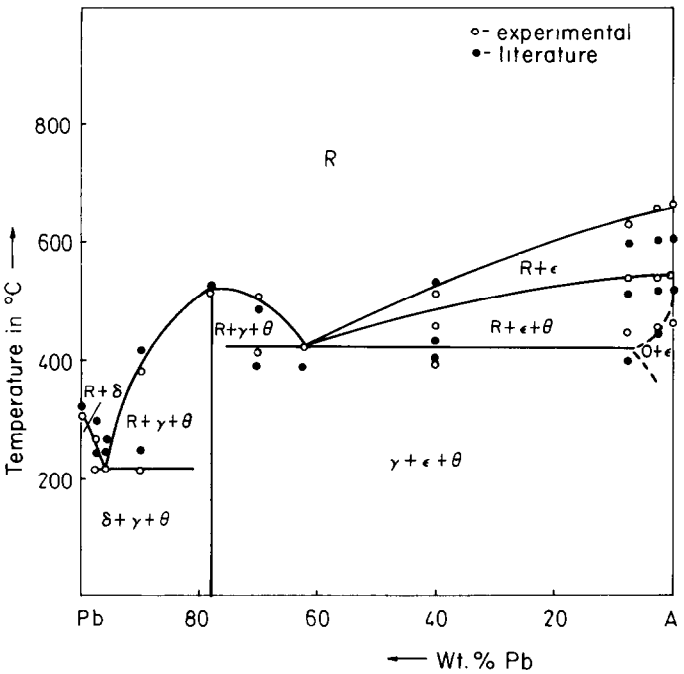

Fig. 2. The phase diagram of the quasi-binary section A–Pb in the ternary diagram Pb–Bi–Mg.

of the space diagram and enthalpy isotherm diagram for the temperature interval 350–1000 K; these are shown in Figs. 3 and 4, respectively. According to the Oelsen thermodynamic analysis [10–12], the next step is graphic planimetry, as shown in Fig. 5, which enables further quantitative thermodynamic analysis.

The construction of the tangent for determination of $-R \ln a_{Pb}$ at 873 K is shown in Fig. 6. The results of the Oelsen quantitive thermodynamic analysis, which include values for activities, activity coefficients and other partial molar quantities for lead in the range 873–973 K, are given in Table 2.

The dependence of the activity of lead on the molar content at 873, 913 and 973 K is presented in Fig. 6. A negative deviation from Raoult's law indicates good miscibility between the components in the investigated quasi-binary section A–Pb of the ternary system Pb–Bi–Mg.

In the compositional range of the investigated section A–Pb studied, from $x_{Pb} = 1$ to 0.347 (or A_1–A_5), the, activity coefficients for lead are less than unity. With increasing molar content, the activity coefficients for lead decrease uniformly. Also, with increasing temperature, the activity coefficients increase for all the studied compositions.

The values of the partial molar quantities derived from known values of the activities and activity coefficients for lead, confirm the conclusions

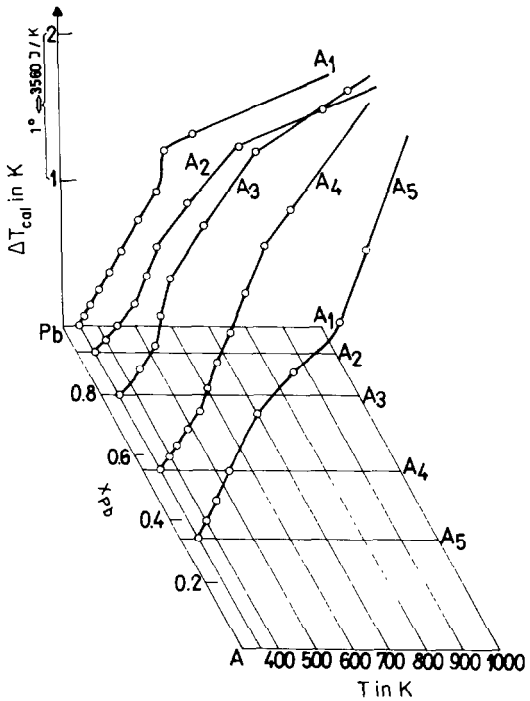

Fig. 3. The space diagram: the temperature change of the calorimeter vs. molar content and temperature.

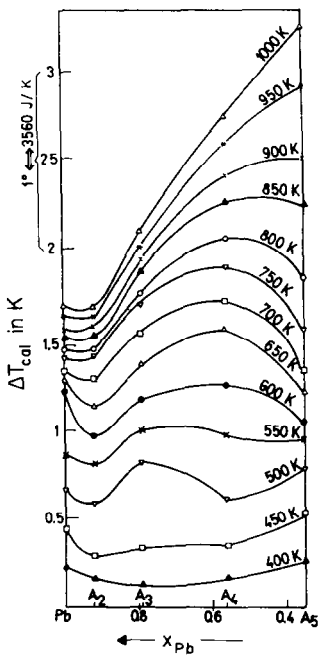

Fig. 4. The enthalpy isotherm diagram for the temperature interval 350–1000 K.

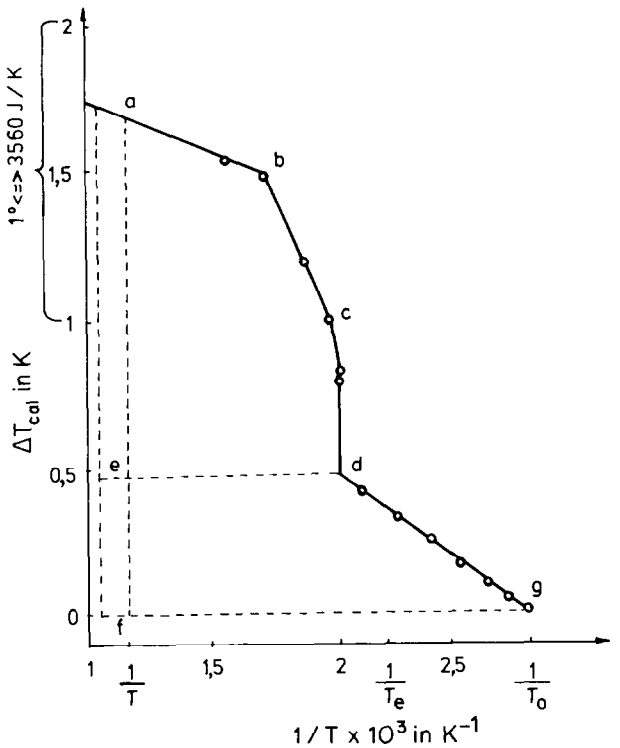

Fig. 5. Graphic planimetry (for sample A3).

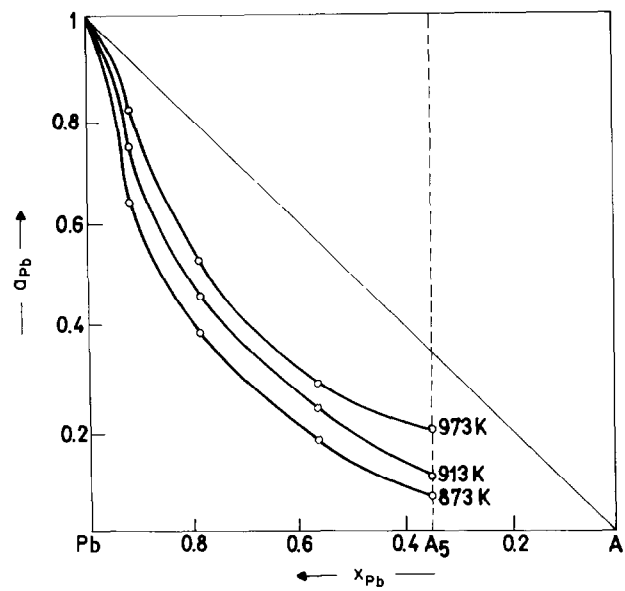

Fig. 6. Activity vs. molar content of lead at 873, 913 and 973 K.

TABLE 2

Results of the Oelsen quantitative thermodynamic analysis

No	T/K	a_{Pb}	γ_{Pb}	$G^{xs}_{Pb} = RT \ln \gamma_{Pb}$ in J mol^{-1}	$G^{M}_{Pb} = RT \ln a_{Pb}$ in J mol^{-1}
A1	873	1	1	0	0
A2		0.641	0.696	−2630	−3239
A3		0.382	0.483	−5282	−7023
A4		0.183	0.318	−8316	−12446
A5		0.075	0.202	−11609	−19301
A1	893	1	1	0	0
A2		0.676	0.736	−2276	−2907
A3		0.406	0.516	−4912	−6692
A4		0.204	0.360	−7585	−11802
A5		0.091	0.259	−10030	−17878
A1	913	1	1	0	0
A2		0.749	0.815	−1553	−2194
A3		0.458	0.572	−4240	−6061
A4		0.239	0.422	−6549	−10865
A5		0.112	0.323	−8578	−16618
A1	933	1	1	0	0
A2		0.768	0.836	−1390	−2048
A3		0.498	0.633	−3547	−5408
A4		0.242	0.428	−6583	−11006
A5		0.122	0.352	−8099	−16319
A1	953	1	1	0	0
A2		0.796	0.866	−1140	−1808
A3		0.522	0.663	−3256	−5151
A4		0.245	0.433	−6632	−11144
A5		0.129	0.372	−7835	−16226
A1	973	1	1	0	0
A2		0.825	0.898	−870	−1556
A3		0.540	0.686	−3049	−4985
A4		0.286	0.505	−5527	−10126
A5		0.204	0.588	−4296	−12859

about the thermodynamic behavior of the investigated system with respect to Raoult's law. The partial Gibbs energy of mixing for lead decreases with increasing temperature, which means that the lead tends to volatize and a change in structural characteristics appears in the solution. Therefore, the temperature at which lead is refined from bismuth using magnesium must be controlled.

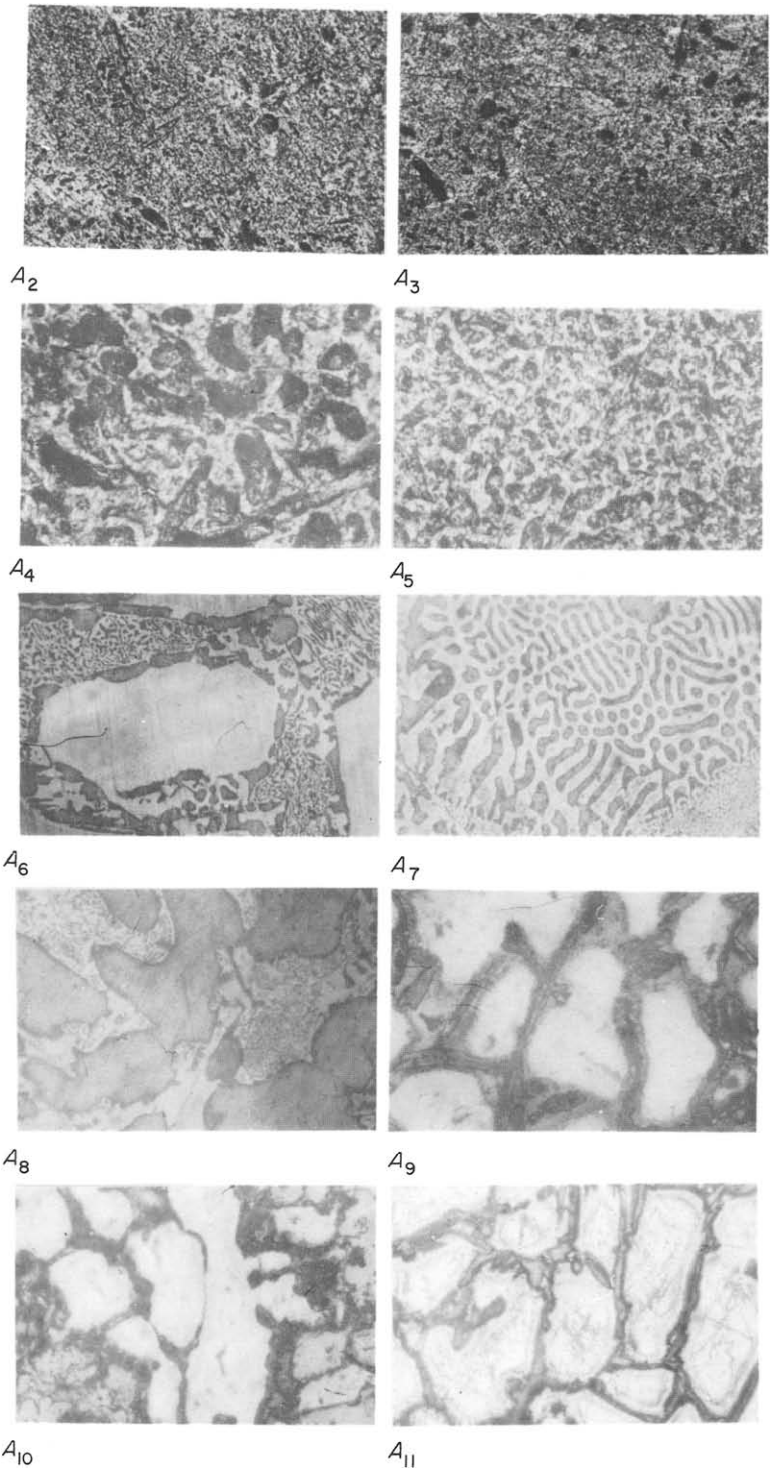

Fig. 7. Micrographs of characteristic samples. Original magnifications: A2–A5, ×200; A6 and A7, ×500; A8 and A9, ×750; A10 and A11, ×500.

TABLE 3

Results of the XRD phase characterizations

A1 nm	A2 nm	A3 nm	A4 nm	A5 nm	A6 nm	A7 nm	A8 nm	A9 nm	A10 nm	A11 nm
0.1422 Pb	0.1422 Pb	0.1102 Pb	0.1232 Pb	0.1232 Pb	0.1304	0.1199 Mg_2Pb	0.1304 Mg_2Pb	0.1257	0.1240	0.1292 Bi_2Mg_3
0.1492 Pb	0.1488 Pb	0.1131 Pb	0.1422 Pb	0.1422 Pb	0.1385	0.1277	0.1385 Mg_2Pb	0.1340	0.1257 Bi_2Mg_3	0.1340
0.1585	0.1741 Pb	0.1232 Pb	0.1488 Pb	0.1488	0.1422	0.1304 Mg_2Pb	0.1475	0.1364	0.1292 Bi_2Mg_3	0.1364 Bi_2Mg_3
0.1676 Pb_2O_3	0.2461 Pb	0.1422 Pb	0.1659	0.1561	0.1484	0.1337	0.1517 Mg_2Pb	0.1385	0.1340 Mg	0.1438
0.1753 Pb	0.2840	0.1488 Pb	0.1747 Pb	0.1611	0.1556	0.1364	0.1556 Mg_2Pb	0.1407	0.1362 Mg	0.1471 Mg
0.1975 Pb_2O_3	0.3199	0.1744 Pb	0.2461 Pb	0.1676	0.1605	0.1385 Mg_2Pb	0.1576	0.1446	0.1381 Mg	0.1484 Bi_2Mg_3
0.2461 Pb		0.1959	0.2599	0.1747 Pb	0.1676	0.1519 Mg_2Pb	0.1699 Mg_2Pb	0.1471	0.1403 Bi_2Mg_3	0.1556 Bi_2Mg_3
0.2840 Pb		0.2461 Pb	0.2771	0.1962	0.1741	0.1556 Mg_2Pb	0.1912	0.1488 Bi_2Mg_3	0.1450 Bi_2Mg_3	0.1600 Mg
0.2989		0.2778	0.2840 Pb	0.2461 Pb	0.1962	0.1597	0.1959 Mg_2Pb	0.1556 Bi_2Mg_3	0.1471 Mg	0.1676 Bi_2Mg_3
0.3199 Pb_2O_3		0.2840 Pb	0.2989	0.2778	0.2043	0.1699 Mg_2Pb	0.2050 Mg_2Pb	0.1605 Mg	0.1483 Bi_2Mg_3	0.1759 Bi_2Mg_3
		0.2989	0.3199	0.2840 Pb	0.2385	0.1897	0.2397 Mg_2Pb	0.1676 Bi_2Mg_3	0.1519 Bi_2Mg_3	0.1860 Bi_2Mg_3
		0.3199	0.3341	0.3091	0.2461	0.1959 Mg_2Pb	0.2461	0.1762 Bi_2Mg_3	0.1551 Bi_2Mg_3	0.1897 Mg
				0.3199	0.2840	0.2043 Mg_2Pb	0.2614	0.1897 Mg	0.1580	0.1959 Bi_2Mg_3
					0.3199	0.2280	0.2771	0.1967 Bi_2Mg_3	0.1602 Mg	0.2008 Bi_2Mg_3
					0.3300	0.2392 Mg_2Pb	0.3199	0.2097 Bi_2Mg_3	0.1670 Bi_2Mg_3	0.2079 Bi_2Mg_3
						0.2448	0.3412 Mg_2Pb	0.2325 Bi_2Mg_3	0.1759 Bi_2Mg_3	0.2258
						0.2785	0.3952 Mg_2Pb	0.2461 Mg	0.1839 Bi_2Mg_3	0.2325 Bi_2Mg_3
						0.2840 Pb		0.2614 Mg	0.1897 Mg	0.2448 Mg
						0.3199		0.2738 Bi_2Mg_3	0.1935 Bi_2Mg_3	0.2614 Mg
						0.3412 Mg_2Pb		0.2785 Mg	0.1959 Bi_2Mg_3	0.2727 Bi_2Mg_3
						0.3952 Mg_2Pb		0.3222	0.2008 Bi_2Mg_3	0.2771 Mg
								0.3551 Bi_2Mg_3	0.2088 Bi_2Mg_3	0.3199
									0.2236	0.3524 Bi_2Mg_3
									0.2314 Bi_3Mg_3	0.3667 Bi_2Mg_3
									0.2448 Mg	0.3998
									0.2599 Mg	
									0.2706 Bi_2Mg_3	
									0.2771 Mg	
									0.3199	
									0.3524 Bi_2Mg_3	
									0.3667 Bi_2Mg_3	

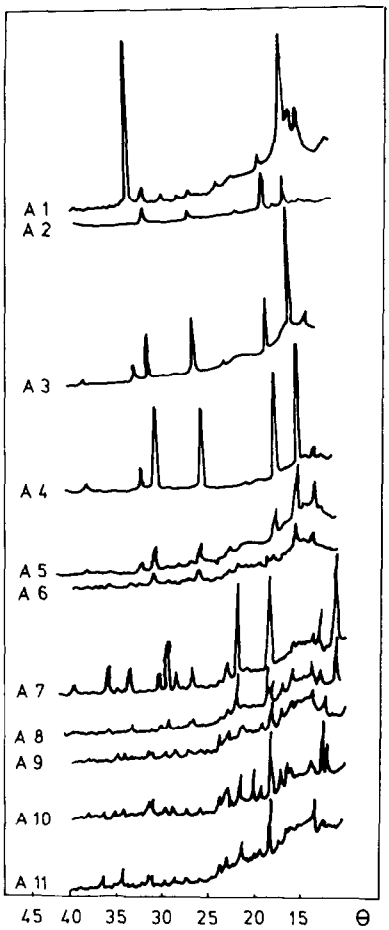

Fig. 8. Diffractograms of the studied samples.

For the phase analysis, metallography and X-ray diffraction were used. Micrographs of typical samples are shown in Fig. 7.

Diffractograms of the studied samples are presented in Fig. 8, and the X-ray diffraction results are given in Table 3. From Table 3, it may be seen that many reflections recorded by the X-ray analysis are not identified because of the absence of ASTM standards for ternary compounds appearing in the ternary system Pb–Bi–Mg. Nevertheless, the results of the metallographic and X-ray investigations confirm the phase structure of the studied samples and agree with the constructed phase diagram of the quasi-binary section A–Pb in the ternary system Pb–Bi–Mg.

REFERENCES

1 M.P. Smirnov, Rafinirovanie svinca i pererabotka poluproduktov, Moskva Metallurgia, 1977, pp. 195–226.
2 B. Dobovisek and A. Paulin, Rud. Met. Zb., 3–4 (1965) 373–387.

3 G. Cacciamani, G. Borzone, A. Saccone and R. Ferro, J. Less-Common Metals, 154 (1989) 109–113.
4 B. Dobovisek, L.A. Meckovski and A. Rosina, Rud. Met. Zba, 2 (1967) 105–109.
5 S. Chen and K.C. Chou, Calphad, 13 (1989) 79–82.
6 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser and K.K. Kelley, Selected Values of Thermodynamic Properties of Binary Alloys, ASM, Metals Park, Ohio, 1973.
7 M.M. Alger and C.A. Eckert, Ind. Eng. Chem. Fundam., 25(3) (1986) 416–421.
8 W.J. Howell and C.A. Eckert, Z. Metallk., 81 (1990) 335–340.
9 P.I. Fedorov, V.I. Sacnev and A.M. Dolgopolova, Izv. Vuz. Cvetnaja Metallurgia, 2 (1962) 58–63.
10 W. Oelsen, Arch. Eisenhuettenwes., 26 (1955) 519–522.
11 W. Oelsen, E. Schürmann, H.J. Weigt and O. Oelsen, Arch. Eisenhuettenwes, 27 (1956) 487–511.
12 W. Oelsen, F. Bieret and G. Schwabe, Arch. Eisenhuettenwes, 27 (1956) 607–620.