



## Predicting thermodynamic stability of crucible oxides in molten titanium and titanium alloys

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Received 13 June 2005; received in revised form 7 March 2006; accepted 8 March 2006

### Abstract

Titanium is all around us, including in the human body. It is immune to environmental attack, regardless of pollutants. Where other architectural metals exhibit limited lifespan, titanium endures. As durable metal, with interesting properties, titanium and its alloys are perfect for use in many applications.

Since titanium and its alloys have a great specific strength, the improvement of the mechanical properties is of growing importance in the aircraft and space industry. They have been key materials used in all space launchers, spacecrafts, and the space station. It is very interesting to mention that titanium is a promising substrate for hard disk drives, as well as for very interesting application in golf sport.

Titanium and its alloys interstitially dissolve a large amount of impurities such as oxygen and nitrogen, which degrade the mechanical and physical properties of alloys. Ways of eliminating oxygen from titanium and its alloys are important for use in widespread applications.

Crucible oxides i.e. refractory oxides based on CaO, ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, etc. can be used for melting titanium and its alloys. However, the thermodynamic behavior of calcium, zirconium, yttrium on the one side, and oxygen on the other side, in molten Ti and Ti–Al alloys have not been made clear and because of that, it is very interesting for research.

Owing to literature data, as well as these crucibles are cheaper than standard crucibles for melting titanium and titanium alloys, in this paper will be presented the results of predicting thermodynamic analysis with the aim to determine the crucible oxide stability in contact with molten titanium and titanium–aluminum alloys.

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**Keywords:** Thermodynamic analysis; Thermodynamic calculations; Crucible oxides; Titanium; Titanium–aluminum alloys

### 1. Introduction

Titanium is all around us, including in the human body, but it was not known to exist until 1791 when William Gregor, an English priest who found a strong hobby in chemistry, had discovered titanium. He had found titanium when experimenting with the mineral menaccanite (nowa-

days called ilmenite), where he discovered a red–brown constituent that was not yet classified [1]. The term “titanium” was coined in 1795 by German chemist Martin Heinrich Klaproth who also discovered this element to exist in the ore rutile [1,2].

By the late 19th century, several scientists had managed to develop methods to isolate titanium to a purity of 95% for example Lars Nilson and Otto Pettersson [3]. Subsequently, Henry Moissan produced 98% pure titanium in an electric furnace, before a joint venture between Rensselaer Polytechnic and General Electric led by Matthew Hunter achieved 99.9% purity using TiCl<sub>4</sub> [4]. The work of Hunter got significant publicity and was a boost to the industry.

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Still, being able to produce titanium in a laboratory did not give much of an incentive to produce it for industrial applications unless if a relatively low cost production method would be developed. As such, the father of the titanium industry is considered William Justin Kroll from Luxembourg who in the mid-1940s developed the Kroll method that is still in use today at many titanium production facilities [3–5].

Other methods of production have been developing in parallel as well as a scientific pursue on how to fabricate and use titanium. The new methods of producing titanium, such as the Vacuum Distillation process (VDP) help reduce the costs of producing this precious but abundant metal [3]. New developments point to further efficiencies, i.e. if British Titanium Plc with its patent in 2002 and the grant from the US office of Naval Research proves itself right on the FFC-Cambridge process [3].

Titanium is immune to environmental attack, regardless of pollutants. Where other architectural metals exhibit limited lifespan, titanium endures. It withstands urban pollution, marine environments, and the sulfur compounds of industrial areas and is failure-proof in even more aggressive environments [3]. Because it is a durable metal, the coupling of titanium with dissimilar metals does not accelerate galvanic corrosion of the titanium [3,6].

These properties make titanium and its alloys perfect for use in many applications. Since they have a great specific strength, the improvement of the mechanical properties is of growing importance in aerospace applications. Titanium and its alloys have been key materials used in all space launchers, spacecrafts, and the space station [7]. The ubiquitous existence of titanium on the moon could one day prove to be of pivotal importance for humanity's endeavors in outer space [8].

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 [9]. 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. The golf industry has found that lightweight titanium club heads can be bigger than those made of steel, enlarging the "sweet spot" of the club and thus increasing distance and accuracy [3].

Several thousand titanium alloys have been examined on a research and development basis [10]. From this extensive activity, more than hundred compositions have been produced commercially over the past four decades of extensive titanium production [11]. Some old alloys have disappeared from the popular listings and new alloys have been added [3].

Anyway, titanium alloys, available in both commercially pure and alloy grade, can be grouped into three categories

according to the predominant phase or phases in their microstructure alpha, alpha–beta, and beta. Although each of these three general alloy types requires specific and different processing methodologies, each offers a unique suite of properties, which may be advantageous for a given application.

In pure titanium, the alpha phase characterized by a hexagonal close-packed crystalline structure is stable from room temperature at 882 °C [12]. The beta phase in pure titanium has a body-centered cubic structure and is stable from approximately 882 °C to the melting point of about 1688 °C [12].

The selective addition of alloying elements to titanium enables a wide range of physical and mechanical properties to be obtained. Basic effects of a number of alloying elements are as follows [12]:

1. Certain alloying additions, notably aluminum and interstitials (O, N, C), tend to stabilize the alpha phase, i.e., raise the temperature at which the alloy will be transformed completely to the beta phase.
2. Most alloying additions such as chromium, niobium, copper, iron, manganese, molybdenum, tantalum, and vanadium stabilize the beta phase by lowering the temperature of transformation (from alpha to beta).
3. Some elements notably tin and zirconium behave as neutral solutes in titanium and have little effect on the transformation temperature, acting as strengtheners of the alpha phase.

The single-phase and near single-phase alpha alloys of titanium have good weldability. The generally high aluminum content of this group of alloys assures excellent strength characteristics and oxidation resistance at elevated temperatures (in the range of 316–593 °C) [12].

The addition of controlled amounts of beta-stabilizing alloying elements causes some beta phase to persist below the beta transformation temperature, down to room temperature resulting in a two-phase system. Even small amounts of beta stabilizers will stabilize the beta phase at room temperature. A group of alloys designed with high amounts of alpha stabilizers and with a small amount of beta stabilizers are alpha–beta alloys, usually called high alpha or near alpha alloys [6,12].

As larger amounts of beta stabilizers are added, a higher percentage of the beta phase is retained at room temperature. Such two-phase titanium alloys can be significantly strengthened by heat treatment quenching from a temperature high in the alpha–beta range followed by an aging cycle at a somewhat lower temperature [12].

The transformation of the beta phase that would normally occur on slow cooling is suppressed by the quenching. The aging cycle causes the precipitation of fine alpha particles from the metastable beta, imparting a structure that is stronger than the annealed alpha–beta structure.

The high percentage of beta-stabilizing elements in this group of titanium alloys results in a microstructure that

is metastable beta after solution annealing. Extensive strengthening can occur by the precipitation of alpha during aging [12].

## 2. Literature survey

Titanium and its alloys interstitially dissolve a large amount of impurities such as oxygen and nitrogen, which degrade the mechanical and physical properties of alloys. Crucible oxides and refractory oxides based on CaO, ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, etc. can be used for melting titanium and its alloys [13]. Ways of eliminating oxygen from titanium and its alloys are important for use in widespread application. However, the thermodynamic behavior of calcium, magnesium, zirconium, yttrium on the one side, and oxygen on the other, in molten titanium and titanium alloys with aluminum has not been well investigated.

Kubaschewski and Dench [14] and Miyazaki et al. [15] reported the capability of calcium for deoxidizing of titanium is superior to that of magnesium. Ono et al. [16] observed the reduction behavior of titanium oxide with calcium. Okabe et al. [17] reported deoxidation of solid titanium by using calcium–calcium halide fluxes resulting in oxygen contents of 50–70 ppm.

However, few studies on the thermodynamic properties of oxygen in molten titanium have been conducted.

Yahata et al. [18] 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. [19] investigated the removal of oxygen in TiAl powder mixed with CaCl<sub>2</sub> by using Ca–Al vapor at 1373 K. Sakamoto et al. [20] investigated the thermodynamic properties of calcium and oxygen in molten TiAl alloys by melting titanium aluminate in CaO crucible in a vacuum induction furnace, a cold crucible type induction furnace, and an electron beam furnace. Shibata et al. [21] 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. [13] investigated the thermodynamic properties of calcium and oxygen in molten Ti, TiAl and TiAl<sub>3</sub> alloys using calcium-based fluxes. Copland and Jacobson [22] executed the most recent thermodynamic study of Ti–Al–O alloys with the aim to find and determine a possible compressor application in gas-turbine engines. They measured component activities by a special pressure technique designed and fabricated at the NASA Glenn Research Center.

Considering the thermodynamic data for the other constituents of crucible oxides, such as magnesium, zirconium, yttrium and their spinels in molten titanium and titanium alloys, there are not many publications. Work is mainly based on characterizations of the alloy–spinel–corundum equilibrium [23], relationships between oxides CaO–ZrO<sub>2</sub> [24,25], some controversy on the standard Gibbs energy of formation CaO [26,27] and measurements of the specific heat of undercooled TiAl liquid alloys [28]. Also, there are some articles about the thermodynamic description of the Ti–Al based system [29,30], kinetics of phase and structural

Table I  
Activity of Ti and Al in the liquid phase at 1773–2273 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
	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

transformations in some Ti–Al alloys [31,32], thermodynamic or kinetic considerations and modeling for casting titanium alloys with some selected moulds as CaO and ZrO<sub>2</sub> [33–35].

To finish this literature survey, it is also good to mention some articles, which consider the relationship between titanium and oxygen [36–38]. This binary subsystem is very

important from a thermodynamic point of view as well as for the casting of titanium and titanium alloys.

Commercial production of titanium and its alloys started in about 1950s, up to nowadays the very nature of melting titanium and titanium alloys are in a water-cooled furnace using copper crucibles. But the price of copper metal is nowadays very high, which is not so negligible.

Table 2

Solution phases, pure components and special interactions between the components published from FactSage databases at 1873 K and  $X_{Ti} = X_{Al} = 0.5$

T = 1873.00 K

P = 1.00000E+00 atin

V = 0.00000E+00 dm<sup>3</sup>

Stream constituents	Equilibrium amount mole fraction			Amount/mol	Activity
AL <sub>fcc_a1</sub> (s)				5.0000E-01	
Ti <sub>hcp_a3</sub> (s)				5.0000E-01	
Phase: liquid	mol				
Al	5.0000E-01			5.0000E-01	2.9103E-01
Ti	5.0000E-01			5.0000E-01	2.6123E-01
Total:	1.0000E+00			1.0000E+00	1.0000E+00
Phase: Ti3Al	mol			Mole fraction	Activity
Al3Al	0.0000E+00			2.6643E-01	2.7452E-04
Al3Ti	0.0000E+00			1.1243E-02	9.3685E-03
Ti3Al	0.0000E+00			6.9308E-01	1.4287E-01
Ti3Ti	0.0000E+00			2.9248E-02	3.5634E-03
Total:	0.0000E+00			1.0000E+00	6.3566E-01
Phase: TiAl	mol			Mole fraction	Activity
AlAl	0.0000E+00			2.0054E-01	2.1730E-02
AlTi	0.0000E+00			2.4728E-01	5.9524E-01
TiAl	0.0000E+00			2.4728E-01	5.9524E-01
TiTi	0.0000E+00			3.0491E-01	2.8296E-02
Total:	0.0000E+00			1.0000E+00	7.8242E-01
Cp_EQUIL (J K <sup>-1</sup> )	H_EQUIL (J)	S_EQUIL (J K <sup>-1</sup> )	G_EQUIL (J)	V_EQUIL (dm <sup>3</sup> )	
3.89150E+01	3.56813E+04	9.11947E+01	-1.35126E+05	0.00000E+00	
<i>Mole fraction of sublattice constituents in Ti3Al</i>					
Al				2.7767E-01 stoichiometry = 3.0000E+00	
				7.2233E-01	
				9.5951E-01 stoichiometry = 1.0000E+00	
				4.0491E-02	
<i>Magnetic properties for Ti3Al</i>					
Curie temperature = 0.00 K					
Average magnetic moment/atom = 0.0000E+00					
<i>Mole fraction of sublattice constituents in TiAl</i>					
Al				4.4782E-01 stoichiometry = 1.0000E+00	
Ti				5.5218E-01	
				4.4782E-01 stoichiometry = 1.0000E+00	
				5.5218E-01	
<i>Magnetic properties for TiAl</i>					
Curie temperature = 0.00 K					
Average magnetic moment/atom = 0.0000E+00					
			Ti3Al	TiAl	
<i>Mole fraction of system components</i>					
Ti			5.5187E-01	5.5218E-01	
Al			4.4813E-01	4.4782E-01	

Thus the main idea of this paper was to try to use less expensive crucible for melting titanium and titanium alloys and give the answer on a question: can crucible oxides based on  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  be used for melting titanium and its alloys?

Owing of literature data for the crucible oxides stability, as well as these crucibles are cheaper than standard crucibles for melting titanium and titanium alloys, in this paper will be presented the results of predicting thermodynamic

analysis with the aim to determine the crucible oxide stability in contact with molten titanium and titanium–aluminum alloys. The results of the activity–temperature–composition relationship of titanium in Ti–Al were estimated. Also, the stability of crucible oxides in Ti–Al was estimated using the Gibbs free energy data.

This research will try to help shed some light on problems connected with thermodynamics of oxides stability in molten titanium and titanium–aluminum alloys and give

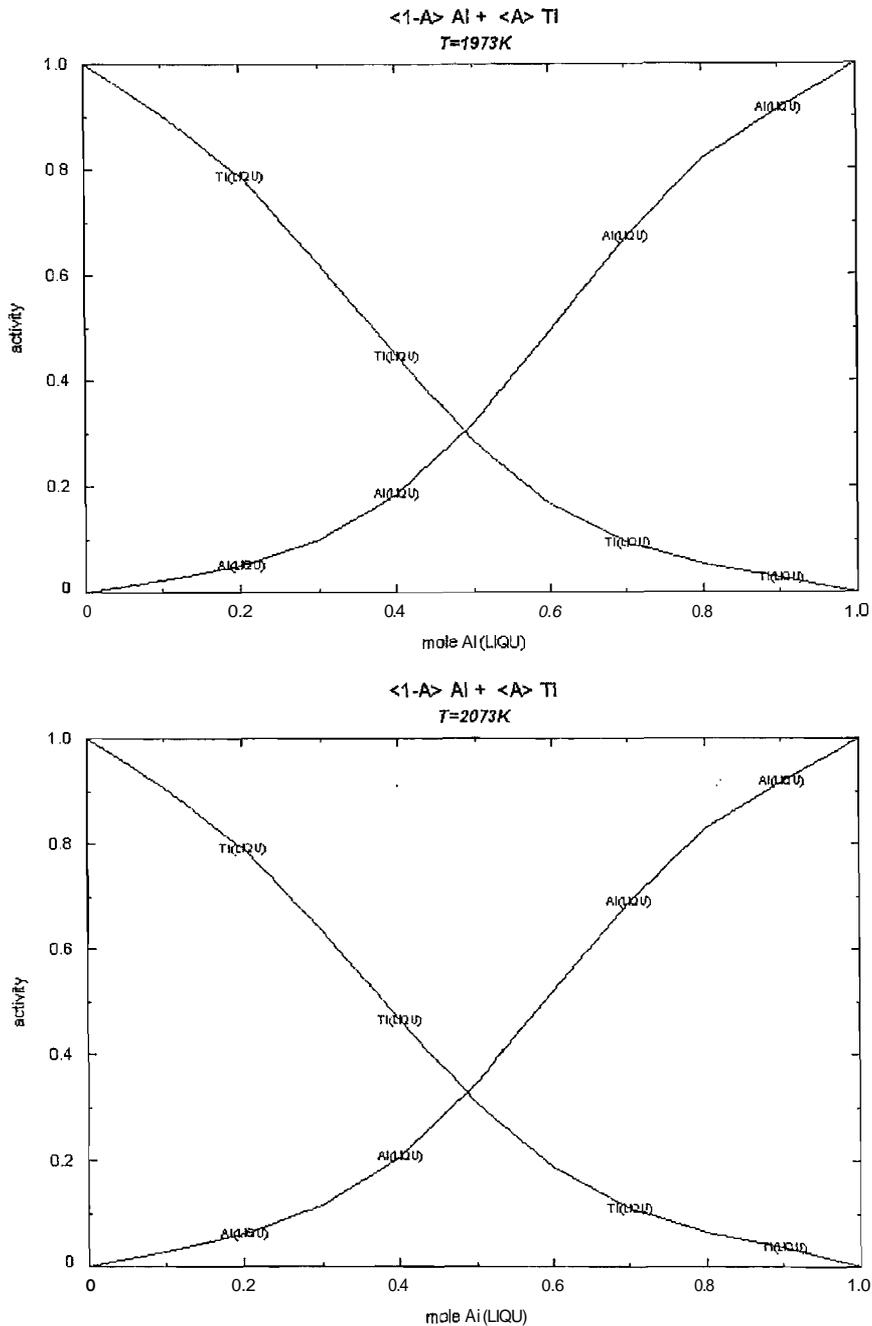


Fig. 1. Ti and Al activity in the liquid phase as function of mole fraction Al at two different temperatures of 1973 and 2073 K.

the answer can crucible oxides be used for melting titanium and its alloys.

### 3. Results and discussion

#### 3.1. Chemical activity of Ti and Al in Ti-Al

The activity of titanium and aluminum in titanium–aluminum alloys is calculated using the FactSage thermochemical software and databases [39]. The activity of Ti and Al as a function of titanium concentration is calculated in the temperature range between 1273 and 2273 K.

Activities of components in the liquid phase are shown in Table 1 and some results of solution phases, pure components and special interactions between the components published from FactSage databases at 1873 K are given in Table 2. The activity–composition diagrams for Ti and Al at 1973 and 2073 K done in FactSage program are shown in Fig. 1.

The obtained results show that the activity coefficient of both components is less than unity and the activity of both titanium and aluminum increase 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, especially oxides, in Ti–Al we need to know the activity of Ti and Al as a function of temperature. The activity–temperature relationship can be expressed as:

$$\ln a_{Ti} = A + B/T \quad (1)$$

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 at 1873 K can be approximated as follows:

$$\ln a_{Ti} = -4.5623 + 6.8302x_{Ti} + 0.7783x_{Ti}^2 - 3.1887x_{Ti}^3 \quad (2)$$

The activity–temperature ( $0.1 < X_{Ti} < 1.0$ ) relationships for Ti–Al alloys for a temperature ranges between 1273 and 2273 K are calculated. Table 3 shows the estimated coefficients for the activity–temperature ( $0.1 < X_{Ti} < 1.0$ ) relationships for Ti in Ti–Al alloys for a temperature range between 1273 and 2273 K. Thus, as a first approximation the activity–temperature relationship of Ti in Ti–Al (Eq. (1)) has been formulated.

Table 3  
Activity–temperature relationship for Ti–Al alloys.  $\ln a_{Ti} = A + B(T/K)^{-1}$

$X_{Ti}$	A	B	Temperature, K
0.1	-10.628	0.0035	1273–2273
0.2	-8.7233	0.0029	1273–2273
0.3	-6.8101	0.0022	1273–2273
0.4	-4.9683	0.0016	1273–2273
0.5	-3.3327	0.0010	1273–2273
0.6	-2.0067	0.0006	1273–2273
0.7	-1.0433	0.0003	1273–2273
0.8	-0.4391	0.0001	1273–2273
0.9	-0.1319	0.00002	1273–2273

Activity–Temperature–Composition Relationship  
for Ti in Ti–Al

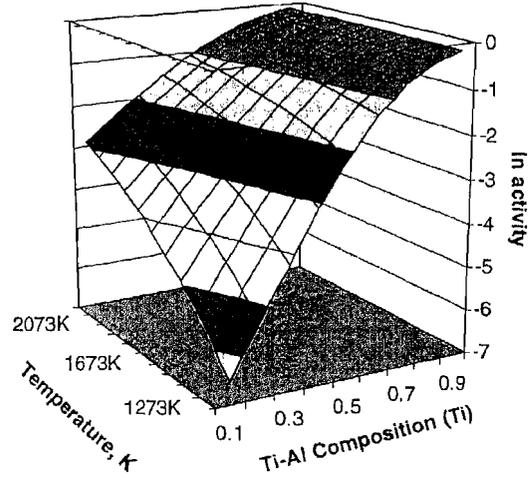


Fig. 2. Activity–temperature–composition relationship for Ti in Ti–Al.

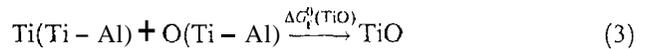
The activity–temperature relationship is shown in Fig. 2. The activity–temperature relationship shows that Ti activity decreases with decreasing Ti inole fraction and with decreasing temperature.

#### 3.2. Thermodynamics of dissolved solutes in Ti–Al

The compatibility of ceramics with Ti–Al will depend on their thermodynamic stability ( $\Delta G_r$ , free energy of reaction) as a function of temperature, titanium concentration, and non-metal solute concentration. To evaluate  $\Delta G_r$ , the activity of the solutes, e.g. oxygen, carbon, etc., has to be known, which depend on the standard free energy of formation,  $\Delta G_f^0$ , of the corresponding Ti-compounds (oxides, carbides, etc). We show here the results of thermodynamics of dissolved solutes (oxygen) as a function of temperature and composition.

The activity relationships for oxygen in Ti–Al can be calculated using equilibrium conditions of saturated solutions. We selected three titanium oxides that may occur in reactions between molten Ti–Al alloys and crucible oxides. Those are TiO, Ti<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>.

Hereafter we give the representative equations for TiO, with similar expressions holding true for the other two oxides considered (TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub>):



where,  $\Delta G_f^0$  is evaluated at temperature *T* as:

$$\Delta G_f^0(TiO) = RT \ln K_e = RT \ln(a_{TiO}/(a_{Ti} \cdot a_O)) \quad (4)$$

where, *R* is the gas constant, *a<sub>i</sub>* is chemical activity of specie *i* and *K<sub>e</sub>* is the equilibrium constant. The activity of TiO is unity, thus Eq. (4) can be solved for the activity of the oxygen:

$$\ln a_O = -\Delta G_f^0(TiO)/RT - \ln a_{Ti} \quad (5)$$

Table 4  
Standard free energy of formation  $\Delta G_f^\theta$  of three Ti-oxides (TiO, Ti<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>)

T, K	TiO	Ti <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
<i>AG of Formation (kJ/mol)</i>			
273	-515.7715	-1441.219	-894.1528
373	-505.9299	-1412.0601	-875.639
473	-496.1496	-1383.2392	-857.2188
573	-486.4601	-1355.2655	-839.0257
673	-476.8721	-1327.8239	-820.9671
773	-467.3919	-1300.8668	-803.0587
873	-458.0209	-1274.3395	-785.2815
973	-448.7561	-1248.1854	-767.6142
1073	-439.5896	-1222.3457	-750.0328
1173	-430.4838	-1196.709	-732.4861
1273	-421.1779	-1170.6691	-714.6749
1373	-412.3048	-1144.9072	-696.9428
1473	-403.556	-1119.3939	-679.278
1573	-394.9282	-1094.1016	-661.6691
1673	-386.4172	-1069.0039	-644.1052
1773	-378.019	-1044.0761	-626.5756
1873	-369.7289	-1019.2943	-609.0702
1973	-361.2915	-994.134	-591.3283
2073		-968.0443	-573.0759

The standard energy of formation of the oxides, TiO, Ti<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are calculated by use of the FactSage thermochemical software and databases [39]. Table 4 lists the energy of formation of the oxides with Table 5 giving the corresponding polynomials.

Table 5  
Polynomial expressions for the standard free energy of formation of Ti-oxides as a function of temperature

Oxides	$\Delta G_f^\theta$	T, K
TiO	$-542.95 + 0.1005T - 3 \times 10^{-6}T^2 - 6 \times 10^{-10}T^3$	273–1973
Ti <sub>2</sub> O <sub>3</sub>	$-1523.1 + 0.3099T - 3 \times 10^{-5}T^2 + 7 \times 10^{-9}T^3$	273–2073
TiO <sub>2</sub>	$-945.42 + 0.1908T - 1 \times 10^{-5}T^2 + 3 \times 10^{-9}T^3$	273–2073

The chemical activity for Ti and O in chosen titanium oxides saturated in Ti–Al in the temperature range from 1273 to 1973 K is already known and modeled in [40].

It has been noticed that the stability of titanium oxides indicated by their large negative formation energy and the activity of oxygen is positive for all values of  $x_{Ti}$  and at all investigated temperatures, which indicated that TiO, Ti<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> is unstable and will be dissolved in Ti–Al liquid.

### 3.3. Thermodynamics of the interactions of ceramics with Ti–Al

We selected six crucible oxides that can be used for melting Ti–Al alloys. Those are: CaO, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>.

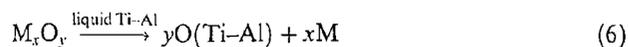
The standard energy of formation of the chosen oxides are calculated by the use of FactSage thermochemical software and databases [39]. Table 6 lists the energy of

Table 6  
Standard free energy of formation  $\Delta G_f^\theta$  of chosen oxides-based ceramics

T, K	CaO	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
<i><math>\Delta G_f^\theta</math>, kJ/mol</i>						
273	-606.0556	-1827.6897	-1044.6254	-571.9478	-1590.1565	-860.8997
373	-595.4404	-1796.5811	-1025.2999	-561.1165	-1558.7587	-842.6393
473	-584.9263	-1766.3701	-1006.1337	-550.2929	-1527.2389	-824.3661
573	-574.5173	-1736.8062	-987.1631	-539.5187	-1495.7968	-806.177
673	-564.1869	-1707.7252	-968.3777	-528.7972	-1464.4887	-788.1162
773	-553.833	-1679.0132	-949.7573	-518.1198	-1433.3168	-770.2165
873	-543.4537	-1650.7049	-931.2801	-507.4747	-1402.2613	-752.5249
973	-533.073	-1622.5472	-912.9263	-496.3872	-1370.3872	-735.0039
1073	-522.6631	-1594.5112	-894.6777	-484.8361	-1337.217	-717.5666
1173	-511.769	-1566.573	-876.3863	-473.2813	-1304.1435	-700.2656
1273	-500.5582	-1538.7129	-857.9828	-461.7257	-1271.1669	-683.1612
1373	-489.3586	-1510.9584	-839.6856	-449.6754	-1238.2865	-666.1254
1473	-478.17	-1483.3201	-821.486	-428.8295	-1205.5006	-649.1513
1573	-466.992	-1455.7281	-803.7321	-408.0792	-1172.8069	-632.2323
1673	-455.8244	-1428.1674	-786.0556	-387.4196	-1140.2028	-615.3625
1773	-444.6666	-1400.5057	-768.4168	-366.846	-1107.6856	-595.9221
1873	-425.3951	-1371.4681	-750.8074	-346.3542	-1075.2523	-576.1819
1973	-405.9763	-1342.0818	-733.2193	-325.9402	-1042.9	-556.4927
2073	-386.6372	-1312.6736	-715.6446	-305.6005	-1010.6257	
2173	-367.3735	-1283.243	-697.6004	-285.3318	-978.4268	
2273	-348.1809	-1253.7894	-679.0228	-265.1311	-946.3003	
2373	-329.0555	-1224.3123	-660.42	-244.9955		
2473	-309.9936	-1194.8113	-641.7921	-224.9223		
2573	-290.9913	-1165.286	-623.1392	-204.9091		
2673	-272.0451	-1135.7363	-604.622	-184.9535		
2773	-253.1511	-1106.1618	-586.3217	-165.0533		
2873		-1076.5623	-567.9969	-145.2065		
2973		-1046.9377		-125.4111		
3073		-1017.288		-105.6652		

formation of the oxides with Table 7 giving the corresponding polynomials.

The reduction reaction of an oxide ceramic ( $M_xO_y$ ) in Ti–Al can be expressed by the following equation:



and the associated free energy of change of the reaction is expressed as:

$$\Delta G_r = 1/x \cdot \{yG_O(\text{Ti-Al}) - \Delta G_f^0(M_xO_y)\} \quad (7)$$

Table 7

Polynomial expressions for the standard free energy of formation of chosen oxides as a function of temperature

Oxides	$\Delta G_f^0$	T, K
CaO	$-629.57 + 0.0959T - 6 \times 10^{-6}T^2 + 8 \times 10^{-9}T^3$	273–2773
$Y_2O_3$	$-1906.7 + 0.3021T - 1 \times 10^{-5}T^2 + 4 \times 10^{-9}T^3$	273–3073
$ZrO_2$	$-1099.3 + 0.2031T - 1 \times 10^{-5}T^2 + 3 \times 10^{-9}T^3$	273–2873
MgO	$-570.73 + 0.0027T + 8 \times 10^{-5}T^2 - 1 \times 10^{-8}T^3$	273–3073
$Al_2O_3$	$-1670.4 + 0.2904T + 3 \times 10^{-5}T^2 - 6 \times 10^{-9}T^3$	273–2273
$SiO_2$	$-917.37 + 0.213T - 4 \times 10^{-5}T^2 + 1 \times 10^{-8}T^3$	273–1973

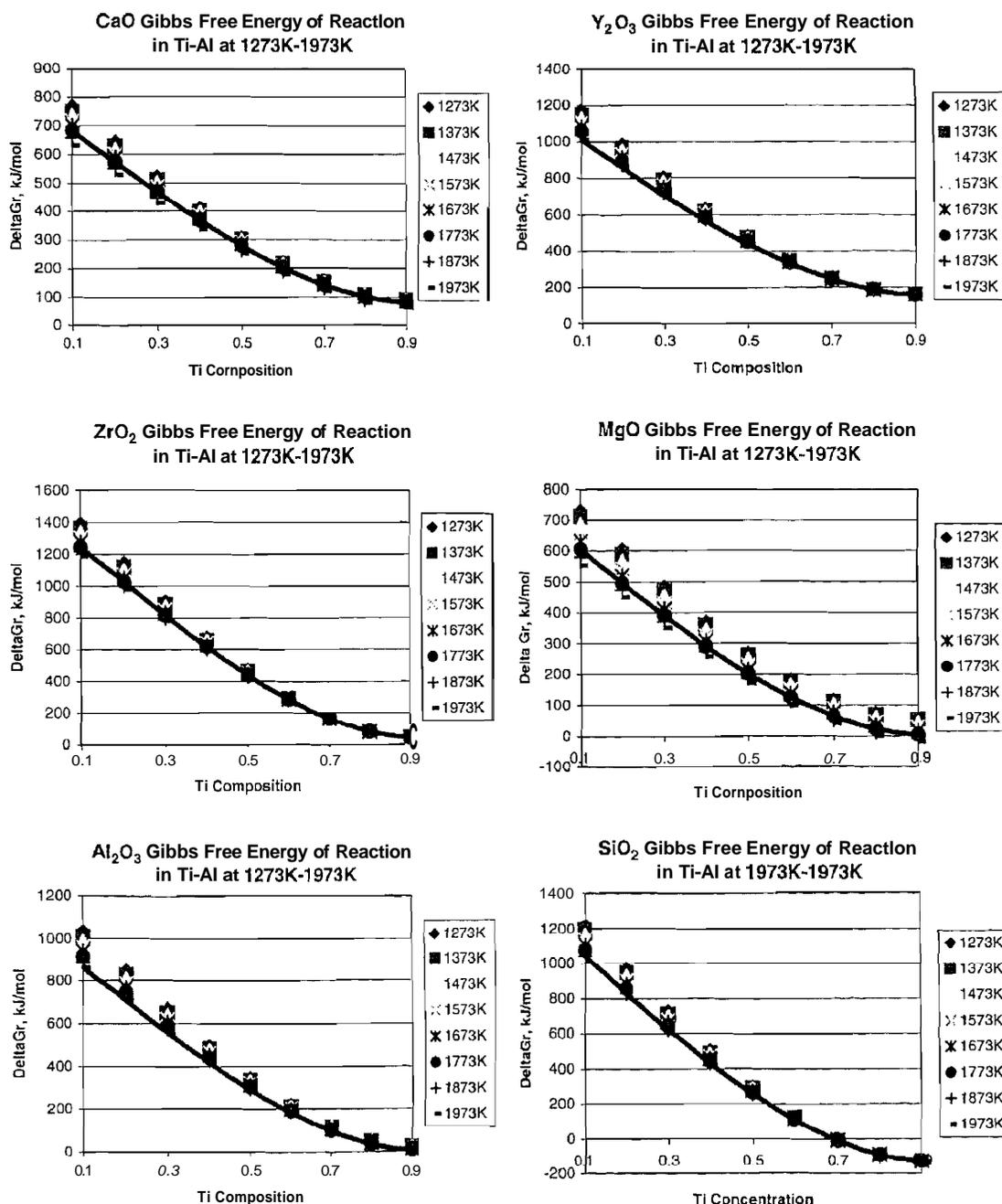


Fig. 3. Free energy changes of reactions of chosen oxides in Ti–Al at 1273–1973 K.

where  $G_O(\text{Ti-Al})$  is the solute free energy in Ti-Al, in this case of oxygen. Eq. (7) represents a relative equilibrium state between the oxygen solute free energy and the Gibbs free energy of the metal oxide formation, which by definition is the thermodynamic driving force  $AG_r$ . For a smaller  $AG_r$ , relative to  $G_O(\text{Ti-Al})$  the oxide is more stable than the oxygen in solution with Ti-Al. This would indicate that the ceramic would be thermodynamically compatible with Ti-Al. In order to evaluate Eq. (7) for the oxides, the Gibbs free energy of formation and the free energy of the associated solutes need to be known. The calculations of the formation energies are shown above, but the solute free energies have to be evaluated using solubility data:

$$\begin{aligned} G_O(\text{Ti-Al}) &= RT \ln a_O = RT \ln a_O^* + RT \ln(x_O/x_O^*) \\ &= \Delta G_f^0(\text{TiO}) - G_{\text{Ti}}(\text{Ti}) + RT \ln(x_O/x_O^*) \end{aligned} \quad (8)$$

where  $a_O^*$  is the oxygen activity at saturation,  $x_O$  is the oxygen concentration,  $x_O^*$  is the oxygen concentration at saturation and  $G_{\text{Ti}} (=RT \ln a_{\text{Ti}})$  is the partial free energy of dissolved titanium. In view of lack of any experimental solubility data it is reasonable to assume some approximations, and a simplified expression can be derived for the solute free energies:

$$G_O(\text{Ti-Al}) = \Delta G_f^0(\text{TiO}) - G_{\text{Ti}}(\text{Ti}) \cdot 0.01 \quad (9)$$

Using Eqs. (7) and (9) the free energy change of reaction for oxide ceramic materials can be evaluated by

$$AG_r = 1/x \cdot \{y[\Delta G_f^0(\text{TiO}) - G_{\text{Ti}}(\text{Ti-Al}) \cdot 0.01] - \Delta G_f^0(\text{M}_x\text{O}_y)\} \quad (10)$$

According to equations given and to the calculated values, the free energy changes of reaction  $\Delta G_r$  of the oxides listed in Table 6 can be calculated. The equations are follow:

$$AG_r = \Delta G_f^0(\text{TiO}) - RT \ln a_{\text{Ti}} \cdot 0.01 - \Delta G_f^0(\text{MO}) \quad (11)$$

$$\Delta G_r = 1/2 \cdot \{3[\Delta G_f^0(\text{TiO}) - RT \ln a_{\text{Ti}} \cdot 0.01] - \Delta G_f^0(\text{M}_2\text{O}_3)\} \quad (12)$$

$$AG_r = \{2[\Delta G_f^0(\text{TiO}) - RT \ln a_{\text{Ti}} \cdot 0.01] - \Delta G_f^0(\text{MO}_2)\} \quad (13)$$

Fig. 3 shows the free energy changes of reaction of oxides listed in Table 6 at temperatures 1273–1973 K. Based on these estimates, all of the selected oxides are stable in liquid Ti-Al at temperature range 1273–1973 K, except for  $\text{SiO}_2$ .

$\text{SiO}_2$  has a negative  $AG_r$  value in liquid Ti-Al at 1273–1973 K for compositions of Ti-Al equal  $X_{\text{Ti}} = 0.7-1$ , which indicates that this oxide is not compatible with Ti-Al. This oxide is thus stable up to 70 mass% Ti and for higher titanium content  $\text{SiO}_2$  would not be stable.

$\text{MgO}$  has a negative  $AG_r$  value in liquid Ti-Al at 1873 K and 1973 K for titanium compositions up  $X_{\text{Ti}} = 0.8$ , which indicates that this oxide will dissolve at these temperatures.

$\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  have positive  $AG_r$  values in Ti-Al in the temperature range 1273–1973 K for all compositions of Ti-Al, which indicates that these oxides do not dissolve. They are compatible with Ti-Al and can be used as materials for crucibles.

The activity–temperature ( $0.1 < X_{\text{Ti}} < 0.9$ ) relationships for selected crucible oxides in the temperature range between 1273 and 1973 K are shown in Table 8.

#### 3.4. Compatibility of ceramic materials with Ti-Al

The thermodynamic stability of ceramic materials was investigated based on the free energy changes of reactions between various oxides. Table 9 summarizes the free energy change of reactions for selected ceramics and Fig. 4 shows a bar-chart representation of their relative stability at 1873 K and the composition  $\text{Ti-Al}_{0.4}$ .

Table 8  
Activity–temperature relationship for free energy changes of reactions of some crucible oxides

$X_{\text{Ti}}$	CaO	$\text{Y}_2\text{O}_3$	$\text{ZrO}_2$
$\Delta G_r, \text{kJ/mol}$			
0.1	$\Delta G_r = 1011.5 - 0.1879 \cdot T$	$AG_r = 1460.5 - 0.2264 \cdot T$	$AG_r = 1767.7 - 0.2933 \cdot T$
0.2	$AG_r = 845.63 - 0.1562 \cdot T$	$AG_r = 1211.6 - 0.1789 \cdot T$	$AG_r = 1435.9 - 0.2299 \cdot T$
0.3	$AG_r = 684.78 - 0.1253 \cdot T$	$AG_r = 970.38 - 0.1325 \cdot T$	$\Delta G_r = 1114.2 - 0.1682 \cdot T$
0.4	$AG_r = 534.75 - 0.0967 \cdot T$	$AG_r = 745.33 - 0.0896 \cdot T$	$\Delta G_r = 814.13 - 0.111 \cdot T$
0.5	$AG_r = 401.3 - 0.0719 \cdot T$	$AG_r = 545.15 - 0.0524 \cdot T$	$AG_r = 547.23 - 0.0613 \cdot T$
0.6	$AG_r = 290.18 - 0.0523 \cdot T$	$AG_r = 378.47 - 0.0231 \cdot T$	$AG_r = 324.99 - 0.0222 \cdot T$
0.7	$AG_r = 207.15 - 0.0395 \cdot T$	$AG_r = 253.94 - 0.0039 \cdot T$	$AG_r = 158.94 + 0.0034 \cdot T$
0.8	$AG_r = 157.99 - 0.035 \cdot T$	$AG_r = 180.18 + 0.0029 \cdot T$	$AG_r = 60.604 + 0.0125 \cdot T$
0.9	$AG_r = 148.43 - 0.0401 \cdot T$	$AG_r = 165.85 - 0.0048 \cdot T$	$AG_r = 41.496 + 0.0022 \cdot T$
	MgO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$
0.1	$AG_r = 1062.1 - 0.257 \cdot T$	$AG_r = 1355.8 - 0.2496 \cdot T$	$AG_r = 1597.9 - 0.2955 \cdot T$
0.2	$AG_r = 896.21 - 0.2253 \cdot T$	$AG_r = 1106.9 - 0.202 \cdot T$	$AG_r = 1266.1 - 0.2321 \cdot T$
0.3	$\Delta G_r = 735.36 - 0.1944 \cdot T$	$AG_r = 865.66 - 0.1557 \cdot T$	$\Delta G_r = 944.39 - 0.1703 \cdot T$
0.4	$AG_r = 585.33 - 0.1658 \cdot T$	$\Delta G_r = 640.61 - 0.1128 \cdot T$	$\Delta G_r = 644.33 - 0.1131 \cdot T$
0.5	$\Delta G_r = 451.88 - 0.141 \cdot T$	$AG_r = 440.43 - 0.0756 \cdot T$	$AG_r = 377.42 - 0.0635 \cdot T$
0.6	$AG_r = 340.76 - 0.1214 \cdot T$	$AG_r = 273.75 - 0.0463 \cdot T$	$AG_r = 155.19 - 0.0244 \cdot T$
0.7	$AG_r = 254.74 - 0.1086 \cdot T$	$AG_r = 149.22 - 0.0271 \cdot T$	$AG_r = -10.861 + 0.0012 \cdot T$
0.8	$AG_r = 208.57 - 0.104 \cdot T$	$AG_r = 75.464 - 0.0202 \cdot T$	$AG_r = -109.2 + 0.0103 \cdot T$
0.9	$AG_r = 199.01 - 0.1092 \cdot T$	$AG_r = 61.134 - 0.028 \cdot T$	$\Delta G_r = -128.31 - 1 \cdot 10^{-5} \cdot T$

**Table 9**  
Calculated stability of ceramics in Ti–Al<sub>0.4</sub> at 1873 K (listed in order of descending stability)

Oxides	AG <sub>r</sub> , kJ/mol
Y <sub>2</sub> O <sub>3</sub>	335.204
ZrO <sub>2</sub>	283.409
CaO	192.222
Al <sub>2</sub> O <sub>3</sub>	187.030
MgO	113.378
SiO <sub>2</sub>	109.489

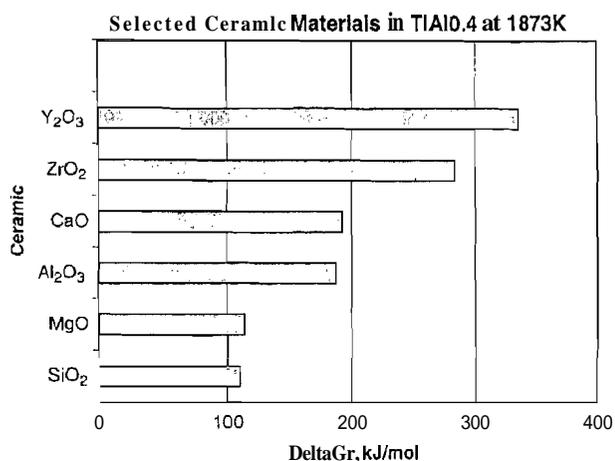


Fig. 4. Estimated AG, of selected ceramics in Ti–Al<sub>0.4</sub> at 1873 K.

Based on this thermodynamic analysis the most stable ceramics are Y<sub>2</sub>O<sub>3</sub>, followed by ZrO<sub>2</sub>, and then the CaO.

According to modeled and calculated values, we can suggest follows positive value of  $\Delta G_r$ , which leads to stable crucibles:

- for titanium alloys to 10 mass% of aluminum, the  $\Delta G_r$  is approximately 50 kJ/mol.
- for titanium alloys to 20 mass% of aluminum, the AG, is approximately 100 kJ/mol.
- for titanium alloys to 30 mass% of aluminum, the AG, is approximately 150 kJ/mol.
- for titanium alloys to 40 mass% of aluminum, the AG, is approximately 200 kJ/mol.
- for titanium alloys to 50 mass% of aluminum, the AG, is approximately 250 kJ/mol.
- for titanium alloys more than 50 mass% of aluminum, the AG, is approximately 300 kJ/mol.

Although it will be depend of composition of an alloy and activity–temperature relationship for free energy change of reactions for selected ceramics (equations given in Table 8).

#### 4. Conclusions

The results of predicting thermodynamic analysis was shown that the crucible oxide stability in contact with

molteii titanium and titanium–aluminum alloys depend of temperature and compositions of alloys. The crucible oxides Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CaO and Al<sub>2</sub>O<sub>3</sub> can be successfully used for melting titanium and its alloys, while MgO and SiO<sub>2</sub> can be used only for some alloys, but not for titanium.

If we know compositions of an alloy and according to the activity–temperature relationship for free energy change of reactions for selected ceramics, we can very easily calculate which crucible oxides will be suitable for melting the alloy.

#### Acknowledgement

First author would like to thank the Alexander von Humboldt Foundation for the supporting and funding granted to this research work.

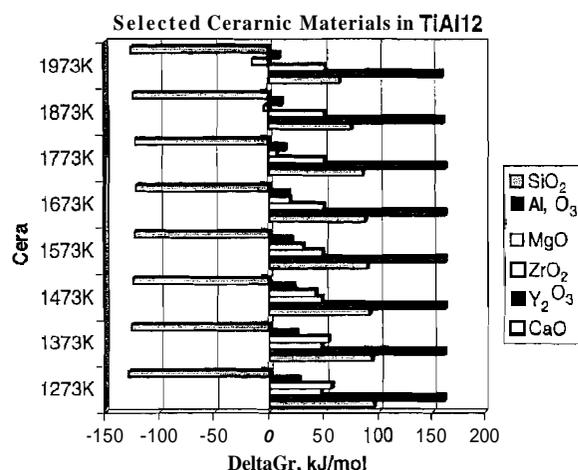


Fig. A.1. Estimated AG, of selected ceramics in TiAl12 alloy.

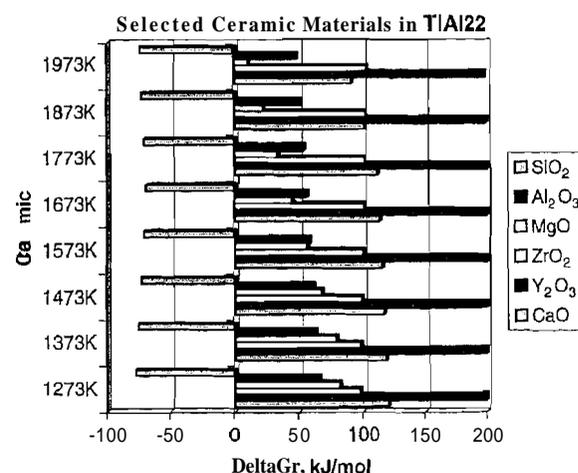


Fig. A.2. Estimated AG, of selected ceramics in TiAl22 alloy

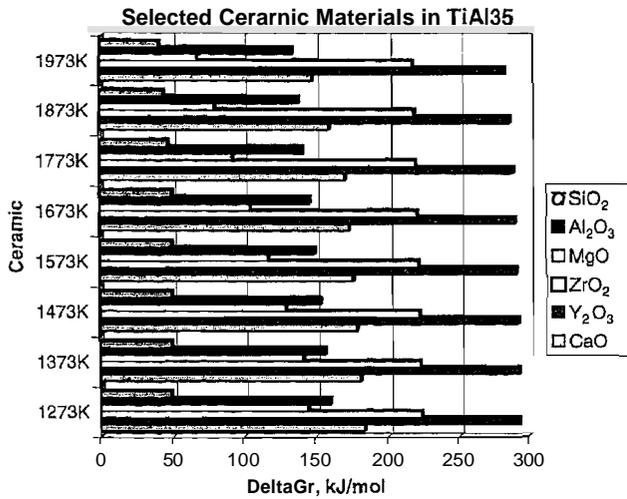


Fig. A.3. Estimated AG, of selected ceramics in TiAl35 alloy.

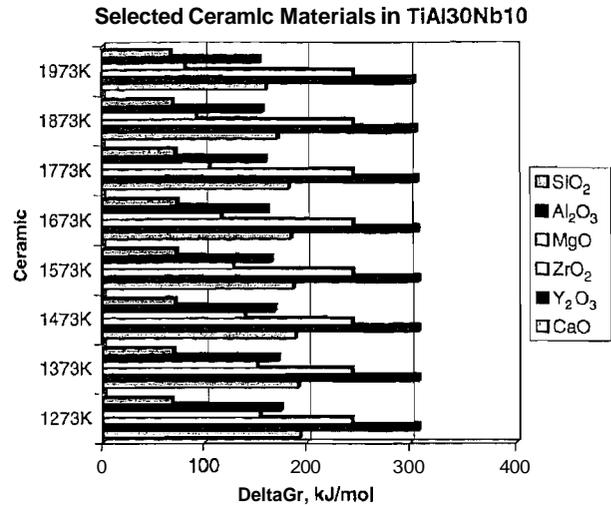


Fig. A.6. Estimated AG, of selected ceramics in TiAl30Nb10 alloy.

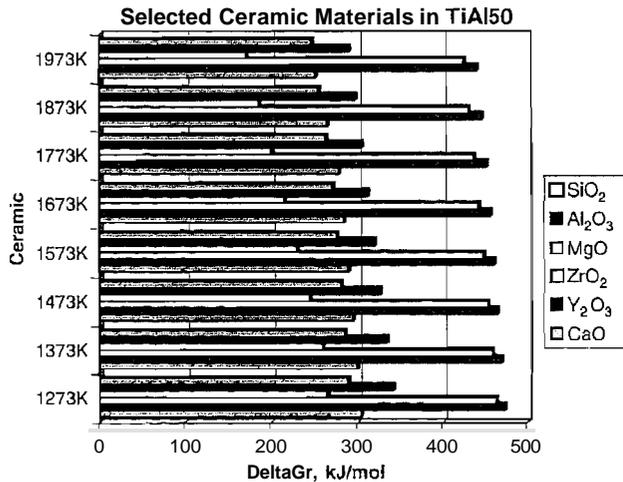


Fig. A.4. Estimated AG, of selected ceramics in TiAl50 alloy.

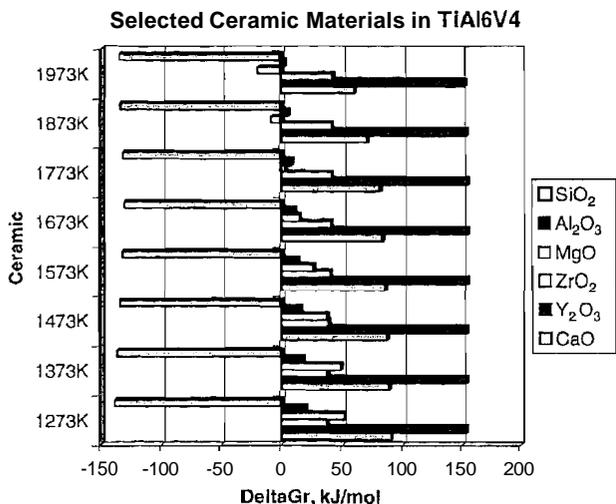


Fig. A.5. Estimated AG, of selected ceramics in TiAl6V4 alloy.

## Appendix A

Hereafter we give you a bar-chart representation of selected ceramics relative stability for some commercial Ti–Al alloy at temperature range 1273–1973 K calculated in this paper (see Figs. A.1–A.6).

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