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Predicting thermodynamic properties in Ti–Al binary system by FactSage

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Abstract

The results of predicting thermodynamic properties in Ti–Al binary system were shown in this paper. The activity of titanium and aluminum in titanium–aluminum alloys were calculated using FactSage thermochemical software and databases. The activity of Ti and Al as a function of titanium concentration was calculated in the temperature range between 1773 K and 2273 K. The activity–temperature ($1.0 > X_{Ti} > 0.1$) relationships for Ti–Al alloys for a temperature ranges between 1773 K and 2273 K were calculated, too. Some predicting thermodynamic results were compared to available experimental results. A good agreement has been noticed.

Keywords: Thermodynamics; Calculation; Predicting; FactSage; Ti–Al binary system

1. Introduction

Titanium belongs to the fourth group of the periodic table and is comparatively strong and ductile transition metal. Titanium is relatively exceptional among metallic elements, since it exhibits various valences, ranging from two to four by the existence of numerous oxides. The high strength and low density of titanium are related to specific electronic states of titanium, which allow the formation of relatively strong bonds between titanium atoms [1]. Theoretically, the attractive mechanical properties, including the lightweight, strength to weight ratio, high ductility, and low thermal conductivity, result in more functional and comfortable use [1].

Titanium can be alloyed with various elements to change its characteristics, primarily to improve the mechanical property, such as strength, high temperature performance, creep resistance, weldability, response to ageing heat treatments, and formability [2]. Unalloyed titanium shows low strength and poor wear resistance. Pure titanium undergoes a transition from a hexagonal close packed structure (α-phase) to a body centered cubic structure (β-phase) at 883 °C. It remains in this crystallographic structure until melting at 1672 °C [1,2]. Alloying elements can be added to stabilize one or the other of these phases by either raising or lowering the transition temperatures [2]. Elements such as Al, Ga, and Sn, with the interstitial elements (C, O, and N) stabilize the α-phase, resulting in alpha titanium alloy. On the other hand, elements such as V, Nb, Ta, and Mo, stabilize the β-phase [1]. There are also titanium alloys, whose compositions at room temperature present a mixture of alpha-stabilizers and beta-stabilizers. Alpha titanium alloy, generally used in aerospace industries, is weldable, more oxidation-resistant, and superior in high-temperature strength. But alpha titanium alloy is difficult to form or cold work at room temperature. In contrast, beta titanium alloy has weldability and a good formability at lower temperatures, which may be suitable, for example of the dental applications [2]. Alpha–beta titanium alloys are commonly strong, owing to the duplex phase structure. Alpha–beta titanium

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alloys are more formable than alpha alloys but somewhat more difficult to weld. Aluminum, a typical alpha stabilizer, increases the alpha–beta transition temperature and maintains the improved mechanical properties over pure titanium. Other alpha stabilizers include oxygen, which forms interstitial solid solutions to titanium [1,2].

Titanium and its alloys has been the key materials used in all space launchers, spacecrafts, and the space station. Titanium and its alloys have application in jet engines, airframes, industrial applications, power generation, chemical processing, petroleum, other industries, emerging applications, computer industry (titanium is a promising substrate for hard disk drives), automotive industry, geothermal power generation, composites, as well as, its specialized applications as human implants, and other applications. Titanium is also now found in a wide variety of consumer products such as jewellery, watchcases, eyeglasses, bicycles and clocks, and has found interesting applications in sport.

According to many and extensive application and used especially titanium–aluminum alloys in various fields, it is necessary to know thermodynamic behaviour of this binary system as the base binary system for the other alloys based on Ti–Al system.

The Ti–Al binary system as well as its phase diagram has long been a topic of interest because of the variability in the results reported by different researchers. Two such examples of this binary system are assessed by Murray [3] and by Kattner et al. [4]. These two diagrams exhibit several discrepancies not only in the equilibrium temperatures and the compositions but also in their phase relations. Particularly noticeable are the disagreement associated with the equilibria at high temperatures in Ti–Al aluminides, which are considered to arise mainly due to oxygen contamination. Kainuma et al. [5] have summarized such uncertainties and have carried out some investigations in the Ti–Al binary system. Because titanium aluminides are potential candidates as high temperature light materials, a redetermination of the phase diagram in this region, using specimens with low levels of oxygen contamination, has become a priority.

In 1978, Kaufman and Nesor [6] reported their pioneering work on the calculation of the phase diagram in the Ti–Al binary system, assuming all the intermetallic compounds to be of stoichiometric composition. Gros et al. [7] published a thermodynamic assessment of the phase equilibria between the liquid, β-Ti, α-Ti and α_2-Ti_3Al phases in the Ti-rich region of the diagram. The Gibbs energies of both the ordered α_2-Ti_3Al and disordered α-Ti phases were described by the unified two-sublattice model. Murray [8] also applied the same unified formalism to the Gibbs energy of the three ordered phases, while Ohnuma et al. [9] experimentally studied the phase equilibria between the Ti-rich solid phases which were determined on specimens with carefully controlled low levels of oxygen contamination.

Also, there are some articles about thermodynamics description of Ti–Al based system [10,11], kinetics of phase and structural transformation in some Ti–Al alloys [12,13], thermodynamics, kinetic consideration and modeling for casting titanium alloys with some selected mould as CaO and ZrO_2 [14–16], as well as work Reddy et al. [17] about thermodynamic properties of Ti–Al intermetallics and Saunders et al. [18] about integrated approach to the calculation of materials properties for titanium alloys.

However, a few studies on the thermodynamic properties of oxygen in molten titanium–aluminum alloys have been conducted. Yahata et al. [19] deoxidized titanium in an electron beam furnace by adding excess aluminum. This mixture formed an aluminum suboxide vapor leaving a Ti–Al alloy with low oxygen content. Okabo et al. [20] investigated the removal of oxygen in TiAl powder mixed with $CaCl_2$ by using Ca–Al vapor at 1373 K. Sakamoto et al. [21] investigated the thermodynamic properties of calcium and oxygen in molten TiAl alloys by melting titanium aluminide in CaO crucible in a vacuum induction furnace, a cold crucible type induction furnace, and an electron beam furnace. Shibata et al. [22] studied the thermodynamic properties of calcium and oxygen in TiAl at 1843 K melted in a cold crucible type of induction furnace. Tsukihashi et al. [23] investigated the thermodynamic properties of calcium and oxygen in molten Ti, TiAl and $TiAl_3$ alloys using calcium-based fluxes. Copland and Jacobson [24] presented the newest thermodynamics study of Ti–Al–O alloys in the aim to find and determine a possible compressor application in gas-turbine engines. They measured component activity by a special pressure technique designed and fabricated at the NASA Glenn Research Center. Also, there are some works which corresponded with measurement of the specific heat TiAl undercooled liquid alloys [25], as well as with computer modeling in ternary and multi alloys based on this binary system [26–28] and equilibrium electrochemical synthesis diagrams of these binaries [29].

According to literature survey, it can be noticed that many scientists worked on the Ti–Al binary system and there were various interesting and differencing data and results. In the aim of contributing with some more data and approaches of thermodynamic description and determination of these investigated binaries, in this work the results of thermodynamic calculations in Ti–Al are done using FactSage thermochemical software and databases. The activity–temperature-composition relationships of titanium and aluminum in Ti–Al in the wide temperature range between 1773 K and 2273 K are estimated. The predicting thermodynamic properties in this system are presented too and some of them are compared to available experimental results. A good agreement has been noticed.

Those results present a contribution to a better knowledge of this binary system.

2. Results of thermodynamic calculations in Ti–Al and discussion

The activity of titanium and aluminum in titanium–aluminum alloys is calculated using the FactSage thermo-

chemical software and databases [30]. The activity of Ti and Al as a function of titanium concentration is calculated in the temperature range between 1773 K and 2273 K. The obtained results are shown in Table 1 and the activity–composition diagrams for Ti and Al at 1873 K done in FactSage program are shown in Fig. 1.

Based on the activity data of Table 1, the activity relationship for Ti and Al depending on Ti composition at temperatures 1773–2273 K was calculated as follows:

$$a_i = A + Bx_i + Cx_i^2 + Dx_i^3, \quad T = \text{const}; \quad i = \text{Ti, Al} \tag{1}$$

The results are given in Table 2.

The dependences of Ti and Al activity on Ti content are shown in Figs. 2 and 3, respectively.

Table 1, as well as Figs. 1–3, show that the activity coefficient of both components is less than unity and the activity of both titanium and aluminum increases with the temperature increasing, there is negative deviation from Raoult's law and thus good miscibility between the components.

To assess the stability of compounds in Ti–Al system we need to know the activity of Ti and Al as a function of temperature. The activity–temperature relationship can be expressed as

$$\ln a_{\text{Ti}} = A + B/T \tag{2}$$

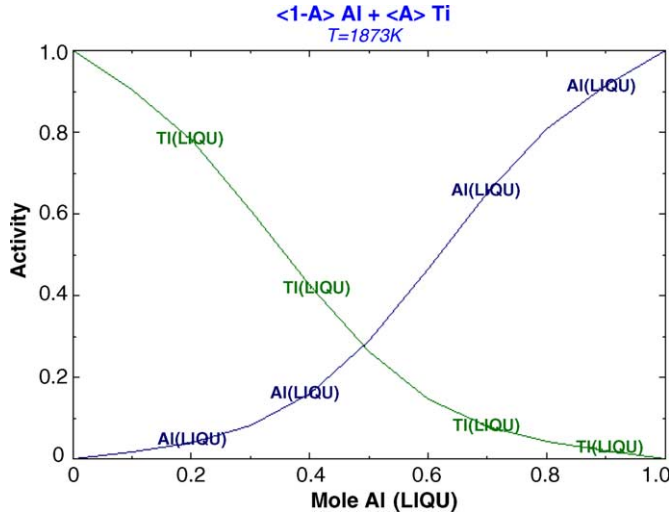

Fig. 1. Ti and Al activity in the liquid phase as function of mole fraction Al at temperature 1873 K.

The coefficients A and B need to be determined. Based on the activity data calculated by FactSage, the composition-based (X_{Ti}) activity relationship for Ti in the temperatures range between 1773 K and 2273 K can be approximated as follows:

$$\ln a_i = A + Bx_i + Cx_i^2 + Dx_i^3, \quad T = \text{const}; \quad i = \text{Ti, Al} \tag{3}$$

Table 1
Activity of Ti and Al in the temperature range from 1773 K to 2273 K

X_{Ti}	1773 K		1873 K		1973 K	
	a_{Ti}	a_{Al}	a_{Ti}	a_{Al}	a_{Ti}	a_{Al}
0	0	1	0	1	0	1
0.1	0.015141	0.91191	0.020727	0.91426	0.027485	0.91637
0.2	0.032151	0.79919	0.041609	0.80936	0.052459	0.81860
0.3	0.064489	0.63285	0.078649	0.65378	0.094007	0.67319
0.4	0.12757	0.43767	0.14703	0.46617	0.16703	0.49335
0.5	0.23813	0.26243	0.26123	0.29103	0.28389	0.31938
0.6	0.40118	0.13875	0.42316	0.16141	0.44393	0.18492
0.7	0.59423	0.066993	0.60958	0.082052	0.62371	0.098450
0.8	0.77232	0.030590	0.77915	0.039369	0.78535	0.049389
0.9	0.90274	0.012534	0.90404	0.016800	0.90521	0.021859
1	1	0	1	0	1	0
X_{Ti}	2073 K		2173 K		2273 K	
	a_{Ti}	a_{Al}	a_{Ti}	a_{Al}	a_{Ti}	a_{Al}
0	0	1	0	1	0	1
0.1	0.035467	0.91829	0.044707	0.92003	0.055217	0.92163
0.2	0.064677	0.82705	0.078218	0.83479	0.093026	0.84191
0.3	0.11045	0.69121	0.12785	0.70800	0.14610	0.72366
0.4	0.18743	0.51928	0.20810	0.54400	0.22893	0.56756
0.5	0.30605	0.34737	0.32767	0.37489	0.34872	0.40190
0.6	0.46358	0.20910	0.48218	0.23377	0.49978	0.25880
0.7	0.63676	0.11607	0.64885	0.13478	0.66007	0.15446
0.8	0.79099	0.060617	0.79615	0.073008	0.80088	0.086505
0.9	0.90627	0.027728	0.90724	0.034412	0.90812	0.041902
1	1	0	1	0	1	0

Table 2
Activity–composition relationship for Ti and Al at 1773–2273 K, $a_i = A + Bx_i + Cx_i^2 + Dx_i^3$

T (K)	A	B	C	D	X_i
Titanium					
1773	0.0308	−0.7503	3.2250	−1.4809	0.1–0.9
1873	0.0290	−0.6617	3.1308	−1.4769	0.1–0.9
1973	0.0274	−0.5619	2.9999	−1.4471	0.1–0.9
2073	0.0261	−0.4521	2.8356	−1.3937	0.1–0.9
2173	0.0252	−0.3337	2.6413	−1.3189	0.1–0.9
2273	0.0246	−0.2077	2.4198	−1.2244	0.1–0.9
Aluminum					
1773	1.0191	−0.9633	−1.8714	1.8464	0.1–0.9
1873	1.0145	−0.8286	−2.0499	1.8922	0.1–0.9
1973	1.0103	−0.7102	−2.1834	1.9088	0.1–0.9
2073	1.0065	−0.6069	−2.2755	1.8989	0.1–0.9
2173	1.0030	−0.5178	−2.3295	1.8648	0.1–0.9
2273	1.0000	−0.4420	−2.3486	1.8088	0.1–0.9

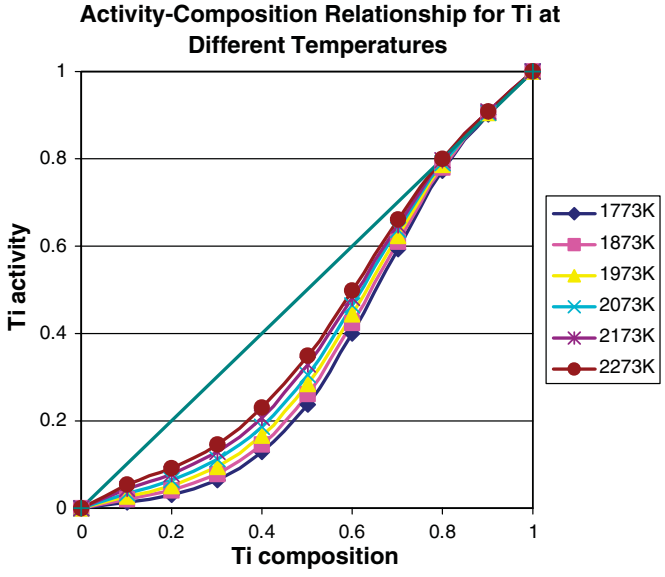

Fig. 2. Dependence of Ti activity on Ti content in the temperature range 1773–2273 K.

The obtained results are given in Table 3.

The activity–temperature ($1.0 > X_{Ti} > 0.1$) relationships for Ti–Al alloys for a temperature ranges between 1773 K and 2273 K are calculated. Table 4 shows the estimated coefficients for the activity–temperature ($1.0 > X_{Ti} > 0.1$) relationships for Ti in Ti–Al alloys for a temperature range between 1773 K and 2273 K. Thus, as a first approximation the activity–temperature relationship of Ti in Ti–Al (Eq. 2) has been formulated.

The activity–temperature relationship is shown in Fig. 4. The activity–temperature relationship shows that Ti activity decreases with decreasing Ti mole fraction and with decreasing temperature, i.e. Ti activity increases with increasing Ti fraction and with increasing temperature.

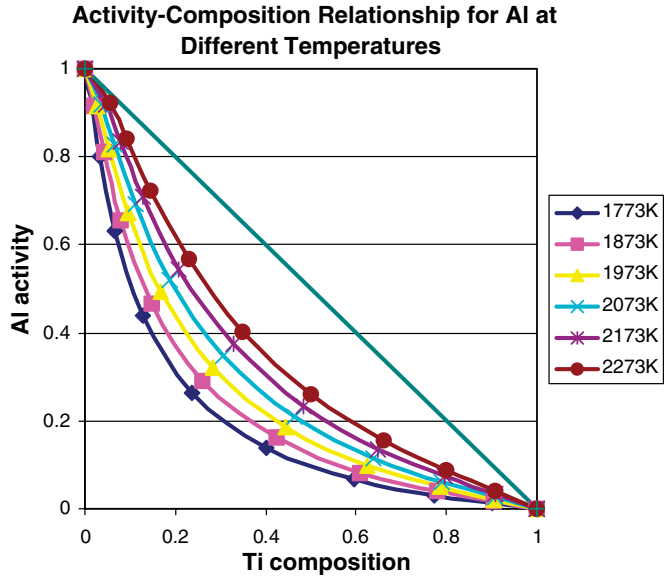

Fig. 3. Dependence of Al activity on Ti content in the temperature range 1773–2273 K.

Table 3
Logarithm activity–composition relationship for Ti and Al at 1773–2273 K, $\ln a_i = A + Bx_i + Cx_i^2 + Dx_i^3$

T (K)	A	B	C	D	X_i
Titanium					
1773	−4.9376	7.4197	0.8965	−3.5371	0.1–0.9
1873	−4.5623	6.8302	0.7783	−3.1887	0.1–0.9
1973	−4.2249	6.3000	0.6729	−2.8761	0.1–0.9
2073	−3.9201	5.8213	0.5769	−2.5933	0.1–0.9
2173	−3.6433	5.3858	0.4919	−2.3378	0.1–0.9
2273	−3.3908	4.9889	0.4136	−2.1042	0.1–0.9
Aluminum					
1773	−0.1584	1.3980	−8.5472	1.9812	0.1–0.9
1873	−0.1425	1.1792	−7.4912	1.4599	0.1–0.9
1973	−0.1281	0.9826	−6.5419	0.9913	0.1–0.9
2073	−0.1151	0.8047	−5.6835	0.5673	0.1–0.9
2173	−0.1034	0.6437	−4.9058	0.1836	0.1–0.9
2273	−0.0926	0.4965	−4.1955	−0.1670	0.1–0.9

Table 4
Activity–temperature relationship for Ti–Al alloys, $\ln a_{Ti} = A + B(T/K)^{-1}$

X_{Ti}	A	B	Temperature (K)
0.1	−8.7202	0.0026	1773–2273
0.2	−7.1569	0.0021	1773–2273
0.3	−5.6044	0.0016	1773–2273
0.4	−4.1063	0.0012	1773–2273
0.5	−2.7704	0.0008	1773–2273
0.6	−1.6827	0.0004	1773–2273
0.7	−0.8884	0.0002	1773–2273
0.8	−0.3855	0.00007	1773–2273
0.9	−0.1231	0.00001	1773–2273

Calculated activity of titanium and aluminum from this work are graphically compared with literature results [11] in Figs. 5 and 6, respectively. Results presented in Figs. 5

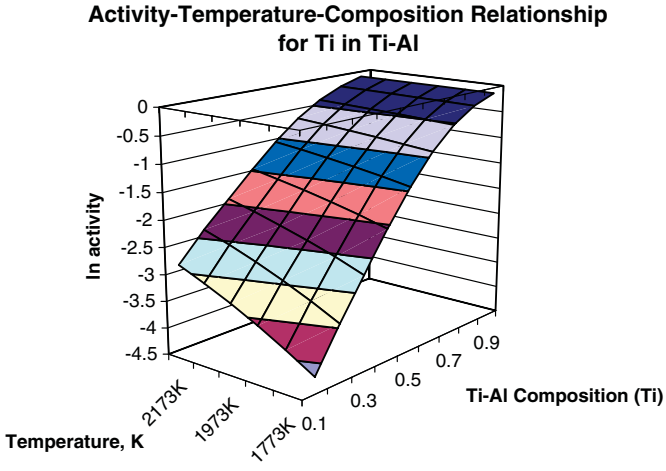

Fig. 4. Activity–temperature–composition relationship for Ti in Ti–Al.

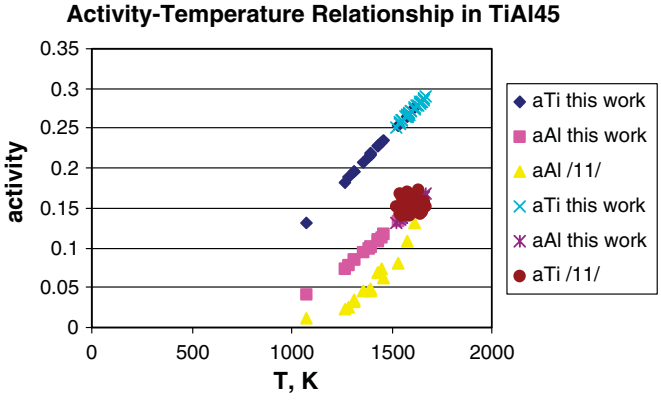

Fig. 5. Comparison between experimentally obtained and calculated values for titanium and aluminum activity in TiAl45 alloy at different temperatures.

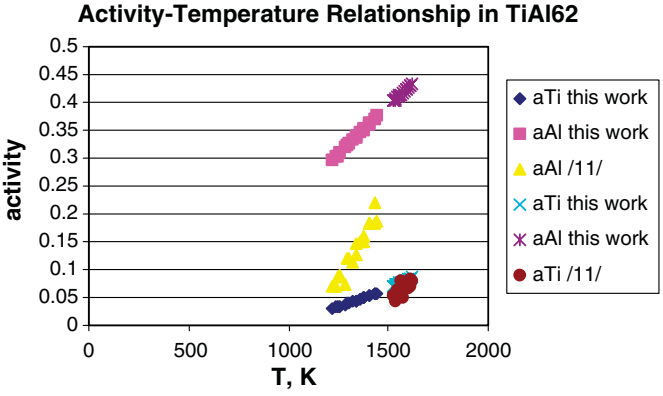

Fig. 6. Comparison between experimentally obtained and calculated values for titanium and aluminum activity in TiAl62 alloy at different temperatures.

and 6 show good agreement between calculated and literature results for two different alloys TiAl45 and TiAl62. Good agreement can be noticed especially for titanium activity, which is even better on higher temperatures.

3. Conclusions

In consideration of above mention as well as titanium and titanium–aluminum alloys large use and application in almost all important branches and fields of techniques, it is very important to know completely thermodynamic determination and description of titanium–aluminum based system. Because of that, thermodynamic properties of the Ti–Al binary system were investigated.

The activity of titanium and aluminum in Ti–Al alloys was calculated at temperature 1773–2273 K as well as the activity–temperature relationship for Ti–Al alloys as a function of titanium concentration. The activity coefficient of both components is less than unity and the negative deviation from Raoult's law is noticed and thus good miscibility between the components. The activity of titanium and aluminum in whole temperature range increase with temperature increasing.

Comparison of the obtained and calculated results with literature data and experimentally obtained are done in Ti–Al45 and Ti–Al62 alloys. Comparison shows good agreement for the titanium activity especially at higher temperature and slight disagreement with aluminum activity.

Results presented in this paper are contribution to the more complete thermodynamic description of Ti–Al binary system and may be useful for the further thermodynamic assessment of this system and in particular for ternary and multi component systems based of this binary.

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