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ALUMINIUM ACTIVITY IN THE (α) Ti ALUMINIUM – TITANIUM SOLID ALLOYS BY EMF METHOD

AKTYWNOŚĆ ALUMINIUM W STAŁYCH STOPACH (α) Ti Z UKŁADU ALUMINIUM-TYTAN Z POMIARÓW SIŁ ELEKTROMOTORYCZNYCH

The equilibrium EMF's were measured for the Al-Ti solid alloys in the region of $\alpha(\text{Ti})$ phase by means of the concentration cells. Experiments were conducted at the temperatures 923 K, 1014 K, 1041 K and 1061 K and in the concentration range from $X_{\text{Al}} = 0.0222$ to 0.1237. Next, the temperature-concentration dependence of excess Gibbs energy of Al was worked out (Redlich-Kister relation) and used to calculate the partial and integral thermodynamic functions (excess Gibbs energy, enthalpy of solutions, excess entropy and activity of aluminium and titanium, integral enthalpy of mixing and excess entropy).

W pracy prezentowane są pomiary sił elektromotorycznych (SEM) ogniów stężeniowych dla stałych stopów w obszarze występowania fazy (α) Ti. Badania wykonano dla temperatur 923 K, 1014 K, 1041 K oraz 1061 K oraz w zakresie stężeń od 0.0222 – 0.1237 ułamka molowego Al. Wyliczone z pomiarów SEM nadmiarowe energie swobodne aluminium opracowano temperaturowo-stężeniową zależnością Redlicha-Kistera, którą następnie wykorzystano do obliczenia cząstkowej nadmiarowej – energii swobodnej i entropii, entalpii rozpuszczania aluminium i tytanu oraz entalpii mieszania i nadmiarowej entropii mola roztworu. Uzyskane wyniki porównano z wcześniejszymi nielicznymi danymi dostępnymi w literaturze.

1. Introduction

The efforts undertaken in the last decade of the past century to find new materials characterised by very good strength, low creeping and good oxidation resistance at elevated temperature were concentrated on the multicomponent alloys based on the intermetallic phases from the Al-Ni and Al-Ti systems and these efforts are continued. The automotive and aircraft industries, the energetic and the missiles factories are particularly interested in

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new materials possessing the mentioned extraordinary mechanical and chemical properties at high temperatures. The alloys based on γ -TiAl intermetallic phase are especially interesting because apart from good mechanical properties they are very resistant to high temperature corrosion. This is the effect of the formation on the surface of the alloy of very thin Al_2O_3 film protecting the bulk of the alloy from the penetration of oxygen what is observed in the case of pure titanium causing fast destruction elements made of this metal.

Although, there are many publications on the Al-Ti system (Fig. 1), most of them are concerned with the corrosion, the strength or the creeping properties. Only a few papers deal with the thermodynamic properties such as enthalpy of formation or mixing or the activity of the components.

This lack of great interest in thermodynamic investigations is probably caused by serious difficulties in the measurements and preparation of alloys due to the high reactivity of Al with oxygen and Ti with oxygen and nitrogen at high temperatures.

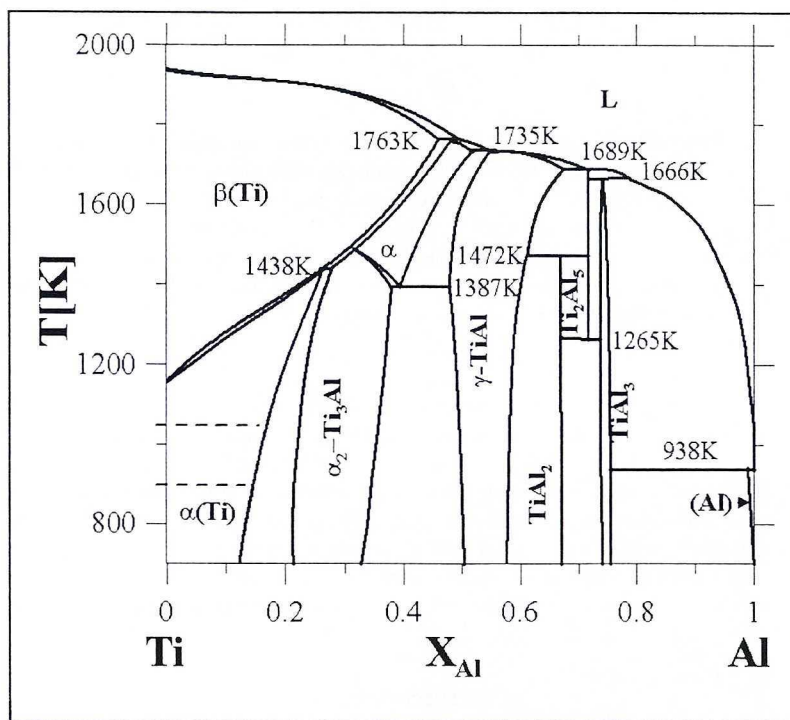


Fig. 1. Phase diagram of the Al-Ti system [1]. Dotted lines on the (α) Ti region indicate the range of measurements of this study

Hence of the special value are the measurements of enthalpy of mixing and activity realized by Esin and coworkers [2, 3], the enthalpy of formation of intermetallic phases obtained by Kubashevski et al. [4, 5] and Rzyman et al. [6, 7], the activity of aluminum measured by Samokhval et al. [8] and Reddy et al. [9] by the EMF method

with solid electrolytes and the activity of Al and Ti determined by Hoch and Usell [10] using the effusion method and Knudsen's cell.

Two years ago, at the Institute of Metallurgy and Materials Science in Kraków there were initiated the studies of the activity and diffusion of the Ni-Al alloys [11] and in 2002 activity measurements of Al in the Al-Ti system were started. In the next 2–3 years a study on the activity and diffusion in the solid alloys in the entire range of components is planned. The main aim of this study is to present the data of aluminium activity measured in the (α)Ti solid phase, i.e. for the Al-Ti alloys with low concentration of Al, as the first step in the thermodynamic investigations of the aluminium-titanium system by EMF method of concentration cells with the liquid electrolyte. The thermodynamic data obtained from EMF study and critically assessed with the other literature data will be finally used for the calculation of the phase diagram.

2. Experimental

The activity measurements in the binary Al-Ti solid alloys have been conducted using the EMF's method of the concentration cells (Fig. 2) which can be written schematically as follows:

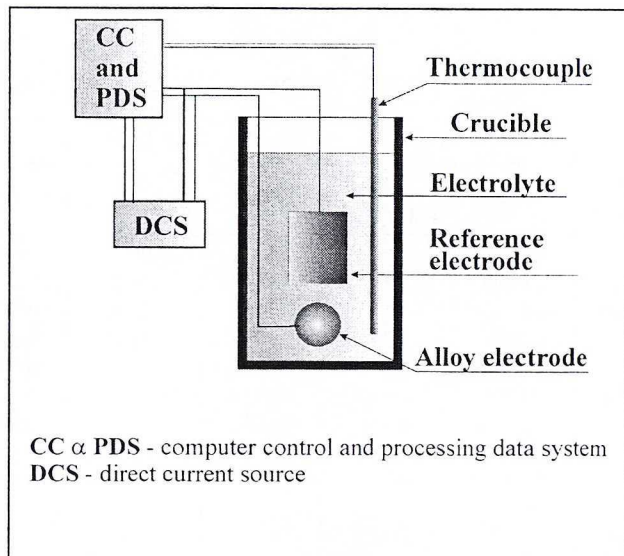
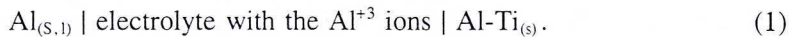


Fig. 2. Scheme of the electrochemical cell employed in investigations of the Al-Ti solid alloys

Using solid or liquid aluminium as the reference electrode, the experiments were performed in the range of (α)Ti solid alloys. The Al-Ti alloys were prepared by direct

electrolytical deposition of Al at the solid Ti thin foil with the thickness 0.1 or 0.05 mm. The Al and Ti metals were of the purity 99.999% at. and 99.95% at., respectively. The LiCl-LiF eutectic with the addition of about 5% at. of AlF_3 was used as electrolyte and prepared by 2 hrs bubbling of a salt mixture by HCl (gas) first, and next by argon. The colorless salts after bubbling, were poured out into alumina crucibles and held in the glove-box with the high purity argon. Before the experiment the salts were grained to fine lumps and placed in the cell. Tantalum wire was used as a connection of Al and Al-Ti electrodes, and the Ni-Mo thermocouple was used for temperature measurements. The measurement cell is shown schematically in Fig. 2. The emfs data were controlled and monitored by a computer supplied with a special software.

3. Results and discussion

The measurements of the electromotive forces were carried out for the Al-Ti solid alloys at the temperatures 923 K, 1014 K, 1041 K and 1061 K and for alloy composition changing from 0.0222 to 0.1237 mole fraction of aluminum. The concentrations of alloys were changed by coulometric titration of Al at the thin Ti foil. The measured equilibrium electromotive forces were used for calculation of the excess Gibbs energy of Al in solid (α)Ti alloys taking into consideration the correction on melting of Al and transformation of Al from BCC to FCC structure applying the relations published by Dinsdale [12]. The obtained values have been listed in Table 1.

TABLE 1
Calculated values of excess Gibbs energy of Al in (α)Ti solid alloys

T = 923 K		T = 1014 K		T = 1041 K		T = 1061 K	
X_{Al}	G_{Al}^{ex} [kJ mol ⁻¹]	X_{Al}	G_{Al}^{ex} [kJ mol ⁻¹]	X_{Al}	G_{Al}^{ex} [kJ mol ⁻¹]	X_{Al}	G_{Al}^{ex} [kJ mol ⁻¹]
0.0222	-102.48	0.0609	-83.64	0.0371	-92.99	0.0266	-95.05
0.0276	-96.80	0.0690	-82.96	0.0488	-86.43	0.0394	-90.87
0.0329	-95.00	0.0770	-80.26	0.0603	-82.55	0.0518	-83.45
0.0382	-91.51	0.0848	-77.31	0.0715	-77.27	0.0639	-73.99
0.0434	-88.99	0.0925	-74.92	0.0824	-74.10	0.0758	-68.82
0.0486	-83.95	0.1001	-71.70	0.0931	-71.91	0.0873	-65.73
0.0537	-83.12	0.1075	-68.80	0.1036	-68.78	0.0985	-63.96
0.0587	-82.65	0.1149	-67.82	0.1138	-65.45	0.1095	-61.82
0.0637	-81.17	0.1221	-67.35	0.1237	-61.57	0.1202	-61.03
0.0687	-80.12						
0.0737	-78.59						
0.0784	-77.92						
0.0832	-77.51						

The data from Table 1 were in the next step described by the Redlich-Kister relation [13] of the following form:

$$G_{\text{Al}}^E = X_{\text{Ti}}^2 [(-82.52293 + 0.02572T) + 48.32137 (3 - 4X_{\text{Ti}})] \quad (2)$$

with the standard deviation 3.1 kJ/mole.

According to the Gibbs-Duhem equation the values of G_{Al}^E in $\alpha(\text{Ti})$ are described by the equation:

$$G_{\text{Ti}}^E = X_{\text{Al}}^2 [(-82.52293 + 0.02572T) + 48.32137 (1 - 4X_{\text{Ti}})]. \quad (3)$$

and the integral excess Gibbs energy is represented by the relation:

$$G^E = (1 - X_{\text{Ti}}) X_{\text{Ti}} [(-82.52293 + 0.02572T) + 48.32137 (1 - 2X_{\text{Ti}})]. \quad (4)$$

Basing on the Eqs (2–4) there were calculated the values of excess Gibbs energy at 1041 K, partial enthalpy of solution, excess entropy for Al and Ti and the integral excess entropy and enthalpy of mixing and activity. The values of the partial thermodynamic function for aluminum and titanium, integral heat of mixing and excess molar entropy are presented in Table 2 and in Figures 3–6. The integral enthalpy of mixing and the excess entropy calculated from Eq 4 are shown in Table 2 and in Fig 7. The activities of Al and Ti at four temperatures: 923 K, 1014 K, 1041 K and 1061 K presented in Table 3 were calculated using the well known relation:

$$a_{\text{Al(Ti)}} = \exp \left(\frac{G_{\text{Al(Ti)}}^{\text{ex}}}{RT} + \ln X_{\text{Al(Ti)}} \right). \quad (5)$$

The excess Gibbs energy of Al and Ti were calculated applying Eqs 2 and 3.

TABLE 2

Partial thermodynamic functions of Al and Ti calculated from Eqs 2 and 3. and integral enthalpy and integral excess entropy calculated using Eq 4.

X_{Al}	H_{Al} [kJ/mol]	S_{Al}^E [kJ/mol K]	G_{Al}^E (1041 K) [kJ/mol]	H_{Ti} [kJ/mol]	S_{Ti}^E [kJ/mol K]	G_{Ti}^E (1041 K) [kJ/mol]	S^E [kJ/mol K]	H [kJ/mol]
0.00	-130.80	-25.72	-104.03	0	0	0	0	0
0.01	-126.35	-25.21	-100.10	-0.02	0	-0.02	-0.25	-1.29
0.02	-121.95	-24.70	-96.23	-0.09	-0.01	-0.08	-0.50	-2.53
0.03	-117.66	-24.20	-92.46	-0.20	-0.02	-0.18	-0.75	-3.72
0.04	-113.46	-23.71	-88.78	-0.35	-0.04	-0.31	-0.99	-4.88
0.05	-109.36	-23.21	-85.20	-0.54	-0.06	-0.48	-1.22	-5.99
0.06	-105.37	-22.73	-81.71	-0.78	-0.09	-0.68	-1.45	-7.05
0.07	-101.47	-22.25	-78.31	-1.05	-0.13	-0.92	-1.67	-8.08
0.08	-97.66	-21.77	-75.00	-1.36	-0.16	-1.19	-1.89	-9.06
0.09	-93.95	-21.30	-71.77	-1.70	-0.21	-1.48	-2.11	-10.00
0.10	-90.33	-20.83	-68.64	-2.08	-0.26	-1.81	-2.31	-10.91
0.11	-86.80	-20.37	-65.59	-2.50	-0.31	-2.17	-2.52	-11.77
0.12	-83.36	-19.92	-62.63	-2.94	-0.37	-2.56	-2.72	-12.59

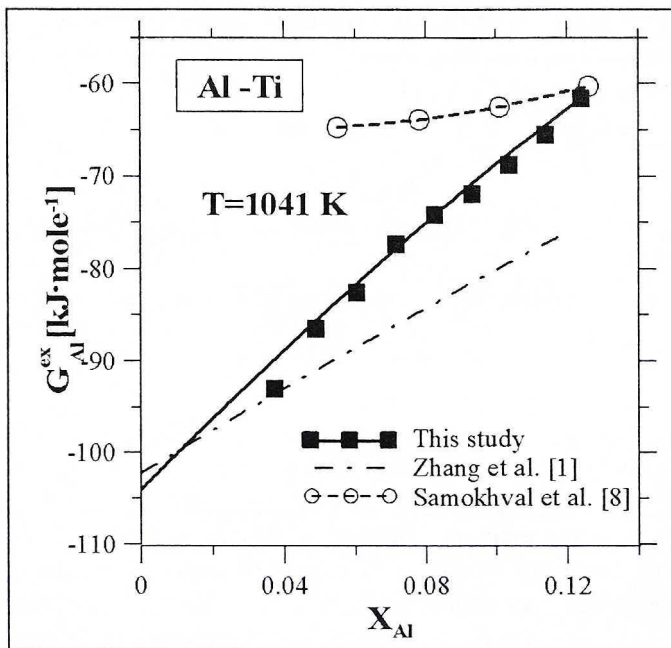


Fig. 3. The excess Gibbs energy of Al for the dilute Al-Ti solid alloys. Squares and solid line are the data from this study, circles and dashed line are related to the data of Samokhval et al. [8] and dotted line represents values calculated from the optimized thermodynamic parameters [1]

TABLE 3
Activities of aluminum and titanium calculated using Equation 5 at temperatures
923 K, 1014 K, 1041 K and 1061 K

X_{Al}	Activity of aluminum * 10^4				Activity of titanium			
	923 K	1014 K	1041 K	1061 K	923 K	1014 K	1041 K	1061 K
0	0	0	0	0	1	1	1	1
0.01	0.0001	0.0006	0.0009	0.0013	0.9874	0.9877	0.9877	0.9878
0.02	0.0005	0.0020	0.0030	0.0039	0.9698	0.9709	0.9711	0.9713
0.03	0.0012	0.0048	0.0069	0.0089	0.9477	0.9500	0.9505	0.9510
0.04	0.0026	0.0099	0.0140	0.0180	0.9216	0.9254	0.9264	0.9271
0.05	0.0053	0.0189	0.0265	0.0337	0.8918	0.8975	0.8990	0.9001
0.06	0.0101	0.0345	0.0476	0.0599	0.8590	0.8668	0.8689	0.8704
0.07	0.0184	0.0603	0.0823	0.1027	0.8236	0.8338	0.8365	0.8384
0.08	0.0326	0.1022	0.1380	0.1707	0.7863	0.7989	0.8022	0.8046
0.09	0.0562	0.1687	0.2252	0.2763	0.7475	0.7625	0.7665	0.7694
0.10	0.0946	0.2722	0.3594	0.4376	0.7077	0.7252	0.7298	0.7332
0.11	0.1560	0.4305	0.5623	0.6793	0.6675	0.6872	0.6925	0.6963
0.12	0.2521	0.6683	0.8638	1.0357	0.6271	0.6491	0.6550	0.6592

The partial excess Gibbs energy of aluminum at 1041 K obtained in this study are shown in Fig. 3 together with the data from literature [1] and [8]. Data of Samokhval et al. [8] from EMF method with the solid electrolyte for lower Al concentrations are higher than those in the present work and those calculated from optimized thermodynamic parameters of Zhiang et al. [1]. The values of this study are located between those from [1] and [8] and for very low Al concentrations are close to the data of Zhiang et al. [1], reaching for 0.1237 mole fraction of Al the values obtained by Samokhval et al. [8]. Maximal differences between the data of [1] and those from the present study are about 15 kJ/mole for most Al concentrated alloys ($X_{Al} \sim 0.12$) while the values cited by [8] and those of the present work differ by about 20 kJ/mole for $X_{Al} = 0.055$.

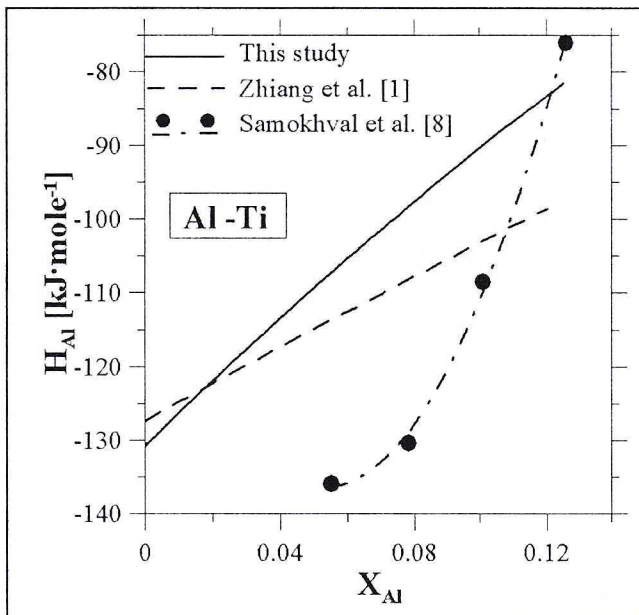


Fig. 4. The enthalpy of solution of Al obtained in this study (solid line) together with the data of Samokhval et al. [8] and values calculated from relation given by Zhiang et al. [1]

The most negative values of partial enthalpy of mixing of Al, presented in Fig. 4, were obtained by Samokhval et al. [8] in the central region of the investigated concentrations. The data calculated from the optimized thermodynamic parameters [1] show higher values than those of [8], similarly as the data of this study for concentrations higher than 0.025 mole fraction of Al. The limiting values of H_{Al} calculated from Eq. 2 and those from [1] are close to -130.8 kJ/mole. The observed maximal differences are located in the vicinity of $X_{Al} = 0.08$ and are close to 35 kJ/mole both for data of [1] and data from this study.

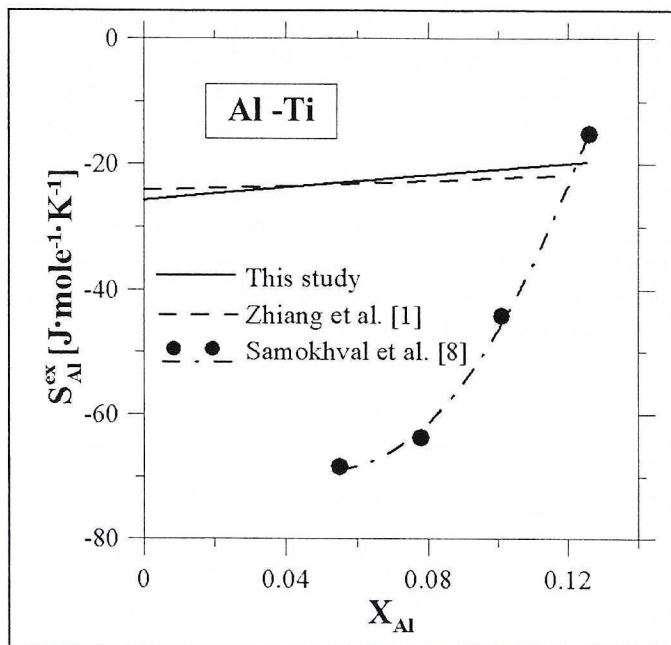


Fig. 5. Excess entropies of Al obtained in this study (solid line), from EMF study by [8] (full points and dotted line) and values calculated from optimized thermodynamic parameters worked out by [1] (dashed line)

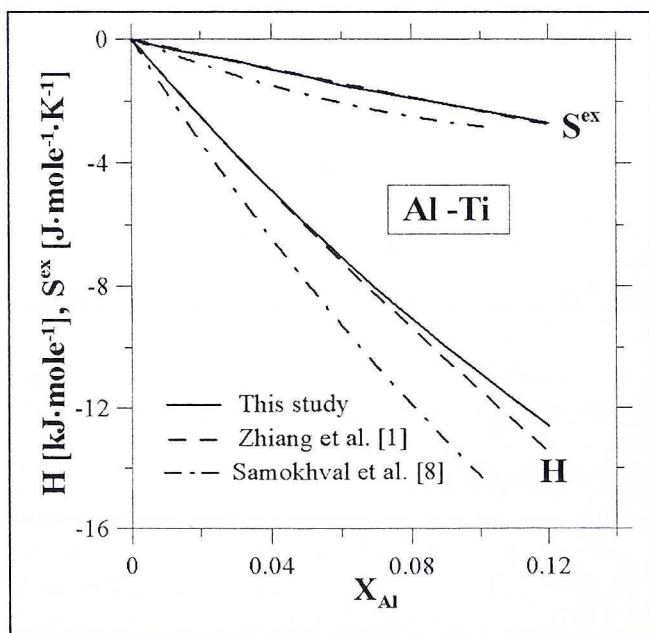


Fig. 6. Integral enthalpy of mixing and integral excess entropy for the Al-Ti dilute solid solutions. Solid line – this study, dashed line – Zhiang et al. [1], and dotted line – Samokhval et al. [8]

A good agreement between the values of our excess entropy of Al and those from [1] is observed in the whole concentration range (Fig. 5). The values of this thermodynamic function obtained in this study change from -25.72 J/mole K ($X_{\text{Al}} = 0$) to -19.92 J/mole K for $X_{\text{Al}} = 0.12$. The data of [1] are almost constant and exhibit a slow increasing tendency from about -24 J/mole K for $X_{\text{Al}} = 0$ to -22 J/mole K for $X_{\text{Al}} = 0.12$. The data presented by Samokhval and coworkers [8] for the Al concentrations close to 0.06 are about three times lower than those obtained in this work and calculated from the relation presented in paper [1].

The excellent agreement between the enthalpy of mixing and the integral excess entropy of the solid Al-Ti alloys is observed in Fig. 6. The data of enthalpies of mixing from this study and those calculated from optimized thermodynamic parameters [1] differ by about 0.5 kJ/mol, for the highest concentration of Al (0.12 molar fraction) while the excess entropy is practically the same. The values in Fig. 6 measured by Samokhval et al. [8] show lower values than either those from this work or from paper [1].

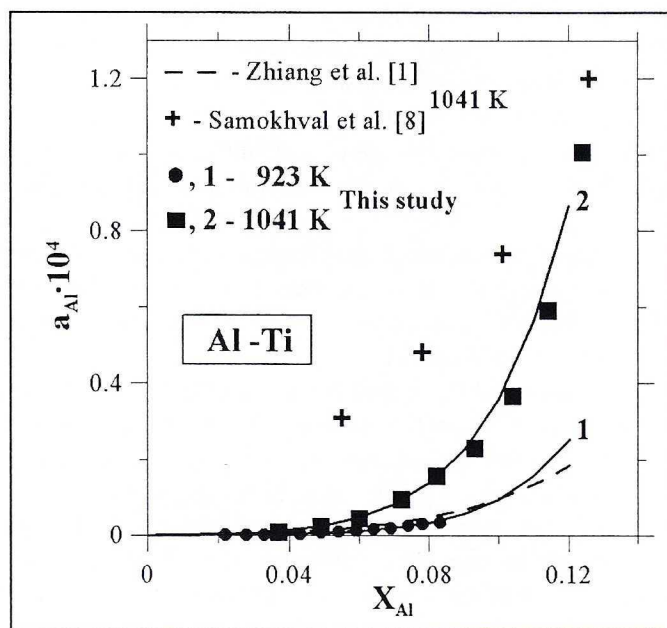


Fig. 7. Activity of Al at 923 K and 1041 K from this work (solid lines, squares and full points), measured by [8] at 1041 K – crosses, and calculated at 1041 K from the optimized thermodynamic parameters [1] – dashed line

Activity values of aluminium obtained in this study at 923 K, 1041 K (continuous lines, full circles, squares) are presented in Fig. 7 together with those from [1] (crosses) and [8] (dashed line) at 1041 K. The values measured by Samokhval et al. [8] are much higher both than the data of this study and those calculated using optimized thermodynamic parameters given by Zhiang et al. [1]. Activity values measured in this work at 1041 K are found between the data presented in [1] and [8], and in the concentration range from 0 to

0.06 mole fraction of Al they are closer to the data of Zhiang et al. [1]. For higher concentrations, the activities [1] at 1041 K are almost the same as those obtained in this study at 923 K.

4. Summarising

The EMF measurements conducted at the temperatures 923 K, 1014 K, 1041 K and 1061 K have shown that the $\alpha(\text{Ti})$ solid alloys are characterized by negative deviations from the ideal solutions and the calculated excess Gibbs energy of Al values obtained in this study (Fig. 3) at 1041 K are between those measured by [8] and calculated using the optimized thermodynamic parameters worked out by Zhiang et al. [1].

The enthalpy of solution of Al obtained in this study (Fig. 4) varies from -130.8 kJ/mole for $X_{\text{Al}} = 0$ to -83.4 kJ/mole for $X_{\text{Al}} = 0.12$, and is lower than that of [8] with a maximal difference of about 30 kJ/mol for concentrations close to 0.08 mole fraction of Al. Data of H_{Al} given by [1] show good agreement with values obtained in the present work (Eq. 2) only for $X_{\text{Al}} < 0.05$. At higher concentrations, higher differences are observed reaching for $X_{\text{Al}} = 0.12$ deviations of almost 17 kJ/mole.

The excess entropy of Al obtained in this work and those from [1] show comparable values in the $\alpha(\text{Ti})$ solid solutions and they are much higher than the data of [8]. Only for the most concentrated alloys the excess entropies from this work, [1] and [8] are close to each other (Fig. 5).

The integral enthalpy of mixing and excess entropy obtained by the authors and [1] are characterized by very low differences. The excess entropies are almost the same and the difference in the heat of mixing is lower than 1 kJ/mole for $X_{\text{Al}} = 0.12$. More negative results are shown by the values of Samokhval et al. [1].

The experimental values of Al activities and those calculated at 1041 K basing on Eq. 3 are located between the values from the optimized thermodynamic parameters [1] (except activities for very dilute Al solution) and those measured by [8]. A good agreement between our data and those calculated from [1] is observed for $X_{\text{Al}} < 0.1$.

This work is the first part of the investigations of Al-Ti solid alloys. The study will be continued in the next years for the measurements of Al activity in the entire range of concentrations to provide against the lack of experimental data either at temperatures lower than 900 K or the higher concentrations of Al. Finally, a new optimization and the calculation of the Al-Ti phase diagram is planned using all information available in the literature on the activity, enthalpy of mixing and enthalpy of formation of intermetallic phases.

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