

Thermodynamic Properties of Alloys of the Binary Al-Sm, Sm-Sn and Ternary Al-Sm-Sn Systems

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(Submitted July 7, 2014; in revised form October 6, 2014; published online November 12, 2014)

Mixing enthalpies of the liquid binary Al-Sm ($0 < x_{\text{Sm}} < 0.15$; $0.37 < x_{\text{Sm}} < 1$), Sm-Sn ($0 < x_{\text{Sn}} < 0.13$; $0.56 < x_{\text{Sn}} < 1$) alloys and ternary Al-Sm-Sn alloys (along the three concentration sections: $(\text{Sm}_{0.87}\text{Sn}_{0.13})_{1-x}\text{Al}_x$ ($0 < x < 0.32$); $(\text{Sm}_{0.44}\text{Sn}_{0.56})_{1-x}\text{Al}_x$ ($0 < x < 0.12$); $(\text{Al}_{0.85}\text{Sm}_{0.15})_{1-x}\text{Sn}_x$ ($0 < x < 0.032$)) were determined by an isoperibolic calorimetry technique at 1410–1670 K. Thermodynamic properties of liquid Al(Sn)-Sm alloys were described in the whole concentration range using the model of ideal associated solution. Thermodynamic activities of components of the Al(Sn)-Sm melts demonstrate large negative deviation from the ideal behavior, and the mixing enthalpies are characterized by significant exothermic effects. The minimum value of the mixing enthalpy of the Al-Sm melts is -47.1 ± 0.5 kJ/mol at $x_{\text{Sm}} = 0.35$ ($T = 1500$ K, undercooled melt), Sm-Sn is -67.7 ± 0.5 kJ/mol at $x_{\text{Sn}} = 0.48$ ($T = 1450$ K, undercooled melt). The obtained results were compared with the data from survey of the binary Al(Sn)-Sm systems and with the values calculated by the different models from the data for the binary boundary subsystems of the ternary Al-Sm-Sn system.

Keywords activity, aluminum, calorimetry, enthalpy, phase diagram, samarium, tin, thermodynamics

1. Introduction

In the last decades, the interest of different scientific groups for the alloys containing aluminum, tin and rare-earth metals (Ln) has been increasing. This was caused by the possibility to obtain the materials with specific physico-chemical properties (such as amorphous and nanocrystalline) based on these elements. However, thermodynamic and other physico-chemical properties of their melts in the wide range of temperature have not been studied yet. At high temperatures, the investigation of such alloys is complicated due to their intensive ability to react with refractory materials and oxygen. So, computational works in this field are predominating; a recent one by Jin et al.^[1] contains the review and the estimation of the thermodynamic properties and phase diagrams of the Al-La(Ce, Pr, Nd, Sm) systems. But some of the data obtained^[1] significantly differ from the ones determined by our scientific group before. Additionally, the results^[1] were derived from quite limited experimental information. This made the further investigation of these objects actual, especially determining the physically based dependences of thermodynamic properties of the Al-Ln alloys on the atomic number of lanthanide.

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The properties of alloys of the Al-Sm system cannot be forecasted reliably from the data for the analogous Al-Ln systems due to two reasons. Firstly, the neighbor systems Al-Pm (not investigated because of the radioactivity of Pm) and Al-Eu (with europium having a complex of properties uncommon for the lanthanides) cannot be taken as examples. Secondly, samarium also differs in physical (anomalous volatility) and chemical (existence of the compounds of divalent Sm) properties. Thus, the investigations of the systems containing Sm are especially interesting.

The limited data on the thermodynamic properties of the Ln-Sn alloys are controversial, too. Mostly, they relate to the alloys at low temperatures containing less than 25% Ln. The melting temperatures of the most refractory compounds in the central range of the phase diagrams are still unknown, and their estimated values differ in several hundred degrees. The interaction of Al with the binary Ln-Sn alloy is expected to be intensive at high contents of lanthanides and very weak at high contents of tin. The refractory Ln_5Sn_3 compound seems to be a delimiter for these types of interaction.

2. Literature Review

2.1 Al-Sm

The Al-Sm system was initially investigated by Casteels and Buschow et al.^[2–4] in the aluminum-rich range by thermal, micrographic, x-ray, and microprobe analyses. The liquidus curve was not determined at high Sm contents, because of the high vapor pressure of samarium. The congruent melting of the $\text{Al}_{11}\text{Sm}_3$ compound was proposed, as well as its catatectic decomposition at 1343 K, unlike the other $\text{Al}_{11}\text{Ln}(\text{Pr}, \text{Nd})_3$ compounds with two allotropic forms in the solid state. Kononenko et al.^[5] studied the Al-rich part

of the phase diagram by the DTA, metallography, and x-ray analyses. Saccone et al.^[6] investigated the whole concentration range of the Al-Sm system using the thermal analysis, micrography, microprobes and x-ray diffraction, and supposed the solid-state transition of Al₁₁Sm₃ at 1343 K. Then, Zhou and Napolitano^[7] investigated the Al₁₁Sm₃ phase using microstructural, microchemical analyses and x-ray diffraction, as well as the first-principles calculation involving VASP.^[8] They confirmed the stability of this phase from 1655 down to 1343 K. Gschneidner et al. reported the melting and phase transition temperatures for Sm in Ref 9. Wernick^[10] found the Laves-C15 structure for Al₂Sm, and Buschow^[11] established the Ni₂Si-type structure for this compound. Buschow^[4] found five intermetallics: Al₄Sm, Al₃Sm, Al₂Sm, AlSm, and AlSm₂. However, Saccone^[6] and Delsante et al.^[12] showed the existence of Al₁₁Sm₃ instead of Al₄Sm, with structure being similar to the Al₁₁La₃.^[13] Delsante^[12] confirmed the catatctic decomposition reaction of the Sm₃Al₁₁.

Pasturel et al.^[14] determined the limiting partial enthalpy of Sm in Al ($\Delta\bar{H}_{\text{Sm}}^{\infty} = -171.5$ kJ/mol) at 966 K, $0 < x_{\text{Sm}} < 0.002$. Colinet et al.^[15] investigated the formation enthalpy of the Al₂Sm compound ($\Delta_f H = -54.3$ kJ/mol), through heat of its dissolution in liquid aluminum. Borzone et al.^[16] determined the enthalpies of formation of some solid alloys at $0.27 < x_{\text{Sm}} < 0.83$ by direct calorimetry.

The properties of the Al-Sm system were assessed in Ref 6,17,18; Jia et al.^[17] used the thermodynamic parameters for liquid phase from Ref 6. Zhou and Napolitano^[18] introduced a model considering the formation of the Al₂Sm associate. The invariant reaction Liq. \rightarrow Al(FCC) + Al₃Sm is at 919.5 K,^[18] that is higher than obtained experimentally by Buscho,^[4] 903 K.

Zhou^[18] showed the ratio $\Delta_{\text{mix}} H^{\text{liquid}} / \Delta_f H^{\text{Al}_2\text{Ln}}$ (at $x_{\text{Ln}} = 0.3333$) to be relatively constant. Jin^[1] determined this ratio to be equal to 0.62 for the Al-Pr(Nd) systems, hence $\Delta_{\text{mix}} H^{\text{liquid}} = -34$, derived from $\Delta_f H^{\text{Al}_2\text{Ln}} = -55$ kJ/mol of atom.

Kulikova et al.^[19] conducted the calculation of mixing enthalpies, excess Gibbs energies, and the activities of components in the Al-Sm melts using the ideal associated solutions model. It is unclear what initial information was taken in that work. Therefore, the obtained minimum value of the integral mixing enthalpy of the Al-Sm melts, $\Delta H_{\text{min}} = -59$ kJ/mol, strongly differs from the data by other authors, and is difficult to interpret. Moreover, that value was calculated for a very high temperature, 1873 K. As Kulikova et al.^[19] stated, “Zhou^[18] considered the formation of the only associate (Al₂Sm), and in Ref 7 the associate model was not used at all; so the values $\Delta H_{\text{min}} = -44.5$ kJ/mol at 1200 K^[18] and -42.5 kJ/mol at 1200 K^[7] are underestimated”. This argument seems unacceptable for us. Indeed, by changing the thermodynamic parameters of the associates or the coefficients of the polynomial dependences of the thermodynamic properties, it is possible to obtain any value of ΔH_{min} . That value depends on the input data used in the model, but not on the number of associates or even whether the association is considered at all.

Actually, the model of associated solutions does not mean the existence of the associates as stable groupings in a real melt. However, the precision of the results obtained with this model is often much better, comparing to the polynomial dependences on concentration.

Zhou and Napolitano did not predict the existence of the temperature dependence of the mixing enthalpies of the Al-Sm melts in Ref 7. On the other hand, their further results^[18] are characterized by a significant dependence of ΔH_{min} on temperature (-44.5 kJ/mol at 1200 K, -37 kJ/mol at 1873 K). Kulikova^[19] gave polynomial coefficients for the integral mixing enthalpies of the Al-Sm melts at three temperatures (1873, 1960 and 2100 K). But it can be seen that all those dependences are erroneous, because they strongly deviate from the concentration dependences presented in the figure and discussed in the text.^[19] Such large deviation renders the results obtained by Kulikova et al.^[19] very doubtful.

The purpose of our work is calorimetric investigation of the Al-Sm melts in the wide concentration range, and calculation of the thermodynamic properties of the liquid and solid Al-Sm alloys, based on the whole set of the data on thermodynamics and phase equilibria available in literature. At the present time there is quite controversial information on the thermodynamic properties of the Al-Sm melts in literature, and this makes the purpose of our work especially actual.

2.2 Sm-Sn

Bulanova et al.^[20] made the literature review for the Sm-Sn system in 1994, and there have appeared hardly any new datum on this subject since that time. Percheron^[21] investigated the phase diagram of the Sm-Sn system using DTA, x-ray diffraction and MSA. It was determined that the compounds Sm₅Sn₃ and SmSn₃ melt congruently at 1778 and 1363 K, respectively, along with Sm₄Sn₃, Sm₅Sn₄, and Sm₂Sn₃ melting peritectically at 1713, 1693 and 1378 K, respectively. The Sm₁₁Sn₁₀ compound forms and decays peritectically, existing in the narrow temperature interval only (1443-1513 K). The latter data, along with the ones for the formation of Sm₄Sn₃, are dubious. In accordance with Yermenko et al.,^[22] the melting temperatures of the Sm₅Sn₃ and Sm₅Sn₄ compounds are significantly underestimated. So, they were reinvestigated by Bulanova^[23] and determined to be 1878 and 1793 K correspondingly. Borzone^[24] observed the SmSn₂ phase, though before Iandelli^[25] this phase was shown not to exist. Weitzer et al.^[26] found such phases in the Sm-Sn alloys as SmSn₂, Sm₃Sn₇ and Sm₂Sn₅. Their compositions are close to each other ($x_{\text{Sn}} = 0.667, 0.7, \text{ and } 0.714$), and their possible equilibria with liquid alloys should be peritectical, situated in the near-horizontal part of liquidus curve at $0.667 < x_{\text{Sn}} < 0.75$. So, the existence of these compounds does not affect the shape of liquidus very much.

No homogeneity ranges for the compounds of samarium with tin were found. In the Sm-Sn system, three eutectic reactions were defined: at 1179 K (11% Sn), 1353 K (67%

Table 1 Experimental thermodynamic data in literature for the Al-Sm and Sm-Sn binary systems

Property	Technique		Value	References
Al-Sm				
$\Delta\bar{H}_{Sm}^{\infty}$ ($0 < x_{Sm} < 0.002$) at 966 K	Calorimetry of dissolution in liquid Al		-171.5	[14]
$\Delta_f H(\text{Al}_{11}\text{Sm}_3)$	Modeling		-23.91	[1]
			-31.15	[6]
			-32.5	[18]
			-49.25	[1]
$\Delta_f H(\text{Al}_3\text{Sm})$	Modeling		-47.5	[6]
$\Delta_f H(\text{Al}_2\text{Sm})$	Modeling		-55	[1]
			-55	[6]
$\Delta_f H(\text{Al}_2\text{Sm})$	Calorimetry of dissolution in liquid Al		-54.3	[15]
$\Delta_f H(\text{AlSm})$	Modeling		-48.5	[1]
			-49	[6]
$\Delta_f H(\text{AlSm}_2)$	Modeling		-34.33	[1]
			-38	[6]
$\Delta_f S(\text{Al}_{11}\text{Sm}_3)$	Modeling		0.6	[1]
			-4	[6]
$\Delta_f S(\text{Al}_3\text{Sm})$	Modeling		-2.14	[1]
			-14.44	[6]
$\Delta_f S(\text{Al}_2\text{Sm})$	Modeling		-6.23	[1]
			-15.79	[6]
$\Delta_f S(\text{AlSm})$	Modeling		-3.95	[1]
			-16.33	[6]
$\Delta_f S(\text{AlSm}_2)$	Modeling		-1.68	[1]
			-13.93	[6]
Property	Technique	T, K	Value	Reference
Sm-Sn				
$\Delta_f H(\text{SmSn}_3)$	Direct calorimetry		-56.0	[28]
	Calorimetry of dissolution in liquid tin		-56.3 ± 1.5	[29]
$\Delta_f H(\text{Sm}_2\text{Sn}_3)$	Calorimetry of dissolution in liquid tin		-72.7 ± 2.0	[29]
$\Delta_f H(\text{Sm}_5\text{Sn}_3)$	Calorimetry of dissolution in liquid tin		-63.6 ± 3.4	[29]
$\Delta_{\text{melt}} H(\text{SmSn}_3)$	Direct calorimetry	1345	16.7 ± 0.8	[28]
$\Delta_{\text{melt}} S(\text{SmSn}_3)$	Direct calorimetry	1345	12.4 ± 0.6	[28]
$\Delta\bar{H}_{Sm}$ ($0 < x_{Sm} < 0.25$)	E.m.f. for heterogeneous alloys	700–1030	-301.3 ± 4.9	[25,31]
$\Delta\bar{S}_{Sm}$ ($0 < x_{Sm} < 0.25$)			-101.9 ± 5.6	
$\Delta\bar{H}_{Sm}$ ($0 < x_{Sm} < 0.25$)	E.m.f. for heterogeneous alloys	700-1014	-291.6 ± 1.6	[33]
$\Delta\bar{S}_{Sm}$ ($0 < x_{Sm} < 0.25$)			-127.2 ± 1.6	
$\Delta\bar{H}_{Sm}$ ($0 < x_{Sm} < 0.25$)	E.m.f. for heterogeneous alloys	1000	-293.8 ± 0.9	[32]
$\Delta\bar{S}_{Sm}$ ($0 < x_{Sm} < 0.25$)			-129.3 ± 1.2	
$\Delta\bar{H}_{Sm}^{\infty}$	E.m.f. for homogeneous liquid alloys	800-1000	-237.9 ± 7.2	[25]
$\Delta\bar{S}_{Sm}^{\text{ex},\infty}$			-62.0 ± 7.0	
$\Delta_{\text{dissol}} \bar{H}_{Sm}^{\infty}$	Isoperibol calorimetry of dissolution in liquid Sn	600	-209.2	[34]
	?	750	-221.8 ± 8.4	[35]
$\Delta H(0 < x \equiv x_{Sm} < 0.32)$	Calorimetry of dissolution in liquid tin	828	-240.5 ± 10.5	[36]
		967	-190.8	[29]
	Tian-Calvet calorimetry	1203	-277	[37]
	Tian-Calvet calorimetry	1203	$x(1-x) \times (-277 + 105.4x)$	[37]

Values are in kJ/mol for enthalpies and in J/(mol K) for entropies

Sn), and 502 K (99.8% Sn). The catatectic decomposition of β -Sm into α -Sm and liquid is observed at 1189 K. Lebedev et al.^[27] determined the solubility of Sn in the solid Sm

using e.m.f. method in the temperature range 823-1023 K, and described it by the equation $\lg x_{Sm} = 2080 - 3316/T$. Palenzona^[28] determined the formation enthalpy of the

SmSn₃ compound by the direct calorimetry, and Percheron et al.^[29] did this (along with the other two compounds) by the dissolution in the liquid Sn. Also, Colinet et al.^[30] estimated the formation enthalpies of the compounds in the Sm-Sn system using the Miedema theory (Table 1).

For SmSn₃, good agreement between the experimental values of $\Delta_f H$ ^[28,29] is observed, but the calculated value^[30] is much less exothermic. For Sm₂Sn₃, there is a good agreement between the calculated^[30] and experimental^[29] values. The formation enthalpy of Sm₅Sn₃ is doubtful. It is hard to assume that the most refractory compound in this system forms with a lesser heat effect than Sm₂Sn₃, forming in a peritectical reaction at the temperature in 500 K lower than melting of Sm₅Sn₃. Percheron et al.^[29] considered the formation of these compounds only (Sm₅Sn₃, Sm₂Sn₃, SmSn₃). The enthalpy and entropy of melting of SmSn₃ were determined by Palenzona.^[28] $\Delta_{melt} H = 16.7 \pm 0.8$ kJ/mol of atom and $\Delta_{melt} S = 12.4 \pm 0.6$ J/(mol of atom · K), which corresponds to the melting temperature 1345 K.

Kober, Lebedev et al.^[27,31-33] studied the thermodynamic properties of the dilute solutions of Sm in liquid Sn in the two-phase region (melt + SmSn₃) by the e.m.f. technique at 700-1030 K (Table 1). In the region of homogeneous solution, the temperature dependence of the activity coefficient of Sm was described by the equation $\lg \gamma_{Sm} = 3243 - 12425/T$.^[27] Due to the data for this region, $\Delta \bar{H}_{Sm}^\infty = -237.9 \pm 7.2$ kJ/mol, $\Delta \bar{S}_{Sm}^{ex,\infty} = -62.0 \pm 7.0$ J/(mol K). From the data of the other works, the $\Delta \bar{H}_{Sm}^\infty = -209.2$ kJ/mol at 600 K,^[34] -221.8 ± 8.4 at 750 K,^[35] -240.5 ± 10.5 at 828 K,^[36] -190.8 at 967 K.^[29] As estimated by Colinet,^[30] $\Delta \bar{H}_{Sm}^\infty = -172$ kJ/mol, and $\Delta H_{min} = -43$ kJ/mol. The latter value differs strongly from both the data for the solid compounds in the Sm-Sn system and for the melts of some other Ln-Sn systems; so, it is unreliable.

Berrada et al.^[37] investigated the mixing enthalpies of alloys of the Sm-Sn system (along with the Pb-Sm system) for $0.69 < x_{Sn} < 1$ at 1203 K (930°C). They obtained very large negative partial mixing enthalpies of samarium ($\Delta \bar{H}_{Sm}^\infty = -277$ kJ/mol). However, due to the available phase diagram, the SmSn₃ compound melts at 1090°C (quite higher than the temperature by Ref 37). So, these results should represent the properties of heterogeneous alloys at $x_{Sn} < 0.93$, i.e. for the majority of the studied alloys. This also explains why the data^[37] are significantly scattered. If the reaction of samarium with the heterogeneous alloy would be complete, the mean value of the observed “ $\Delta \bar{H}_{Sm}$ ” for $0.75 < x_{Sn} < 1$ will be equal to

$$4\Delta_f H(\text{SmSn}_3) - \Delta_{melt} H(\text{Sm}) - 3\Delta_{melt} H(\text{Sn}) \\ = 4 \cdot (-56.3) - 10.5 - 3 \cdot 7.2 = -257.3 \text{ kJ/mol.}$$

This is rather close to the results.^[37] However, such heterogeneous reactions are usually problematical and incomplete, hence the scattered results.

All the data from literature listed above are gathered in the Table 1.

3. Experimental Part

The whole description of the experimental technique was presented by us in Ref^[38]. The experiments were carried out in a high temperature isoperibolic solution calorimeter working up to 1850 K in purified helium atmosphere under a pressure of 150000 Pa. A massive molybdenum block with two crucibles—the melt container and the reference crucible—is placed in the constant-temperature zone of the furnace with a coaxial molybdenum heater. We used aluminum AB00 99.99%, samarium 99.88% and tin 99.99% for experiments. Samples of aluminum had masses 0.005-0.02 g, samarium samples were 0.013-0.035 g, and tin samples 0.01-0.035 g. Being solid at $T = 298$ K, they were dropped into the melt in the crucible (the calorimetric bath) from a revolving container through a ceramic tube. Molybdenum is inert against samarium and tin, but interacts with aluminum at some point. So, molybdenum crucibles were used for the alloys Al-Sm ($0.37 < x_{Sm} < 1$), Sm-Sn and for the sections $(\text{Sm}_{0.87}\text{Sn}_{0.13})_{1-x}\text{Al}_x$ ($0 < x < 0.32$) and $(\text{Sm}_{0.44}\text{Sn}_{0.56})_{1-x}\text{Al}_x$ ($0 < x < 0.12$) of the ternary system. For the Al-Sm alloys in the range $0 < x_{Sm} < 0.15$ and the section $(\text{Al}_{0.85}\text{Sm}_{0.15})_{1-x}\text{Sn}_x$ ($0 < x < 0.032$), the crucibles made of aluminum oxide were used, because Al₂O₃ is inert against aluminum, tin and only small concentrations of samarium. However, there should be a threat of the Al₂O₃ + Sm → Sm₂O₃ + Al reaction, if the concentration of samarium were greater.

Unfortunately, samarium is quite a volatile metal. Its vapor interacts with some parts of the calorimeter, and that may cause the failure of the device. In addition, the quantity of metal in the crucible decreases with time, and the exact value of this decrease at the given moment is impossible to determine. That is why we attempted to conduct all the experiments at as low temperature as possible, though keeping the alloy liquid. In particular, the Al-Sm alloys in the range $0 < x_{Sm} < 0.15$ and $(\text{Al}_{0.85}\text{Sm}_{0.15})_{1-x}\text{Sn}_x$

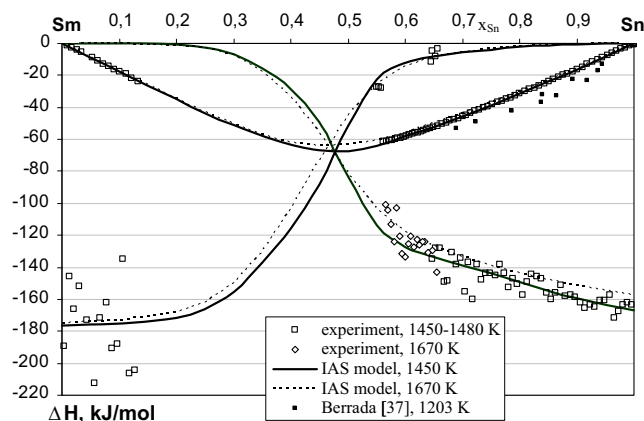


Fig. 1 Partial and integral mixing enthalpies of melts of the Sm-Sn system at 1450-1670 K, obtained in our experiments (points) and approximated by IAS model at 1450 and 1670 K (lines)

Table 2 Partial and integral mixing enthalpies of melts of the Al-Sm(-Sn) system (kJ/mol)

x_{Sm}	$-\Delta H$	$-\Delta\bar{H}_{Sm}$	x_{Sm}	$-\Delta H$	$-\Delta\bar{H}_{Sm}$	x_{Sm}	$-\Delta H$	$-\Delta\bar{H}_{Sm}$
Series 1. Experimental points, 1440 K								
0.0076	1.4	180.0	0.0607	11.1	183.2	0.1135	20.2	166.9
0.0152	2.8	183.4	0.0682	12.4	175.0	0.1213	21.5	168.6
0.0229	4.2	186.0	0.0759	13.8	180.6	0.1290	22.8	162.6
0.0306	5.6	187.2	0.0835	15.2	179.7	0.1371	24.1	170.8
0.0382	7.0	181.6	0.0911	16.4	172.1	0.1452	25.4	156.6
0.0456	8.4	182.0	0.0986	17.7	173.0	0.1532	26.7	165.8
0.0532	9.7	176.9	0.1060	19.0	168.8			
x_{Sn}	$-\Delta H$	$\Delta\bar{H}_{Sn}$	x_{Sn}	$-\Delta H$	$\Delta\bar{H}_{Sn}$	x_{Sn}	$-\Delta H$	$\Delta\bar{H}_{Sn}$
Ternary section (Al _{0.85} Sm _{0.15}) _{1-x} Sn _x								
0.0054		26.5	7.0		0.0229		26.0	-1.8
0.0137		26.2	7.4		0.0317		25.7	6.5
x_{Sm}	$-\Delta H$	$-\Delta\bar{H}_{Al}$	x_{Sm}	$-\Delta H$	$-\Delta\bar{H}_{Al}$	x_{Sm}	$-\Delta H$	$-\Delta\bar{H}_{Al}$
Series 2. 1410 K								
0.9805	1.8	90.2	0.7892	18.3	90.3	0.6326	30.2	80.8
0.9586	3.8	93.3	0.7701	19.8	80.1	0.6183	31.4	84.5
0.9354	5.8	87.6	0.7511	21.1	71.9	0.6042	32.5	79.1
0.9130	8.0	96.2	0.7321	22.7	84.1	0.5905	33.6	79.7
0.8908	9.7	79.0	0.7139	24.2	83.9	0.5770	34.6	78.9
0.8698	11.7	93.4	0.6963	25.6	82.5	0.5638	35.6	75.5
0.8488	13.4	82.8	0.6793	26.8	73.1	0.5512	36.4	74.2
0.8284	15.1	83.3	0.6632	27.8	69.4			
0.8090	16.5	74.9	0.6476	29.0	79.4			
x_{Sm}	$-\Delta H$	$-\Delta\bar{H}_{Al}$	x_{Sm}	$-\Delta H$	$-\Delta\bar{H}_{Al}$	x_{Sm}	$-\Delta H$	$-\Delta\bar{H}_{Al}$
1640 K								
0.5384	37.2	68.3	0.4708	41.5	73.9	0.4134	45.3	65.0
0.5262	37.9	68.3	0.4608	42.3	79.5	0.4047	46.0	74.1
0.5143	38.6	67.9	0.4508	43.0	71.6	0.3963	46.4	68.4
0.5028	39.4	74.7	0.4410	43.7	75.0	0.3881	47.0	75.8
0.4918	40.1	72.4	0.4314	44.3	74.7	0.3800	47.2	57.5
0.4813	40.8	73.3	0.4222	44.9	72.3	0.3721	47.7	67.4
x_{Sm}	ΔH	\pm	$\Delta\bar{H}_{Al}$	\pm	$\Delta\bar{H}_{Sm}$	\pm		
IAS model, 1500 K								
0	0	0	0	0	-183.3			4.3
0.1	-18.0	0.3	-0.5	0.0	-174.8			4.1
0.2	-34.4	0.5	-5.1	0.3	-151.5			3.5
0.3	-46.0	0.7	-28.1	1.8	-87.7			2.0
0.4	-45.4	0.7	-63.1	4.1	-18.9			0.4
0.5	-39.6	0.6	-71.9	4.7	-7.2			0.2
0.6	-32.7	0.5	-75.5	5.0	-4.2			0.1
0.7	-25.3	0.4	-78.7	5.2	-2.4			0.1
0.8	-17.5	0.3	-82.6	5.4	-1.2			0.0
0.9	-9.0	0.1	-87.5	5.7	-0.3			0.0
1	0	0	-93.4	6.1	0			0

($0 < x < 0.032$) were studied at 1440 K; $0.55 < x_{Sm} < 1$ at 1410 K, and $0.37 < x_{Sm} < 0.55$ at 1640-1670 K. In the last case, there was still a possibility of formation of the solid

Al₂Sm compound in a small amount, so a lesser statistical weight was given to these data in the range $0.37 < x_{Sm} < 0.43$ while treating the results. The Sm-Sn alloys

Table 3 Partial and integral mixing enthalpies of melts of the Sm-Sn(-Al) system at (kJ/mol)

x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sn}}$	x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sn}}$	x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sn}}$
Series 3. Experimental points, 1450 K								
0.0086	1.6	189.1	0.0626	10.9	212.2	0.1122	19.3	134.5
0.0172	2.9	145.8	0.0725	12.6	171.7	0.1225	21.5	206.3
0.0261	4.4	166.0	0.0823	14.2	161.9	0.1325	23.6	204.0
0.0348	5.7	151.8	0.0922	16.1	190.8			
0.0532	8.9	172.7	0.1018	18.0	187.8			
x_{Al}	$-\Delta H$	$-\Delta\bar{H}_{\text{Al}}$	x_{Al}	$-\Delta H$	$-\Delta\bar{H}_{\text{Al}}$	x_{Al}	$-\Delta H$	$-\Delta\bar{H}_{\text{Al}}$
Ternary section ($\text{Sm}_{0.87}\text{Sn}_{0.13}$) $_{1-x}\text{Al}_x$, 1450 K								
0.0331	26.3	101.1	0.1651	36.3	100.6	0.2916	45.5	95.1
0.0656	28.9	102.6	0.1971	38.9	101.1	0.3230	47.1	80.3
0.1018	31.5	93.6	0.2272	40.9	91.1			
0.1344	33.8	92.5	0.2603	43.2	93.1			
x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sm}}$	x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sm}}$	x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sm}}$
Series 4. Experimental points, 1450 K								
0.9926	1.2	163.8	0.9451	9.0	160.8	0.8932	17.4	158.4
0.9853	2.4	162.2	0.9363	10.4	160.9	0.8848	18.7	157.4
0.9776	3.6	163.7	0.9275	11.9	164.9	0.8764	20.1	158.3
0.9699	4.9	167.3	0.9187	13.3	163.2	0.8680	21.3	151.5
0.9619	6.3	171.5	0.9102	14.7	165.7	0.8596	22.6	156.2
0.9537	7.6	157.1	0.9016	16.1	162.0	0.8512	24.0	160.3
x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sm}}$	x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sm}}$	x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sm}}$
Experimental points, 1480 K								
0.8430	25.2	155.9	0.7693	36.0	143.4	0.7003	45.8	155.5
0.8345	26.5	147.3	0.7612	37.1	138.3	0.6931	46.8	134.2
0.8260	27.7	145.8	0.7532	38.2	145.1	0.6858	47.7	138.1
0.8174	28.9	144.2	0.7453	39.3	144.0	0.6786	48.6	130.8
0.8090	30.1	149.2	0.7375	40.4	143.6	0.6716	49.6	148.6
0.8007	31.4	157.5	0.7299	41.5	147.8	0.6644	50.7	148.8
0.7927	32.6	150.6	0.7223	42.5	138.6	0.6574	51.5	128.3
0.7851	33.7	146.8	0.7149	43.8	160.3	0.6504	52.3	128.2
0.7773	34.9	152.3	0.7076	44.7	136.6	0.6434	53.2	134.6
x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sm}}$	x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sm}}$	x_{Sn}	$-\Delta H$	$-\Delta\bar{H}_{\text{Sm}}$
Experimental points, 1670 K								
0.6517	51.7	142.7	0.6127	56.7	127.5	0.5775	60.5	124.0
0.6444	52.5	129.3	0.6077	57.2	120.8	0.5726	60.9	112.7
0.6374	53.9	130.8	0.6027	57.8	125.4	0.5677	61.3	104.0
0.6325	54.5	124.3	0.5977	58.4	133.7	0.5626	61.6	100.5
0.6277	55.0	124.1	0.5926	59.0	131.2	0.5579	61.7	73.6
0.6228	55.6	125.9	0.5875	59.5	120.5	0.5531	61.9	82.2
0.6178	56.1	122.6	0.5825	59.9	102.7	0.5483	62.1	79.3
x_{Al}	$-\Delta H$	$-\Delta\bar{H}_{\text{Al}}$	x_{Al}	$-\Delta H$	$-\Delta\bar{H}_{\text{Al}}$	x_{Al}	$-\Delta H$	$-\Delta\bar{H}_{\text{Al}}$
Ternary section ($\text{Sm}_{0.44}\text{Sn}_{0.56}$) $_{1-x}\text{Al}_x$, 1670 K								
0.0165	60.9	11.9	0.0558	58.7	7.7	0.0974	56.5	9.4
0.0364	59.7	5.9	0.0765	57.6	7.1	0.1193	55.3	7.2

Table 3 continued

x_{Sn}	ΔH	\pm	$\Delta \bar{H}_{\text{Sm}}$	\pm	$\Delta \bar{H}_{\text{Sn}}$	\pm
Sm-Sn, IAS model, 1450 K						
0	0	0	0	0	-176.6	23.6
0.1	-17.6	0.1	-0.1	0.0	-175.3	23.4
0.2	-35.0	0.2	-0.8	0.0	-171.6	22.9
0.3	-51.4	0.3	-7.0	0.3	-155.0	20.7
0.4	-63.4	0.4	-28.3	1.2	-115.8	15.5
0.5	-67.4	0.4	-83.6	3.5	-51.1	6.8
0.6	-58.2	0.4	-127.6	5.4	-12.0	1.6
0.7	-45.7	0.3	-138.8	5.9	-5.8	0.8
0.8	-31.7	0.2	-149.2	6.3	-2.3	0.3
0.9	-16.3	0.1	-159.3	6.7	-0.4	0.1
1	0	0	-167.0	7.1	0	0

($0 < x_{\text{Sn}} < 0.13$) and $(\text{Sm}_{0.87}\text{Sn}_{0.13})_{1-x}\text{Al}_x$ ($0 < x < 0.32$) were studied at 1450 K, Sm-Sn ($0.64 < x_{\text{Sn}} < 1$) at 1480 K, Sm-Sn ($0.55 < x_{\text{Sn}} < 0.66$) and $(\text{Sm}_{0.44}\text{Sn}_{0.56})_{1-x}\text{Al}_x$ ($0 < x < 0.12$) at 1670 K.

The calibration constant of the calorimeter was determined by adding some samples of the metal, the same as the pure one contained in the crucible (before adding other components)—Al, Sm, or the refractory metal inert to the alloy (Mo). The heat effects observed while the samples dissolved were treated accordingly to the heat balance equation: $K \int_0^{\tau_{\infty}} (T - T_0) dt = \Delta H_T + n_i \Delta H_{298}^T$.

Here ΔH_{298}^T is an enthalpy of heating 1 mol of an additive from 298 K to the temperature of experiment, by Dinsdale;^[39] K is a calibration constant of the calorimeter; n_i is a molar quantity of an additive; $T - T_0 = \Delta T$ is a difference between the temperatures of the crucible with the melt and of the isothermal shell of the calorimeter; t is time.

From the partial mixing enthalpies of one component, the analogous values for the second component were calculated, and then the integral values were obtained (Fig. 1 and 7; Tables 2, 3). These data together with the ones obtained from literature were treated using the model of ideal associated solutions (IAS).^[40] Five associates (Al_4Sm , Al_3Sm , Al_2Sm , AlSm , AlSm_2) were chosen to model the thermodynamic properties of the Al-Sm system. Three associates (Sm_2Sn , SmSn , SmSn_3) were taken for the Sm-Sn system; they are close to the compositions of rather stable intermetallics Sm_5Sn_3 , Sm_5Sn_4 , and SmSn_3 . However, they have simpler compositions, increasing the probability of such atomic combinations in the liquid high-temperature alloys. It appeared that such numbers of the associates are both necessary and sufficient for describing the thermodynamic data within the experimental errors. Given in Tables 2 and 3, these errors were estimated from mean square deviations of experimental points for partial and integral mixing enthalpies from the fitting lines by IAS model. Such estimation gave terminal values of errors, and at other concentrations they were taken proportional to the absolute values of corresponding functions. That is, we

suggested the relative errors being constant for a given function $\Delta \bar{H}_i$ or ΔH . Unfortunately, we could not find more accurate methods of calculating these errors, because of a complex mathematical nature of functions $\Delta \bar{H}_i$ and ΔH from concentration of the melt, which is characteristic for IAS model in comparison to polynomial functions.

One of the criticisms of the associated solution model is about the mathematical formalism implying that distinct molecules exist, which is hard to justify.^[41] However, actually the model merely implies some underlying structure to the liquid, which is quite reasonable, and it does provide functions which allow for the temperature dependence of the enthalpy of mixing and other thermodynamic functions. In the literature, there is a tendency to use as few associates as possible in the model, based on the assumption that diffraction or other structure-sensitive measurements usually reveal no more than two different kinds of chemical short range order. On the contrary, we think that if one kind of associate is assumed, there are no obstacles to consider as many other kinds as possible. A true reason why this is rarely done in practice is rise in computational difficulties with increase in the number of associates. Nevertheless, some works have used as much as five associates for modeling,^[42-45] though most of these imaginable compounds reveal rather low concentrations in the liquid alloys, especially when the composition is far from the stoichiometry of such associates.

Actually, considering a large number of simultaneously possible associates is more general than artificial choosing only one or two among them. So, we cannot agree that an ideal associated model considering five associates is necessarily worse than a regular associated model considering one associate and some interaction energies between the species in the melt. The second variant may seem simpler for someone. But actually we managed to develop an algorithm for quick search of equilibrium point between the species in an ideal associated solution. However, this algorithm fails when the interaction between the species is considered, as in regular associated model. It is similar to the fact that a system of five linear equations is usually simpler to solve than another system of two transcendental equations.

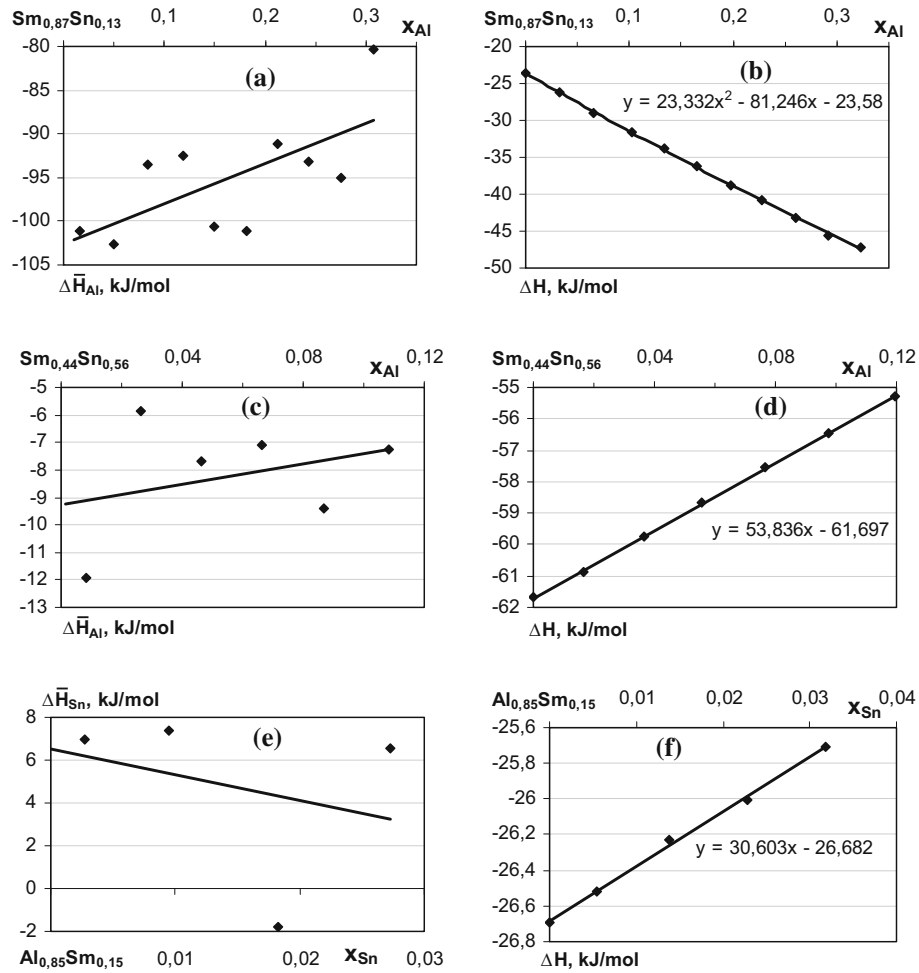


Fig. 2 Partial (a, c, e) and integral (b, d, f) mixing enthalpies of the ternary Al-Sm-Sn system for three sections of the compositional triangle: $(\text{Sm}_{0.87}\text{Sn}_{0.13})_{1-x}\text{Al}_x$ ($0 < x < 0.32$) (a, b—1450 K), $(\text{Sm}_{0.44}\text{Sn}_{0.56})_{1-x}\text{Al}_x$ ($0 < x < 0.12$) (c, d—1670 K), and $(\text{Al}_{0.85}\text{Sm}_{0.15})_{1-x}\text{Sn}_x$ ($0 < x < 0.032$) (e, f—1440 K)

The temperature dependences of the mixing enthalpies of the Al-Sm and Sm-Sn melts are not very large. This may be explained by very intensive interaction between the components, which becomes weaker only at quite high temperatures, >2000 K. So, the differences of experimental temperature within 100-200 K do not cause a violation of the experimental error bounds. Thus, the calculations were made for 1500 K (Al-Sm) and 1450 K (Sm-Sn), which are approximately average of the temperatures of all our experiments conducted in the corresponding systems.

In the end of some series of investigation of mixing enthalpies of binary alloys, several samples of the third component of the ternary Al-Sm-Sn systems were added. This allowed us to obtain partial mixing enthalpies of the third component, and integral enthalpies, along three sections of the Al-Sm-Sn triangle (Tables 2, 3): $(\text{Sm}_{0.87}\text{Sn}_{0.13})_{1-x}\text{Al}_x$ ($0 < x < 0.32$); $(\text{Sm}_{0.44}\text{Sn}_{0.56})_{1-x}\text{Al}_x$ ($0 < x < 0.12$); $(\text{Al}_{0.85}\text{Sm}_{0.15})_{1-x}\text{Sn}_x$ ($0 < x < 0.032$).

The obtained set of partial and integral mixing enthalpies and entropies was approximated by the polynomial dependences which give a less exact estimate of the thermodynamic functions, comparing to IAS model, but make the calculation faster in the case of multicomponent system based on the binary Al-Sm and Sm-Sn subsystems. Let us assume

$$\Delta H = x_2(1 - x_2) \sum_{i=0}^n a_i x_2^i, \quad \Delta \bar{H}_1 = x_2^2 \sum_{i=0}^n b_i x_2^i,$$

$$\Delta \bar{H}_2 = (1 - x_2)^2 \sum_{i=0}^n c_i x_2^i, \quad \Delta S^{\text{ex}} = x_2(1 - x_2) \sum_{i=0}^n d_i x_2^i,$$

$$\Delta \bar{S}_1^{\text{ex}} = x_2^2 \sum_{i=0}^n e_i x_2^i, \quad \Delta \bar{S}_2^{\text{ex}} = (1 - x_2)^2 \sum_{i=0}^n f_i x_2^i,$$

$$b_i = (i + 1)(a_i - a_{i+1}), \quad c_i = (i + 1)a_i,$$

$$e_i = (i + 1)(d_i - d_{i+1}), \quad f_i = (i + 1)d_i.$$

Then the coefficients of the polynomial dependences will have the next values:

Al-Sm ($x_2 = x_{Sm}$):

i	0	1	2	3	4	5
a_i (kJ/mol), 1500 K	-183.3	-222.8	-306.9	4073.9	-6184.5	2730.2
d_i (J/(mol K)), 1500 K	-65.5	-88.3	-402.8	2569.4	-3582.0	1531.9

So, $\Delta\bar{H}_{Sm}^\infty = -183.3 \pm 2.1$; $\Delta\bar{H}_{Al}^\infty = -93.4 \pm 1.9$; $\Delta H_{min} = -47.1 \pm 0.5$ kJ/mol at $x_{Sm} = 0.35$

Sm-Sn ($x_2 = x_{Sn}$):

i	0	1	2	3	4
a_i (kJ/mol), 1450 K	-176.6	-82.1	-1199.3	2822.9	-1531.8
d_i (J/(mol K)), 1450 K	-51.1	8.5	-751.1	1529.6	-794.2

So, $\Delta\bar{H}_{Sn}^\infty = -176.6 \pm 2.1$; $\Delta\bar{H}_{Sm}^\infty = -167.0 \pm 1.9$; $\Delta H_{min} = -67.7 \pm 0.5$ kJ/mol at $x_{Sn} = 0.48$.

Partial and integral mixing enthalpies of melts of the ternary Al-Sm-Sn system for three sections studied by us, approximated by linear and quadratic functions, are presented in the Fig. 2.

4. Thermodynamic Modeling

4.1 The Properties of the Binary Al(Sn)-Sm Alloys

The activities of pure components and the molar fractions of the associates in the melts of the Al-Sm and Sm-Sn systems are presented in the Fig. 3-4, and the parameters of the IAS model are shown in the Table 4.

It is obvious from the Table 4 that the optimized values of the formation enthalpies of the Sm_2Sn_3 and $SmSn_3$ compounds agree with the experimental data by Percheron et al.^[29] For Sm_5Sn_3 , our estimation of the formation enthalpy is more exothermic than obtained in Ref 29. This confirms the speculations by Bulanova et al.^[20] that both melting temperatures and enthalpies of formation of the refractory compounds in the Sm-Sn system are underrated. We found the greatest exothermic effect of formation for the Sm_5Sn_4 compound, not being the most refractory in this system, but closer to the equiatomic composition. This compound stands close to the minimum of the mixing enthalpies of the melts, obtained by extrapolating of our experimental data.

The given parameters of the IAS model correspond to the certain temperature dependences of the thermochemical properties. For the partial mixing enthalpies at infinite dilution ($\Delta\bar{H}_i^\infty$) of the components of melts of the binary Al-Sm and Sm-Sn systems, they are presented in the Fig. 5. For the Sm-Sn system, there were many determinations of $\Delta\bar{H}_{Sm}^\infty$ at low temperatures,^[29,34-36] which did not agree with each other. Our thermodynamic model predicts rather significant temperature dependence of $\Delta\bar{H}_{Sm}^\infty$ in the Sm-Sn melts. However, this dependence is not as strong as necessary to achieve $-230...-250$ kJ/mol when the temperature lowers to 700-800 K. Surely, the corresponding experimental data are not reliable enough, probably due to the kinetic effects caused by the low temperature comparing to the melting temperatures of most intermetallics in the Sm-Sn system.

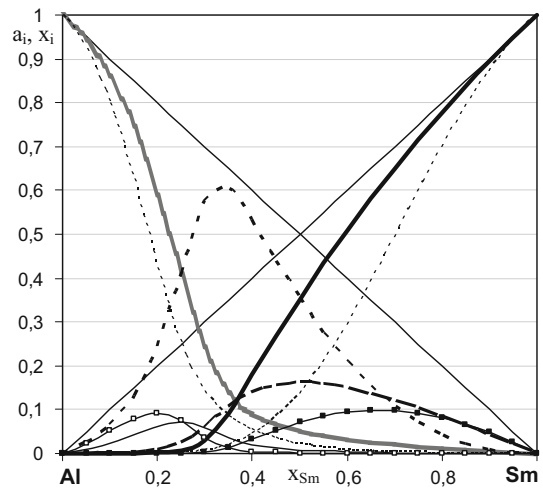


Fig. 3 Activities of the pure components (a_i : — Al, — Sm) and molar fractions of the associates (x_i : —□— Al_4Sm , —○— Al_3Sm , —■— Al_2Sm , —●— $AlSm$, —▲— $AlSm_2$) in the melts of the Al-Sm system at 1500 K, according to the obtained IAS model, compared to estimation by Jin^[1] (a_i : - - - Al, Sm)

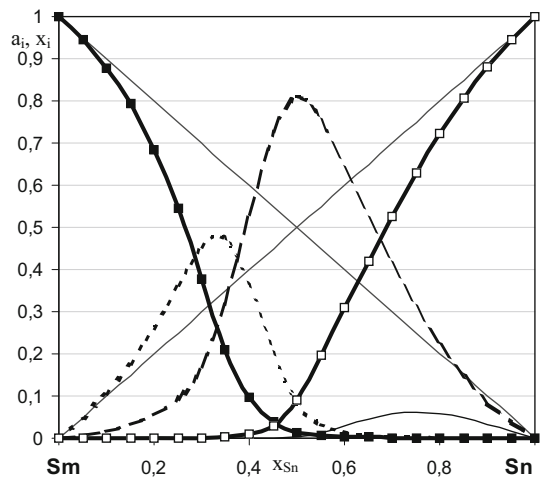


Fig. 4 Activities of the pure components (a_i : —■— Sm, —□— Sn) and molar fractions of the associates (x_i : - - - □ - Sm_2Sn , - - - ○ - $SmSn$, —●— $SmSn_3$) in the melts of the Sm-Sn system at 1450 K, according to the obtained IAS model

4.2 Properties of the Ternary Al-Sm-Sn Melts

For calculating the thermodynamic functions of the ternary alloys from the analogous data for binary boundary subsystems, the latter ones are necessary to transform into the well-known Redlich-Kister polynomial type: $\Delta H_{A-B} = x_A x_B \sum_i L_i^{AB} (x_A - x_B)^i$.

The coefficients of these polynomials are presented in the Table 5.

Then the Redlich-Kister-Muggianu model gives the following description for the mixing enthalpies of the ternary

Table 4 Enthalpies (kJ/mol of atom) and entropies (J/mol of atom/K) of formation of the associates (liq.) and the intermetallics (sol.) in the Al-Sm and Sm-Sn systems

Compound	$\Delta_f H^{liq}$	$\Delta_f S^{liq}$	$\Delta_f H^{sol}$	$\Delta_f S^{sol}$	$\Delta_f H^{sol}$, exper.
Al ₄ Sm	-41.0	-17.4			
Al ₁₁ Sm ₃			-31.6	-2.5	
Al ₃ Sm	-45.7	-20.1	-48.7	-12.6	
Al ₂ Sm	-53.8	-19.6	-52.4	-12.3	-54.3 ^[15]
AlSm	-45.2	-21.2	-46.2	-13.4	
AlSm ₂	-34.9	-16.7	-30.8	-8.1	
Sm ₂ Sn	-60.3	-18.3			
Sm ₅ Sn ₃			-72.2	-15.6	-63.6 ^[29]
Sm ₅ Sn ₄			-75.2	-16.8	
SmSn	-73.0	-23.6			
Sm ₂ Sn ₃			-71.3	-19.2	-72.7 ^[29]
SmSn ₂			-65.1	-17.5	
Sm ₃ Sn ₇			-61.8	-16.6	
Sm ₂ Sn ₅			-60.4	-16.2	
SmSn ₃	-52.4	-24.2	-56.3	-15.0	-56.3 ^[29]

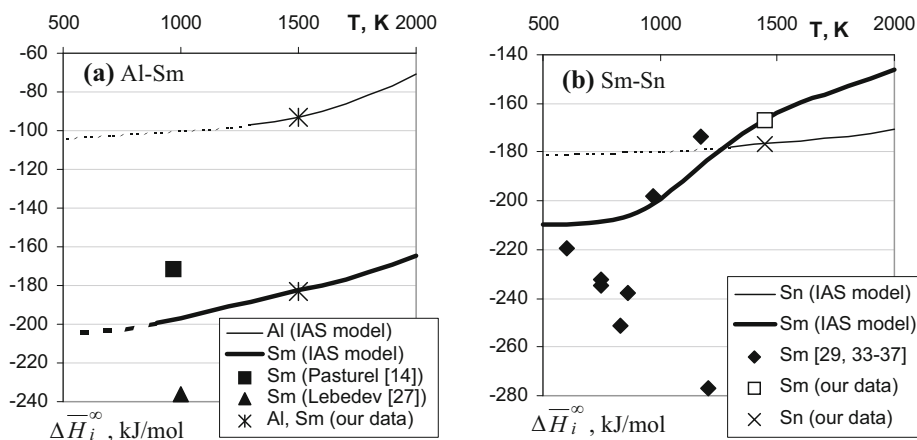


Fig. 5 Temperature dependences of the partial mixing enthalpies at infinite dilution ($\Delta \bar{H}_i^\infty$) of the components of the liquid or under-cooled (dashed lines) melts of the Al-Sm (a) and Sm-Sn (b) systems, accordingly to the IAS model

Table 5 The L_i^{AB} coefficients of the polynomial dependences (13) of the mixing enthalpies of melts of the binary Al-Sm, Al-Sn, Sm-Sn systems (kJ/mol)

System	i = 0	1	2	3	4	5
Al-Sm	-163.4	-143.4	-15.0	183.7	40.1	-85.3
Al-Sn	16.3	-3.5	1.7	-1.7		
Sm-Sn	-260.4	-34.9	184.3	30.1	-95.7	

alloys: $\Delta H_{A-B-C} = \Delta H_{A-B} + \Delta H_{A-C} + \Delta H_{B-C} + x_A x_B x_C (L_0^{ABC} + L_A^{ABC} x_A + L_B^{ABC} x_B + \dots) = x_A x_B \sum L_i^{AB} (x_A - x_B)^i + x_A x_C \sum L_i^{AC} (x_A - x_C)^i + x_B x_C \sum L_i^{BC} (x_B - x_C)^i + x_A x_B x_C (L_0^{ABC} + L_A^{ABC} x_A + L_B^{ABC} x_B + \dots)$.

If the experimental information for the ternary alloys were absent, the L_i^{ABC} coefficients might be assumed as zero.

However, in our case, this would give inaccurate values of the partial mixing enthalpies of the components. We found that the coefficients $L_0^{AlSmSn} = 50$, $L_{Al}^{AlSmSn} = 60$, and $L_{Sm}^{AlSmSn} = -360$ (kJ/mol) help to achieve agreement for the partial mixing enthalpies at infinite dilution of Al and Sn with our experimental values (Fig. 2). The modeling results are presented in the Fig. 6.

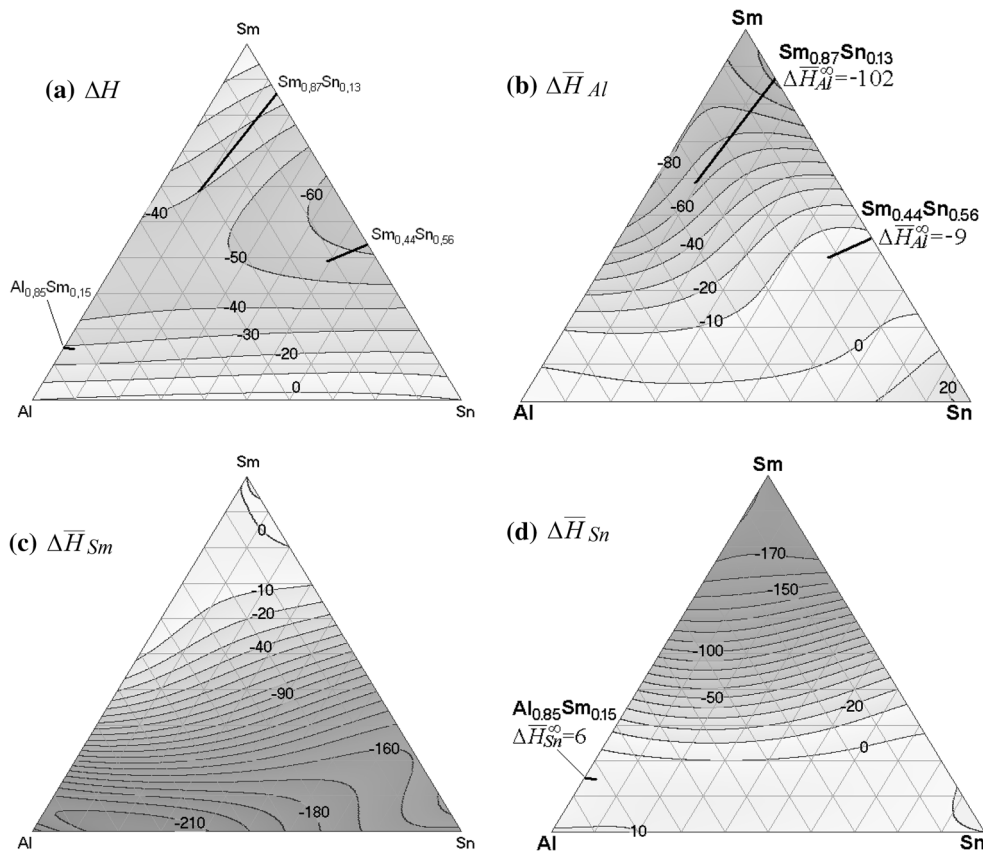


Fig. 6 Integral (a) and partial (b, c, d) mixing enthalpies of the ternary Al-Sm-Sn system (kJ/mol), obtained experimentally and calculated by the Redlich-Kister-Muggianu method

5. Discussion on the Results

Our results for the mixing enthalpies of melts of the Al-Sm system (Fig. 7) have an interstitial position between insufficiently negative^[1,16] and excessively negative^[19] data. The data by Saccone^[6] are close to our results, though having less asymmetric concentration dependence. Surely, the main source of information for modeling by all these authors was the phase diagram, and this can explain the great divergence between their results. From our experience in modeling the thermodynamic properties of many similar systems (for example, Ref 46), even small inaccuracies in the liquidus temperatures can often lead to significant deviations in the calculated activities of components and mixing enthalpies. Thus, at the present time the only approach to correct those errors is confirming them with the direct experimental results on the mixing enthalpies, and actually this was done in our work. We hope that the accuracy of forecasting the thermodynamic properties will increase for the analogous systems in the future, due to the expansion of the corresponding databases.

It is clear from the Fig. 8 that different modeling methods gave dissimilar results for the excess mixing entropies of melts of the Al-Sm system. They can be divided into two groups: (a) with small deviations from the ideal solutions,

–5 to –7 J/(mol K),^[1,18]—(b) with large deviations, –18 to –19 J/(mol K)—^[6] and our model. Correspondingly, the data (a) have large negative values, and the data (b) have moderate values of the mixing Gibbs energies of the melts (Fig. 9). In our model, large negative mixing entropies correspond to the formation of the stable, strongly ordered associates. Unfortunately, mixing entropies are difficult to evaluate accurately from the experimental data (Fig. 8).

Figure 10 shows that the formation enthalpies of the intermetallics, calculated by us, are slightly less exothermic than obtained by Saccone^[6] and Colinet.^[15] Nevertheless, they agree with them, as well as with the results of modeling by Jin^[1] and Zhou.^[18] The greatest deviations are observed for AlSm₂ and Al₁₁Sm₃. The compound AlSm₂ melts at the lowest temperature and has a small area of equilibrium with the melt, so its contribution to the estimation of the liquidus curve of the phase diagram is insignificant. Jin et al.^[1] proposed very small exothermic $\Delta_f H(\text{Al}_{11}\text{Sm}_3)$ that corresponds to very steep liquidus curve in the area of equilibrium of this compound with the melt. We calculated the liquidus curve of the Al-Sm phase diagram in accordance to the obtained thermodynamic model based on IAS. It is clear that this curve matches the experimental points^[2,5,6] no worse than the modeling,^[1] including the area of the equilibrium of Al₁₁Sm₃ with the melt. Thus, the

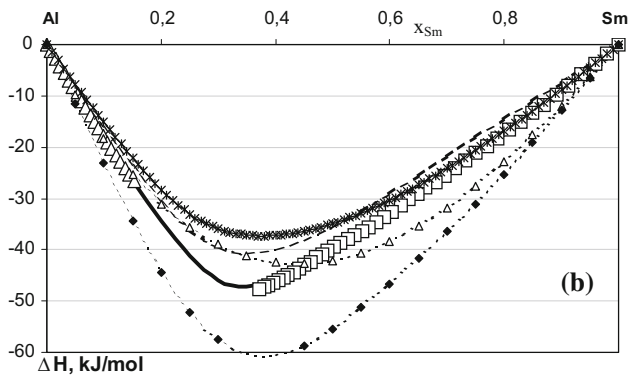
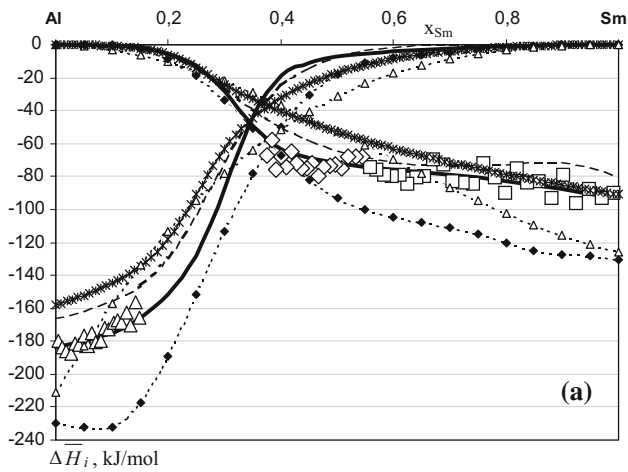


Fig. 7 Partial (a) and integral (b) mixing enthalpies of melts of the Al-Sm system: our experimental data— ΔH_{Al} at 1410 K (\square), 1640 K (\diamond) and ΔH_{Sm} at 1440 K (\triangle); approximated by IAS model at 1500 K (—); data from literature: Saccone,^[6] (- - \triangle - -); Zhou,^[18] (— —); Jin,^[1] 1500 K, MQM (\ast); Kulikova^[19] IAS model (dubious) (- - \ast - -)

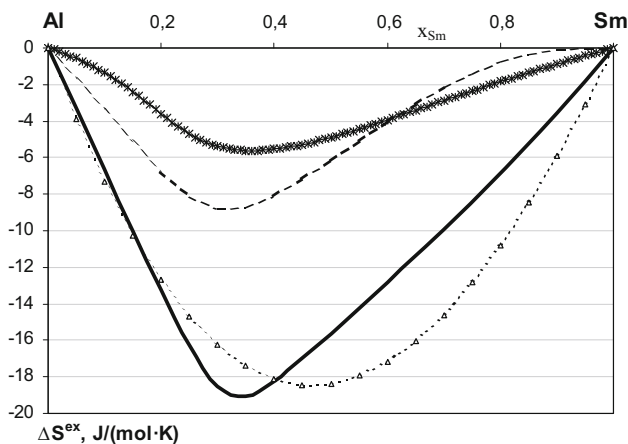


Fig. 8 Excess mixing entropies ΔS^{ex} of melts of the Al-Sm system at 1500 K, calculated by us using the IAS model (—), and the data from literature: Saccone,^[6] (- - \triangle - -); Zhou,^[18] (— —); Jin^[1], MQM (\ast)

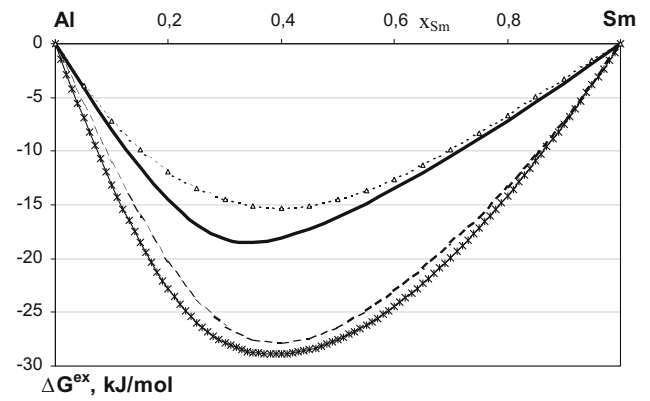


Fig. 9 Excess mixing Gibbs energies ΔG^{ex} of melts of the Al-Sm system, calculated by us using the IAS model (—), and the data from literature: Saccone,^[6] (- - \triangle - -); Zhou,^[18] (— —); Jin^[1] MQM (\ast)

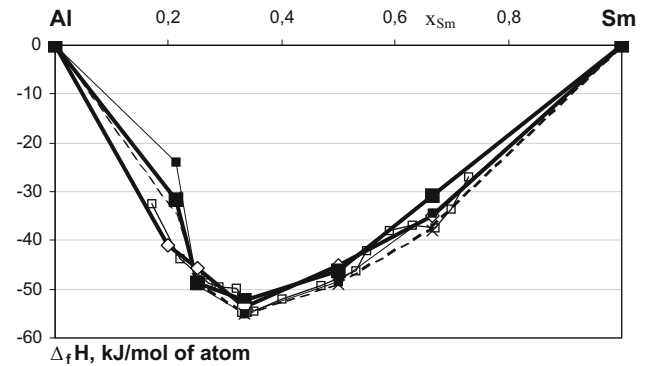


Fig. 10 The enthalpies of formation of the associates in the melts (\diamond) and the intermetallics (\blacksquare) in the solid alloys of the Al-Sm system at 298 K, compared to the data in literature— experimental \square Colinet^[15] calorimetry of dissolution in liquid Al; \square Borzone^[16] direct calorimetry; estimations \times Zhou^[7] (based on the experiment by Borzone^[16]); — — Kulikova^[19] \blacksquare Jin^[1]

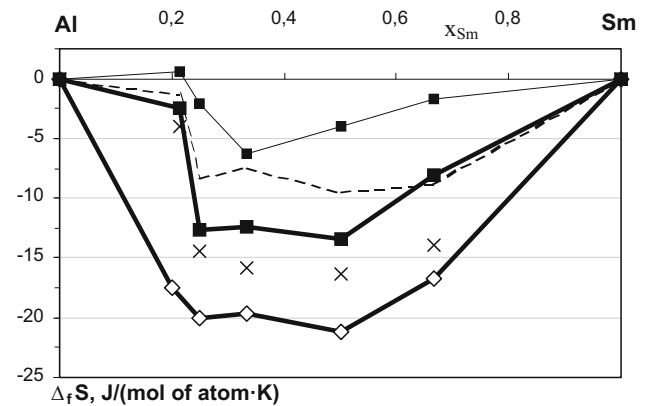


Fig. 11 The entropies of formation of the associates in the melts (\diamond) and the intermetallics (\blacksquare) in the solid alloys of the Al-Sm system at 298 K, compared to the estimations in literature: \times Zhou;^[7] — — Kulikova,^[19] \blacksquare Jin^[1]

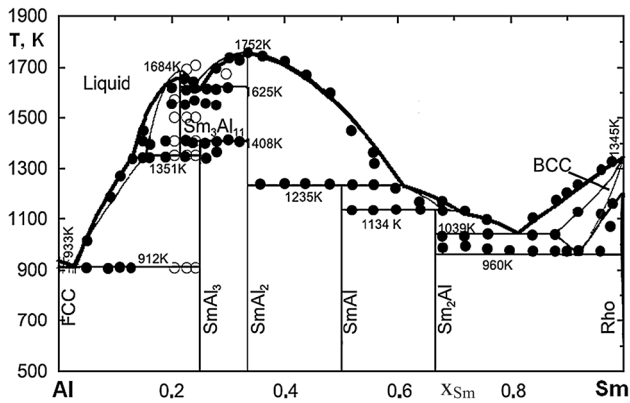


Fig. 12 Phase diagram of the Al-Sm system, calculated by us using the obtained IAS model (bold liquidus curve), compared with the data from literature^[1] (thin lines/curves, modeling) and ^[2], ^[5,6] (experiment)

value of the formation enthalpy of this compound, equal to -23.9 kJ/mol of atom accordingly to Jin et al.,^[1] is hardly possible.

Moreover, too small negative values of the entropies of formation of the intermetallics in the Al-Sm system, $-2 \dots -6$ J/(mol of atom K), and even a positive value for $\text{Al}_{11}\text{Sm}_3$, are proposed by Jin et al.^[1] (Fig. 11). This correlates with small negative mixing entropies of the melts. But the equilibrium of the melts with the solid alloys (the liquidus curve) is described quite adequately in Ref 1. For the conclusion, we choose considerably more negative, -13 J/(mol of atom K), entropies of formation of the Al-Sm compounds. They are closer to the values obtained in Ref 6.

The calculated phase diagram (Fig. 12) is an ultimate confirmation of validity of our thermodynamic model. Some small discrepancies with the experimental data are observed for the solubility of aluminum in the high-temperature (BCC) modification of samarium ($0.85 < x_{\text{Sm}} < 1$). However, our model is suited firstly for dealing with melts, and our experimental data also refer to melts; so, this model describes solid phases less accurately. Moreover, the experimental data in this area are not determined distinctively.

We calculated the liquidus curve of the Sm-Sn phase diagram (Fig. 13) using a model adjusted accordingly to Bulanova et al.^[20] The latter data state that the melting temperatures of the most stable intermetallics are higher comparing to the results of the previous works. These higher temperatures correlate with the analogous parameters for other Ln-Sn systems, and they join the regularities in the fundamental lanthanide properties (mainly, the atomic radii). Apparently, a great part of the liquidus curve calculated by us agrees with experiments and predictions by Bulanova et al.^[20] There are only two regions of disagreement: $0.45 < x_{\text{Sn}} < 0.6$ (which is uncertain in Ref 20), and $0.9 < x_{\text{Sn}} < 1$. These small inconsistencies do not contradict to the validity of the thermodynamic model obtained by us.

As for the ternary Al-Sm-Sn alloys (Fig. 2 and 6), two of their sections— $(\text{Sm}_{0.44}\text{Sn}_{0.56})_{1-x}\text{Al}_x$ ($0 < x < 0.12$) (1670 K) and $(\text{Al}_{0.85}\text{Sm}_{0.15})_{1-x}\text{Sn}_x$ ($0 < x < 0.032$) (1440 K)—confirm our expectations that the main part of interaction between the components relates to the binary

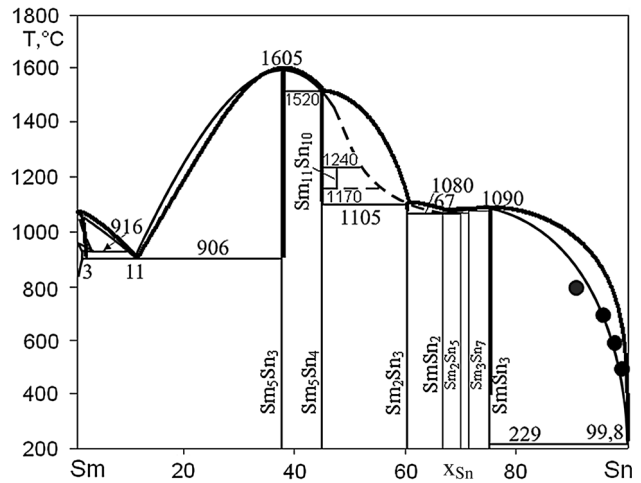


Fig. 13 Liquidus curve of the phase diagram of the Sm-Sn system, calculated using our thermodynamic model (the bold curve), compared with the data^[20]

subsystems. Adding the third component does not give significant energetic effects. The opposite case is observed for the third section— $(\text{Sm}_{0.87}\text{Sn}_{0.13})_{1-x}\text{Al}_x$ ($0 < x < 0.32$) (1450 K). Here we see great negative ($-100 \dots -90$ kJ/mol) partial mixing enthalpies of aluminum. They are explained by a great fraction of nearly free samarium in the $\text{Sm}_{0.87}\text{Sn}_{0.13}$ melt. However, it is difficult to understand the fact that these exothermic effects decrease so slowly with the addition of aluminum—even more slowly than it was observed for pure Sm (Fig. 7). This fact hindered the whole agreement of the mixing enthalpies of the ternary melts with the Redlich-Kister-Muggianu model (Fig. 6). So, this phenomenon is worth being clarified in the future—not surely for Al-Sm-Sn, but at least for some other analogous Al-Ln-Sn systems.

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