Investigation of the Integral Enthalpy of Mixing of the Ternary Ag-Al-Sn System with a Calorimetric Method

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ABSTRACT

The integral enthalpy of mixing of the ternary Ag-Al-Sn system was determined at 1173 K using a calorimetric method. For the determination of the temperature dependency, an additional measurement was performed at 973 K. The substitutional solution model of Redlich–Kister–Muggianu was used for a least square fit of the experimental data in order to get an analytical expression for the integral enthalpy of mixing. The ternary extrapolation models of Kohler, Muggianu, and Toop were applied to calculate the integral enthalpy of mixing and to compare measured and extrapolated values. Additionally calculations of the integral enthalpy of mixing using the Chou model have been carried out. With the calculated data, the iso-enthalpy lines have been determined using the Redlich-Kister-Muggianu model.

1. INTRODUCTION

For all metallurgical processes the knowledge of the thermodynamic properties of alloy systems is necessary. The stability of phases, the reaction path, and many more physical properties depend on it. It is also necessary for all types of calculations, like phase diagram calculations, the calculation of the wetting behaviour and the surface tension.

The aim of thermodynamic investigations is the determination of the partial and integral quantities of metallic systems depending on concentration, temperature and pressure. Various methods are available, depending on the system and on the properties that shall be determined.

Therewith the properties of higher order systems can be calculated. Various extrapolation and calculation models are available and are widely used /1-4/.

2. EXPERIMENTAL PROCEDURE

For the determination of the enthalpy of mixing of the ternary system a Calvet type microcalorimeter (Fa. SETARAM; Lyon) was used. The furnace was adapted to our requirements /5/. The measurements were performed at 1173 K by a direct drop method under Ar flow. An automatic sample drop device was used.

The calorimeter furnace is a twin calorimeter with two separate calorimeter cells, surrounded by thermopiles (TP) with more than 200 pairs of thermocouples each. Each TP is mounted as a ring formed by two concentric cylinders measuring the temperature difference between the inner and outer surface. In this way, the EMF of a TP gives direct information on the heat flow absorbed or produced by the reaction in the cell.

The calorimeter cells are located in the large calorimeter block made of alumina and kanthal which is surrounded by thermal isolating bricks and an electric

resistance heating. The cells are connected in opposition, so that the oscillations of the furnace will be compensated and variations of the temperature differences down to 10^{-5} K can be detected. One cell is usually permanently loaded with a block of about 25 g alumina and serves as the reference cell. This provides similar heat capacity and thermal conductivity in the two cells in order to avoid secondary effects on the calorimeter signal. The furnace further contains two single thermocouples. One measures the sample temperature and the other is used to control the furnace temperature together with a Eurotherm 818 Controller.

All thermocouples are of type S (Pt/Pt-10 mass %Rh). The furnace can be operated from ambient temperature up to 1273 K. The measuring cell is charged with a quartz tube which contains the sample crucible. This quartz tube is connected to the automatic sample introducing unit. The entire system is gas tight and can be evacuated and flushed with a protective gas. Our measurements were performed under a continuous argon flow (30 cm^3/min= 30 x 10^{-6} m^3/min). The obtained signals were automatically recorded and integrated.

The calorimeter is described in more detail in /5/. After each series of drops the calorimeter was calibrated by adding 5 pieces of α-Al_2O_3 (20-40mg) standard of NIST (National Institute of Standards and Technology, Gaithersburg, USA). The temperature in the drop device (DT) and the furnace temperature (FT) were measured before each drop.

The measured enthalpy is given by

$$H_{Signal} = n_i \cdot (H_{Sample,FT} - H_{Sample,DT}) + H_{Reaction} \quad (1)$$

n_i is the amount of the added sample. The relative enthalpy ($H_{Sample,\ FT} - H_{Sample,\ DT}$) was calculated using the polynomials from Dinsdale /6/ for the thermodynamic data of pure elements. The approximate partial enthalpies of Ag, Al, and Sn in the ternary Ag-Al-Sn system could be determined directly by

$$\overline{\Delta H_i} = \left(\frac{H_{Signal}}{n_i}\right) - \left(H_{Sample,FT} - H_{Sample,DT}\right) \quad (2)$$

The integral enthalpy of mixing was calculated by

$$\Delta H_{mix} = H_{bin} + \frac{\sum \overline{H}_{Reaction}}{(n + \sum ni)} \quad (3)$$

n is the molar amount and H_{bin} the integral enthalpy of the metals propounded in the crucible. All metals were of high purity (99.98+ %). Sn rod (Johnson Matthey GmbH, Karlsruhe, Germany) and Al (Johnson Matthey GmbH, Karlsruhe, Germany) were cleaned with a fine sand paper before using. Ag was a product of Ögussa (Vienna, Austria). The Ag shots were heated in a carbon crucible for 10 min at 973 K to remove Ag_2S.

The measurement was carried out by adding aluminium to the molten binary Ag–Sn alloys in the composition range from 0 to 50 at.% Al. For the next cross sections Ag was dropped into the binary Al-Sn alloys and Sn was dropped into the binary Ag-Al alloys. The measurements were carried out at the constant ratios of Al:Sn = 1:1, 1:2, and 1:9, Ag:Sn = 2:1, 1:1, 1:2, and Ag-Al = 1:1 at 1123 K. An additional measurement at the cross section Al:Sn = 1:1 has been performed at 973 K, to check the temperature dependency of the integral enthalpy of mixing in the ternary Ag-Al-Sn system. No temperature dependency has been found, as can be seen in **Fig. 1**. The time interval between drops was 40min.

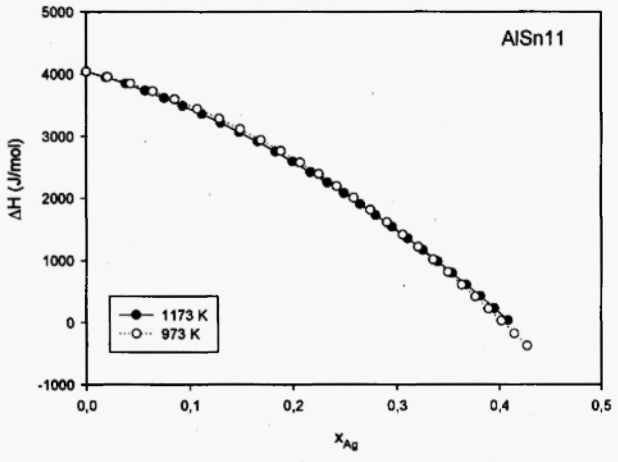

Fig. 1: Comparison of the integral enthalpy of mixing of the ternary Ag-Al-Sn system at 973 K and 1173 K.

2.1 Binary Systems

Silver-aluminium

Few literature data of thermodynamic properties have been found of the binary silver-aluminium, and the scattering of the data is rather large. A thermodynamic evaluation has been performed by Spencer and Kubaschewski /7/, and a compilation of the thermodynamic data has been given by Hultgren *et al.* /8/. Calorimetric measurements have been performed by Itagaki and Yazawa /9/. EMF measurements of have been performed by Massart *et al.* /10/. A comparison of these three data has been made and the results are shown in **Fig. 2**.

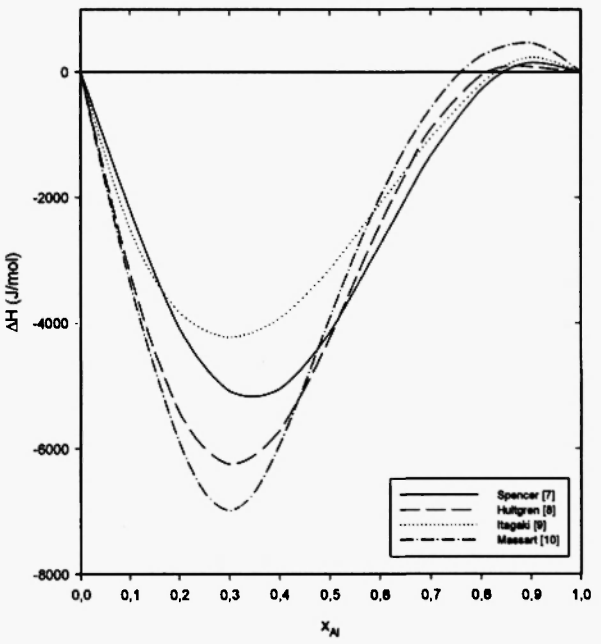

Fig. 2: Comparison of the integral enthalpy of mixing of the binary Ag-Al system given by Spencer and Kubaschewski /7/, Hultgren *et al.* /8/, and Itagaki and Yazawa /9/.

Silver–tin

The most recent work on this system has been done by Luef *et al.* /11/ in the temperature range between 773 K and 1523 K. This work reports negative ΔH values on the silver rich side and positive ones on the tin rich side. Several calorimetric works /12–15/ show the same tendency. The values of Luef *et al.* differ slightly from the values of Castanet. The maximum of the integral enthalpy of mixing was reported at 20 at.%Ag and the minimum at 80 at.%Ag. The numerical values are ΔH_M = 418 J/mol and ΔH_M = –3 201 J/mol, given by Castanet /9/ and ΔH_M = 440 J/mol and ΔH_M = –2 720 J/mol given by Luef *et al.* /11/. Kameda /16/ and Frantik *et al.* /17/ measured the partial molar quantities with an EMF method. Calorimetric and EMF measurements have been performed by Farhi *et al.* /18/. A critical evaluation of this system has been performed by Kubaschewski and Alcock /19/.

Aluminium–tin

Calorimetric measurements were carried out by Wittig and Keil /20/ and the phase diagram is given by McAlister and Kahan /21/. The thermodynamic properties have been evaluated by Heuzey and Pelton /22/. EMF measurements with a liquid electrolyte have been performed by Blot *et al.* /23/ and by Massart *et al.* /24/. A compilation of the thermodynamic data has been given by Hultgren *et al.* /8/ as well.

2.2 Extrapolation models

Three different extrapolation models, the model of Kohler /1/, Muggianu /2/, and Toop /3/ were used to calculate the enthalpy of mixing in the ternary systems. These values have been compared with the experimental data.

2.3 Ternary modelling

The experimental data were treated with a least squares fit using the Redlich–Kister–Muggianu polynomial (Eq. 4) given by Ansara and Dupin /25/ for substitutional solutions. For the determination of the isoenthalpy curves of the integral molar enthalpy of mixing of the ternary Ag–Al–Sn system, shown in **Fig. 3**, the Redlich-Kister-Muggianu model has been used.

$$\Delta H_{mix} = \sum_i \sum_{j>i} \left[x_i\, x_j \sum_v L_{ij}^{(v)} (x_i - x_j)^v \right] + x_A x_B x_C \left(M_{A:B:C}^{(0)} x_A + M_{A:B:C}^{(1)} x_B + M_{A:B:C}^{(2)} x_C \right) \quad (4)$$

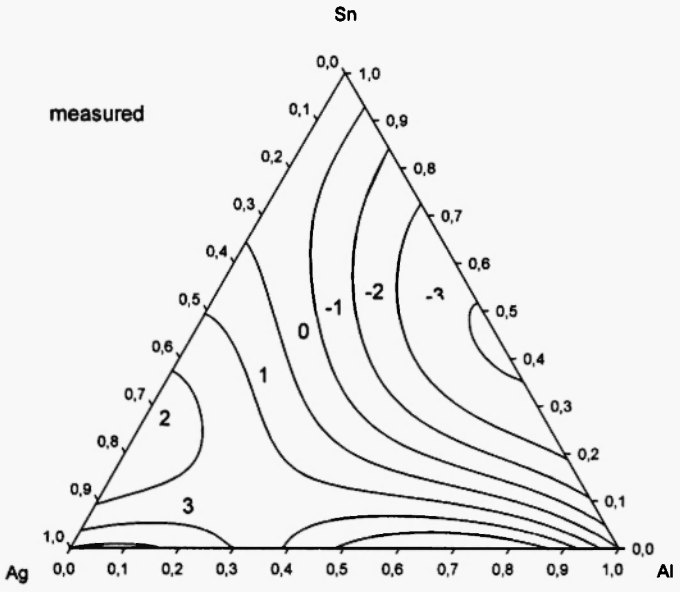

Fig. 3: Iso-enthalpy lines (measured) of the ternary Ag-Al-Sn system at 1173 K in kJ/mol.

Table 1
Binary and ternary interaction parameter

Interaction parameter		v	J mol^{-1}
$L^{(v)}_{Ag,Al}$	(9)	0	-12 590
		1	-18 952
		2	-3.42
$L^{(v)}_{Ag,Sn}$	(11)	0	-3 775
		1	-16 184
		2	-10 526
$L^{(v)}_{Al,Sn}$	(8)	0	16 148
		1	-3 767
		2	2 884
$L^{(v)}_{Ag,Al,Sn}$		0	71 287
		1	40 326
		2	-23 643

i and j are equal 1, 2 and 3 representing the elements Ag, Al and Sn, in the case of this work Ag, Au, and Sn. $L_{i,j}^{(v)}$ (v= 0, 1,...) are the interaction parameters of the binary Ag–Al, Ag–Sn and Al–Sn systems taken from Ref. /7,17,18/ and shown in **Table 1** .

The last term represents the additional enthalpy of mixing due to the ternary interactions where $M_{A:B:C}^{(\alpha)}$ are the excess ternary interaction parameters. **Table 1** shows the results of the least square fit.

2.4 Calculation

For the calculation of the integral enthalpy of mixing the model given by Chou *et al.* /4/ has been used. The binary interaction parameters, shown in Table 1 have been used for the calculation of the ΔH values of the ternary system.

3. RESULTS

No temperature dependency of the integral enthalpy of mixing in the ternary Ag-Al-Sn system could be found as shown in Fig. 1. The integral enthalpy of mixing measured at different cross sections is shown in **Figs. 4-6** and presented in **Tables 2-4.**

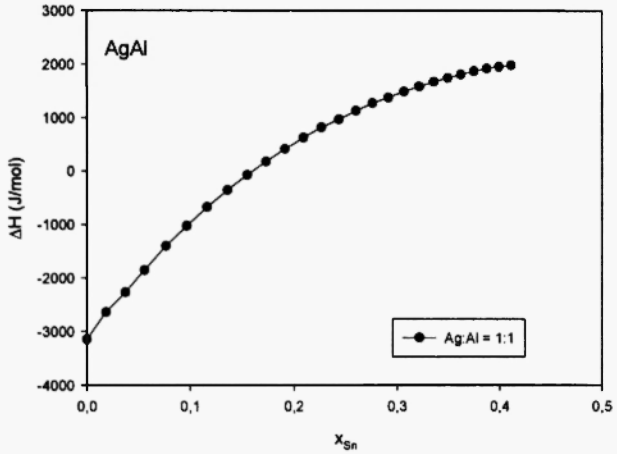

Fig. 4: Integral Enthalpy of mixing of the ternary Ag-Al-Sn system at 1173 K, at the cross sections Al:Sn = 1:2, 1:1, and 2:1.

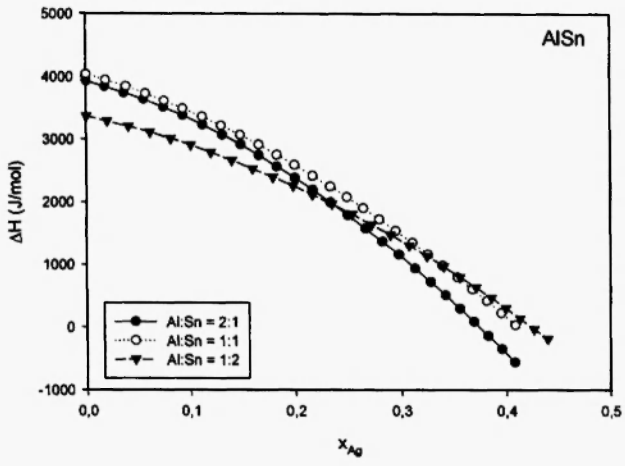

Fig. 5: Integral enthalpy of mixing of the ternary Ag-Al-Sn system at 1173 K, at the cross sections Ag:Sn = 1:2, 1:1, and 2:1.

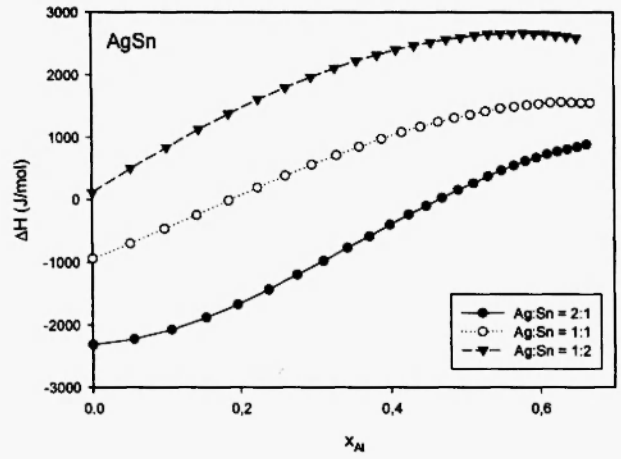

Fig. 6: Integral enthalpy of mixing of the ternary Ag-Al-Sn system at 1173 K, at the cross section Ag:Al = 1:1.

In the case of the Ag-Al-Sn system, the Chou model is a useful tool to calculate the integral enthalpy of mixing, because there is only a small difference between the iso-enthalpy lines determined from the measurements, shown in **Fig. 3** and from the calculation, shown in **Fig. 7**. In **Fig. 8** a comparison of the measurements at the cross section Ag:Sn = 1:2 with the calculated data and the one obtained with the extrapolation models is shown. The values calculated with the Chou model match very good with the measured data whereas there is a rather high difference between the calorimetric values and the extrapolation values, because of the lack of a ternary interaction parameter in these models. In case of the ternary Ag-Al-Sn system, these extrapolation methods do not provide reliable values.

Table 2

Partial and integral enthalpies of mixing resulting from calorimetric measurements at different constant ratios of Al:Sn with Ag dropped from 0 to 55 at.% in the ternary system Ag-Al-Sn at 1173 K

Al:Sn = 1:1			
m_{Al} = 131.96 mg, m_{Sn} = 579.37 mg			
m_{Sn} (mg)	x_{Sn}	$\overline{\Delta H}_{Sn}$ (J mol^{-1})	ΔH_M (J mol^{-1})
			4 037
20.67	0.0192	-813	3 944
21.78	0.0386	-1 195	3 842
21.84	0.0574	-2 064	3 727
21.84	0.0754	-2 372	3 610
22.55	0.0933	-2 808	3 486
24.38	0.1119	-2 903	3 355
24.72	0.1300	-3 585	3 214
25.83	0.1481	-4 012	3 063
26.31	0.1658	-4 282	2 910
26.60	0.1830	-4 907	2 749
26.84	0.1996	-5 123	2 589
28.68	0.2167	-5 427	2 419
28.91	0.2331	-5 670	2 249
29.04	0.2489	-5 986	2 079
29.30	0.2643	-6 401	1 906
29.93	0.2793	-6 761	1 729
32.53	0.2950	-6 835	1 543
33.57	0.3104	-7 089	1 353
33.60	0.3252	-7 337	1 167
33.63	0.3394	-7 520	984
35.42	0.3537	-7 658	797
35.77	0.3676	-7 946	609
36.99	0.3813	-7 937	424
38.98	0.3951	-8 350	228
39.72	0.4086	-8 313	38

Al : Sn = 1 : 2			
m_{Al} = 81.80 mg, m_{Sn} = 719.50 mg			
m_{Ag} (mg)	x_{Ag}	$\overline{\Delta H}_{Ag}$ (J mol^{-1})	ΔH_M (J mol^{-1})
			3 360
20.57	0.0205	-399	3 283
21.57	0.0411	-735	3 198
22.33	0.0616	-964	3 109
22.48	0.0813	-1 800	3 006
23.02	0.1007	-1 803	2 905
23.84	0.1199	-2 496	2 789
26.19	0.1401	-2 826	2 661
27.04	0.1600	-3 136	2 527
27.78	0.1795	-3 084	2 396
27.81	0.1981	-3 627	2 260
28.48	0.2163	-4 026	2 117
30.39	0.2349	-4 130	1 969
32.64	0.2539	-4 571	1 807
32.91	0.2721	-4 871	1 644
33.49	0.2897	-5 136	1 480
35.24	0.3074	-5 360	1 310
35.29	0.3242	-5 828	1 136
35.82	0.3404	-5 738	971
36.23	0.3561	-6 136	802
36.36	0.3711	-6 327	636
36.75	0.3856	-6 590	470
36.88	0.3994	-6 829	305
38.15	0.4131	-6 878	141
39.53	0.4267	-7 061	-25
38.65	0.4396	-7 048	-184
Al : Sn = 2 : 1			
m_{Al} = 189.60 mg, m_{Sn} = 417.55 mg			
m_{Al} (mg)	x_{Al}	$\overline{\Delta H}_{Al}$ (J mol^{-1})	ΔH_M (J mol^{-1})
			3 926
20.80	0.0179	-806	3 841
22.72	0.0368	-1 362	3 741
23.49	0.0555	-1 782	3 634
24.99	0.0747	-2 510	3 509
25.33	0.0933	-3 085	3 376
26.89	0.1123	-3 651	3 229
27.30	0.1308	-4 445	3 070
27.45	0.1486	-4 544	2 913
27.96	0.1660	-5 304	2 745
28.65	0.1831	-6 067	2 564
29.54	0.2001	-6 152	2 384
30.09	0.2166	-6 699	2 196
31.82	0.2334	-7 147	1 996
32.54	0.2498	-7 538	1 792
34.19	0.2663	-7 671	1 584
34.26	0.2821	-8 062	1 376
35.46	0.2978	-8 409	1 162
36.02	0.3130	-8 979	942
36.53	0.3278	-9 050	727
36.65	0.3420	-9 344	514
37.39	0.3559	-9 681	298
37.41	0.3693	-9 723	91
39.07	0.3826	-10 611	-136
39.38	0.3955	-10 252	-347
39.68	0.4080	-10 391	-554
Al:Sn = 1:9			
m_{Al} = 22.52 mg, m_{Sn} = 885.62 mg			
m_{Sn} (mg)	x_{Sn}	$\overline{\Delta H}_{Sn}$ (J mol^{-1})	ΔH_M (J mol^{-1})
			1 348
21.79	0.0238	1660	1 355
23.80	0.0485	1479	1 359
24.33	0.0724	949	1 348
24.52	0.0954	402	1 325
25.45	0.1181	76	1 293
25.78	0.1399	-155	1 258
26.86	0.1616	-742	1 207
28.16	0.1831	-1 060	1 149
28.19	0.2038	-1 368	1 085
29.65	0.2243	-1 689	1 014
31.68	0.2450	-1 981	934
32.78	0.2653	-2 445	843
33.83	0.2853	-2 622	749
34.00	0.3041	-2 897	653
35.06	0.3226	-3 262	549
35.29	0.3402	-3 556	442
35.73	0.3571	-3 673	337
35.87	0.3733	-4 119	225
36.31	0.3888	-4 169	116
37.08	0.4039	-4 451	3
37.09	0.4183	-4 748	-111
38.38	0.4324	-4 979	-230
39.38	0.4462	-4 915	-344
39.53	0.4595	-5 209	-460
39.48	0.4720	-5 339	-577

Table 3
Partial and integral enthalpies of mixing resulting from calorimetric measurements at different constant ratios of Ag:Sn with Al dropped from 0 to 55 at.% in the ternary system Ag-Al-Sn at 1173 K

Ag : Sn = 1 : 1			
m_{Ag} = 738.11 mg, m_{Sn} = 812.30 mg			
m_{Al} (mg)	x_{Al}	$\overline{\Delta H}_{Al}$ (J mol^{-1})	ΔH_M (J mol^{-1})
			-943
20.01	0.0516	3 711	-703
20.10	0.0983	4 112	-466
20.77	0.1419	4 089	-245
22.44	0.1846	4 390	-15
22.82	0.2238	4 247	190
23.95	0.2612	4 304	388
24.38	0.2956	4 111	562
25.62	0.3286	3 840	715
25.83	0.3588	3 671	848
27.72	0.3883	3 666	978
27.80	0.4153	3 328	1 082
27.82	0.4401	3 120	1 168
29.15	0.4639	3 006	1 246
29.30	0.4858	2 782	1 309
30.82	0.5070	2 571	1 361
32.11	0.5274	2 688	1 416
33.91	0.5471	2 507	1 461
34.88	0.5657	2 168	1 490
35.00	0.5830	2 149	1 516
35.19	0.5989	2 045	1 537
37.50	0.6147	1 973	1 554
37.74	0.6293	1 890	1 567
38.04	0.6430	1 232	1 554
38.54	0.6559	1 451	1 550
39.14	0.6680	1 506	1 549
Ag : Sn = 1 : 2			
m_{Ag} = 485.57 mg, m_{Sn} = 1068.90 mg			
m_{Ag} (mg)	x_{Ag}	$\overline{\Delta H}_{Ag}$ (J mol^{-1})	ΔH_M (J mol^{-1})
			113
20.20	0.0527	7 483	501
20.70	0.1012	7 010	835
20.71	0.1450	6 832	1 127
20.73	0.1848	6 429	1 374
22.89	0.2246	6 102	1 605
23.17	0.2612	5 645	1 795
23.73	0.2952	5 481	1 965
24.08	0.3267	5 155	2 107
24.16	0.3555	4 818	2 224
24.85	0.3827	4 527	2 321
25.05	0.4080	4 288	2 401
25.62	0.4317	1 089	2 469
25.96	0.4539	3 764	2 519
26.72	0.4750	3 633	2 562
27.03	0.4947	3 482	2 597
27.96	0.5136	3 392	2 627
28.00	0.5312	3 246	2 649
28.48	0.5478	2 673	2 650
28.71	0.5634	2 887	2 658
29.79	0.5785	2 792	2 663
30.98	0.5931	2 470	2 656
33.06	0.6077	2 334	2 645
35.75	0.6223	2 237	2 629
37.19	0.6363	2 125	2 611
37.64	0.6495	1 978	2 588
Ag : Sn = 2 : 1			
m_{Ag} = 996.27 mg, m_{Sn} = 547.32 mg			
m_{Ag} (mg)	x_{Ag}	$\overline{\Delta H}_{Ag}$ (J mol^{-1})	ΔH_M (J mol^{-1})
			-2 320
22.30	0.0565	-661	-2 226
22.40	0.1072	592	-2 075
23.00	0.1538	1 606	-1 882
23.13	0.1961	2 303	-1 673
25.55	0.2381	2 910	-1 434
25.56	0.2760	3 316	-1 198
25.88	0.3107	3 453	-975
26.16	0.3425	3 502	-768
26.52	0.3719	3 394	-582
26.80	0.3991	3 639	-399
26.81	0.4240	3 464	-239
26.93	0.4471	3 253	-100
26.99	0.4684	3 232	29
30.30	0.4904	3 073	155
30.95	0.5111	2 850	265
31.20	0.5304	3 121	377
31.26	0.5482	2 913	473
31.65	0.5649	2 554	550
32.00	0.5806	2 548	622

32.69	0.5955	2 130	676
33.87	0.6098	2 287	733
35.41	0.6238	1 836	772
36.06	0.6370	1 886	811
38.76	0.6502	1 737	845
39.83	0.6628	1 999	887

Table 4

Partial and integral enthalpies of mixing resulting from calorimetric measurements at a constant ratio of Ag:Au = 1:1 with Al dropped from 0 to 55 at.% in the ternary system Ag-Al-Sn at 1173 K

Ag : Al = 1 : 1			
m_{Ag} = 508.50 mg, m_{Al} = 126.83 mg			
m_{Sn} (mg)	x_{Sn}	$\overline{\Delta H}_{Sn}$ (J mol^{-1})	ΔH_M (J mol^{-1})
			-3 147
21.32	0.0187	24 078	-2 638
22.22	0.0374	16 791	-2 267
22.60	0.0558	19 483	-1 852
26.83	0.0767	18 423	-1 404
26.91	0.1164	15 899	-1 028
27.54	0.1359	15 183	-675
28.59	0.1546	13 658	-359
28.70	0.1728	12 538	-79
29.07	0.1912	11 644	172
30.84	0.2090	10 907	412
31.16	0.2264	9 922	621
31.78	0.2434	9 468	815
32.45	0.2598	7 626	965
32.94	0.2757	8 245	1 123
33.12	0.2912	7 767	1 266
33.88	0.3064	6 129	1 370
34.60	0.3211	6 639	1 483
34.77	0.3351	5 892	1 576
34.89	0.3487	5 869	1 665
34.95	0.3917	5 268	1 738
35.00	0.3746	4 851	1 800
36.39	0.3872	4 960	1 865
36.80	0.3995	4 421	1 916
37.28	0.4114	3 539	1 949
37.66		3 196	1 973

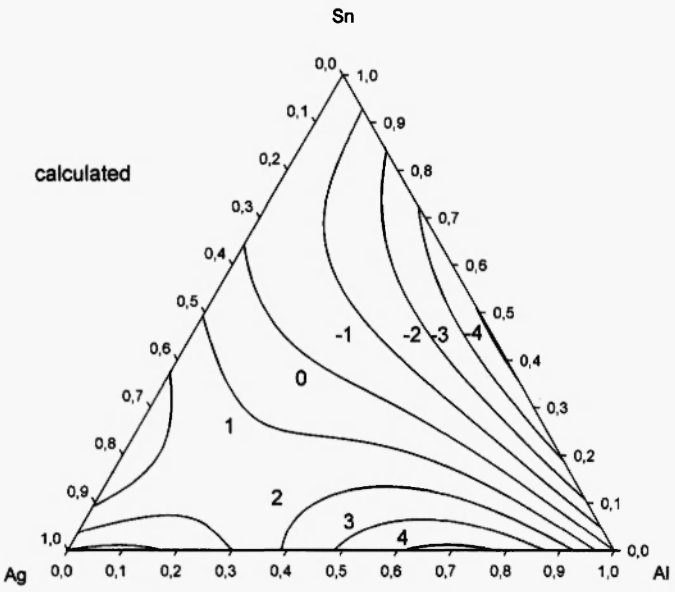

Fig. 7: Iso-enthalpy lines (calculated with the model of Chou) in kJ/mol.

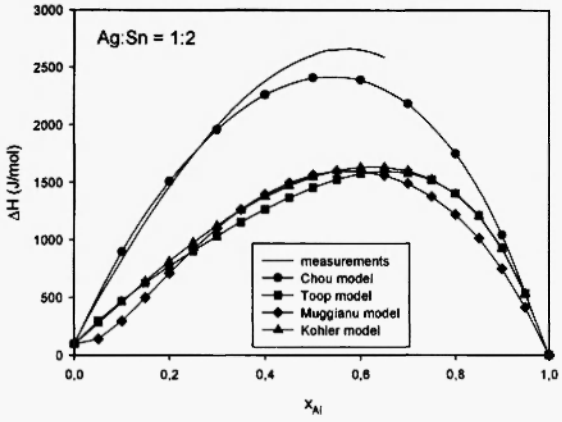

Fig. 8: Comparison of the values of the integral enthalpy of mixing at the cross section Ag:Sn = 1:1 at 1173 K with the values calculated with the model of Chou and with the extrapolation methods of Toop, Muggianu, and Kohler.

4. CONCLUSION

With this investigation a complete set of thermodynamic parameters for the calculation of the

integral enthalpy of mixing at any point in the ternary system has been determined. Calorimetric measurements have been performed at 7 different cross sections to obtain a complete set of the integral enthalpy of mixing of the ternary system Ag-Al-Sn at 1123 K. The temperature dependency of the integral enthalpy of mixing has also been determined. The iso-enthalpy lines and the ternary interaction parameter have been evaluated, and a comparison with data obtained by the calculation model of Chou and the extrapolation methods of Kohler, Muggianu and Toop has been performed.

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