

SELECTION OF CRUCIBLE OXIDES IN MOLTEN TITANIUM AND TITANIUM ALUMINUM ALLOYS BY THERMO-CHEMISTRY CALCULATIONS

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Abstract

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. On the other hand crucible oxides based on CaO, ZrO₂, Y₂O₃, etc., and their spinels (combination of two or more oxides) 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 of 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 selection of thermo-chemistry analysis with the aim to determine the crucible oxide stability in contact with molten titanium and titanium-aluminum alloys.

Keywords: thermo-chemistry calculations, crucible oxides, titanium, titanium-aluminum alloys, thermodynamic stability

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1. Introduction

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. On the other hand, 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 [1]. But the price of copper metal at LME on 25.10.2005 is 4079 US\$/mt, which is not so negligible.

Thus the main idea 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 CaO, MgO, ZrO₂, Y₂O₃, Al₂O₃, SiO₂, and their spinels be used for melting titanium and its alloys?

Kubaschewski and Dench [2] and Miyazaki *et al.* [3] reported the capability of calcium for deoxidizing of titanium is superior to that of magnesium. Ono *et al.* [4] observed the reduction behavior of titanium oxide with calcium. Okabe *et al.* [5] reported deoxidation of solid titanium by using calcium-calcium halide fluxes resulting in oxygen contents of 50 to 70 ppm.

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

Yahata *et al.* [6] 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.* [7] investigated the removal of oxygen in TiAl powder mixed with CaCl₂ by using Ca-Al vapor at 1373 K. Sakamoto *et al.* [8] 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.* [9] studied the thermodynamic properties of calcium and oxygen in TiAl at 1843K melted in a cold crucible type of induction furnace. Tsukihashi *et al.* [10] investigated the thermodynamic properties of calcium and oxygen in molten Ti, TiAl and TiAl₃ alloys using calcium-based fluxes. Copland and Jacobson [11] 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 [12], relationships between oxides CaO-ZrO₂ [13, 14], some controversy on the standard Gibbs energy of formation CaO [15, 16] and measurements of the specific heat of undercooled TiAl liquid alloys [17]. Also, there are some articles about the thermodynamic description of the Ti-Al based system [18,19], kinetics of phase and structural transformations in some Ti-Al alloys [20,21], thermodynamic or kinetic considerations and modeling for casting titanium alloys with some selected mould as CaO and ZrO₂ [22-24].

To finish this literature survey, it is also good to mention some articles, which consider the relationship between titanium and oxygen [25-27]. This binary subsystem is very important from a thermodynamic point of view as well as for the casting of titanium and titanium 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 selection thermo-chemistry analysis with the aim to determine the crucible oxide stability in contact with molten titanium and titanium-aluminum alloys. This paper will try to help shed some light on problems connected with thermodynamics of oxides stability in molten titanium and titanium alloys.

2. Results and discussion

Thermo-chemistry analysis and calculating is done for titanium-aluminum alloys system as the base system of titanium alloys.

The activity of titanium and aluminum in Ti-Al alloys is calculated using the FactSage thermochemical software and databases [28]. The activity of Ti and Al as a function of titanium concentration is calculated in the temperature range between 1273 K and 2273 K. The results in the liquid phase 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 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:

$$\ln a_{Ti} = A + B/T \tag{1}$$

The coefficients A and B need to be determined.

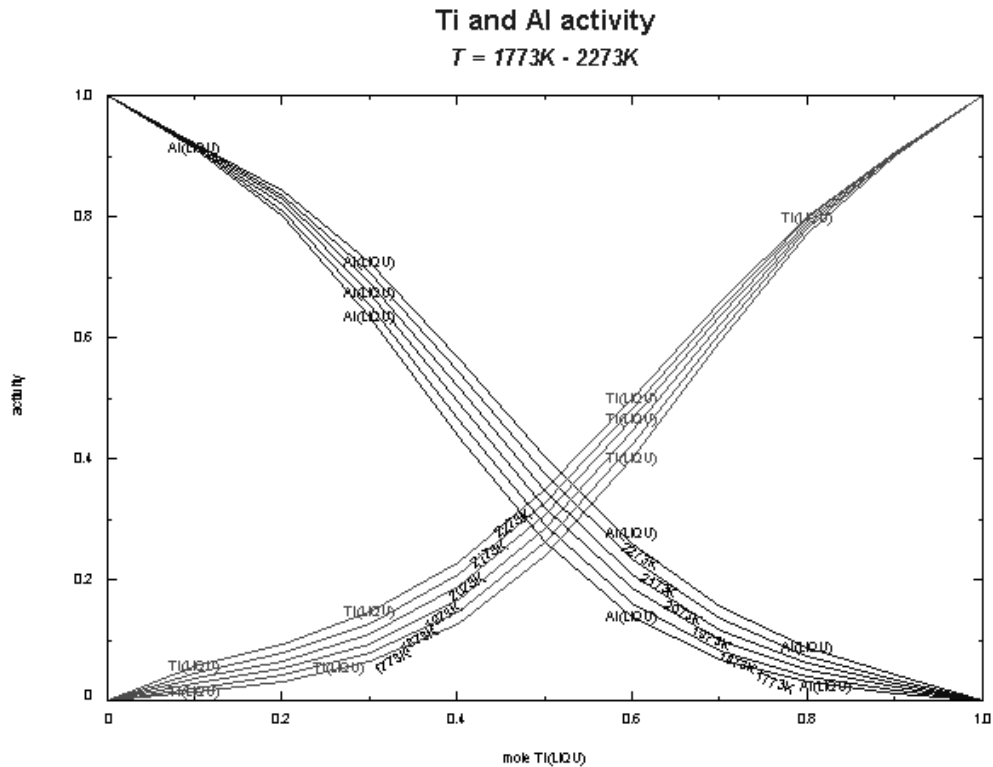


Fig.1. Ti and Al activity in the liquid phase as function of mole fraction Ti at temperature range 1773K - 2273K

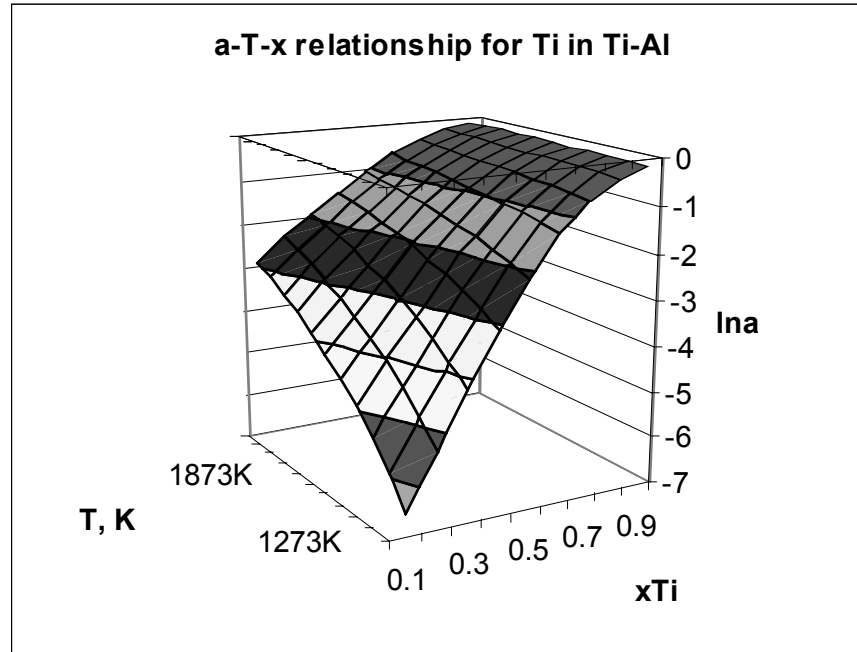


Fig.2. Activity-temperature-composition relationship for Ti in Ti-Al

Based on the activity data and thermo-chemistry calculating by FactSage, the activity-temperature relationship in Ti-Al alloys for titanium composition is shown in Fig.2. This activity-temperature-composition relationship is used for further thermo-chemistry calculations and analysis.

The compatibility of ceramics with Ti-Al will depend on their thermodynamic stability (ΔG_r , free energy of reaction) as a function of temperature, titanium concentration, and oxygen concentration. To evaluate ΔG_r , the activity of oxygen has to be known, which depends on the standard free energy of formation, ΔG_f^θ , of the corresponding oxides. So the next step in our thermo-chemistry analysis was the selection of oxides.

We selected:

- three titanium oxides that may occur in reactions between molten Ti-Al alloys and crucible oxides, in which titanium exists in three different valences: +2, +3 and +4: TiO, Ti₂O₃ and TiO₂;

- six crucible oxides that can be used for melting Ti-Al alloys: CaO, Y₂O₃, ZrO₂, MgO, Al₂O₃ and SiO₂; and
- a few crucible oxides combinations (oxide spinels) that can be used for melting Ti-Al alloys: CaOAl₂O₃, CaO₆Al₂O₃, CaOSiO₂, Al₂O₃SiO₂, Al₂O₃MgO, SiO₂MgO, ZrO₂CaO, ZrO₂SiO₂, Al₂O₃SiO₂CaO and Al₂O₃SiO₂2CaO.

The standard energy of formation of the selected oxides is calculated by use of the FactSage thermochemical software and databases. Table 1 lists the energy of formation of the oxides given in the polynomial expressions as a function of temperatures.

It can be noticed from Table 1 that standard free energy of formation of chosen combination oxides-based ceramics is very low, which indicate those crucible materials are not very stable for titanium and titanium alloys melting. Because of that, we choose only three crucible oxides combination for further calculating and predict thermodynamics of interactions of those oxides with Ti-Al alloys. Those chosen oxides are: CaOAl₂O₃, CaO₆Al₂O₃ and Al₂O₃SiO₂2CaO.

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:

$$\Delta G_r = 1/x \cdot \{yG_O(\text{Ti-Al}) - \Delta G_f^0(M_xO_y)\} \quad (3)$$

where $G_O(\text{Ti-Al})$ is the solute free energy in Ti-Al, in this case of oxygen. Equation (3) 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 ΔG_r . For a smaller ΔG_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.

Table 1. Polynomial expressions for the standard free energy of formation of the selected oxides as a function of temperature

Oxides	ΔG_f^0	T, K
TiO	$-542.95 + 0.1005T - 3 \cdot 10^{-6} T^2 - 6 \cdot 10^{-10} T^3$	273-1973
Ti ₂ O ₃	$-1523.1 + 0.3099T - 3 \cdot 10^{-5} T^2 + 7 \cdot 10^{-9} T^3$	273-2073
TiO ₂	$-945.42 + 0.1908T - 1 \cdot 10^{-5} T^2 + 3 \cdot 10^{-9} T^3$	273-2073
CaO	$-629.57 + 0.0959T - 6 \cdot 10^{-6} T^2 + 8 \cdot 10^{-9} T^3$	273-2773
Y ₂ O ₃	$-1906.7 + 0.3021T - 1 \cdot 10^{-5} T^2 + 4 \cdot 10^{-9} T^3$	273-3073
ZrO ₂	$-1099.3 + 0.2031T - 1 \cdot 10^{-5} T^2 + 3 \cdot 10^{-9} T^3$	273-2873
MgO	$-570.73 + 0.0027T + 8 \cdot 10^{-5} T^2 - 1 \cdot 10^{-8} T^3$	273-3073
Al ₂ O ₃	$-1670.4 + 0.2904T + 3 \cdot 10^{-5} T^2 - 6 \cdot 10^{-9} T^3$	273-2273
SiO ₂	$-917.37 + 0.213T - 4 \cdot 10^{-5} T^2 + 1 \cdot 10^{-8} T^3$	273-1973
CaOAl ₂ O ₃	$-12.747 - 0.0305T + 7 \cdot 10^{-6} T^2 - 1 \cdot 10^{-9} T^3$	273-1873
CaOSiO ₂	$-87.998 - 0.0056T + 8 \cdot 10^{-6} T^2 - 2 \cdot 10^{-9} T^3$	273-2073
Al ₂ O ₃ SiO ₂	$-9.1506 + 0.0101T - 5 \cdot 10^{-6} T^2 + 1 \cdot 10^{-9} T^3$	273-2073
Al ₂ O ₃ MgO	$-24.26 - 0.0027T - 3 \cdot 10^{-6} T^2 + 7 \cdot 10^{-10} T^3$	273-2373
SiO ₂ MgO	$-32.686 + 0.0009T + 1 \cdot 10^{-7} T^2 + 2 \cdot 10^{-12} T^3$	273-2473
Al ₂ O ₃ SiO ₂ CaO	$-85.021 + 0.0202T - 3 \cdot 10^{-5} T^2 + 9 \cdot 10^{-9} T^3$	273-2773
ZrO ₂ CaO	$-34.003 - 0.0167T + 5 \cdot 10^{-6} T^2 - 9 \cdot 10^{-10} T^3$	273-2573
ZrO ₂ SiO ₂	$-19.936 + 0.0075T + 7 \cdot 10^{-7} T^2 + 7 \cdot 10^{-10} T^3$	273-2873
CaO6Al ₂ O ₃	$-15.473 - 0.0478T + 1 \cdot 10^{-5} T^2 - 2 \cdot 10^{-9} T^3$	273-2373
CaOAl ₂ O ₃ 2SiO ₂	$-109.53 + 0.0053T - 3 \cdot 10^{-5} T^2 + 8 \cdot 10^{-9} T^3$	273-2873

In order to evaluate equation (3) 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:

$$G_O(Ti-Al) = RT \ln a_O = RT \ln a_O^* + RT \ln (X_O/X_O^*) = \Delta G_f^0(TiO) - G_{Ti}(Ti) = RT \ln (X_O/X_O^*) \quad (4)$$

where a_O^* is the oxygen activation at saturation, x_O is the oxygen concentration, x_O^* is the oxygen concentration at saturation and $G_{Ti} (=RT \ln a_{Ti})$ is the partial free energy of titanium.

Table 2. Activity-temperature relationship for free energy changes of reactions of selected crucible oxides

ΔG_r , kJ/mol			
X_{Ti}	CaO	Y_2O_3	ZrO ₂
0.1	$\Delta G_r = 1011.5 - 0.1879 \cdot T$	$\Delta G_r = 1460.5 - 0.2264 \cdot T$	$\Delta G_r = 1767.7 - 0.2933 \cdot T$
0.2	$\Delta G_r = 845.63 - 0.1562 \cdot T$	$\Delta G_r = 1211.6 - 0.1789 \cdot T$	$\Delta G_r = 1435.9 - 0.2299 \cdot T$
0.3	$\Delta G_r = 684.78 - 0.1253 \cdot T$	$\Delta G_r = 970.38 - 0.1325 \cdot T$	$\Delta G_r = 1114.2 - 0.1682 \cdot T$
0.4	$\Delta G_r = 534.75 - 0.0967 \cdot T$	$\Delta G_r = 745.33 - 0.0896 \cdot T$	$\Delta G_r = 814.13 - 0.111 \cdot T$
0.5	$\Delta G_r = 401.3 - 0.0719 \cdot T$	$\Delta G_r = 545.15 - 0.0524 \cdot T$	$\Delta G_r = 547.23 - 0.0613 \cdot T$
0.6	$\Delta G_r = 290.18 - 0.0523 \cdot T$	$\Delta G_r = 378.47 - 0.0231 \cdot T$	$\Delta G_r = 324.99 - 0.0222 \cdot T$
0.7	$\Delta G_r = 207.15 - 0.0395 \cdot T$	$\Delta G_r = 253.94 - 0.0039 \cdot T$	$\Delta G_r = 158.94 + 0.0034 \cdot T$
0.8	$\Delta G_r = 157.99 - 0.035 \cdot T$	$\Delta G_r = 180.18 + 0.0029 \cdot T$	$\Delta G_r = 60.604 + 0.0125 \cdot T$
0.9	$\Delta G_r = 148.43 - 0.0401 \cdot T$	$\Delta G_r = 165.85 - 0.0048 \cdot T$	$\Delta G_r = 41.496 + 0.0022 \cdot T$
X_{Ti}	MgO	Al ₂ O ₃	SiO ₂
0.1	$\Delta G_r = 1062.1 - 0.257 \cdot T$	$\Delta G_r = 1355.8 - 0.2496 \cdot T$	$\Delta G_r = 1597.9 - 0.2955 \cdot T$
0.2	$\Delta G_r = 896.21 - 0.2253 \cdot T$	$\Delta G_r = 1106.9 - 0.202 \cdot T$	$\Delta G_r = 1266.1 - 0.2321 \cdot T$
0.3	$\Delta G_r = 735.36 - 0.1944 \cdot T$	$\Delta G_r = 865.66 - 0.1557 \cdot T$	$\Delta G_r = 944.39 - 0.1703 \cdot T$
0.4	$\Delta G_r = 585.33 - 0.1658 \cdot T$	$\Delta G_r = 640.61 - 0.1128 \cdot T$	$\Delta G_r = 644.33 - 0.1131 \cdot T$
0.5	$\Delta G_r = 451.88 - 0.141 \cdot T$	$\Delta G_r = 440.43 - 0.0756 \cdot T$	$\Delta G_r = 377.42 - 0.0635 \cdot T$
0.6	$\Delta G_r = 340.76 - 0.1214 \cdot T$	$\Delta G_r = 273.75 - 0.0463 \cdot T$	$\Delta G_r = 155.19 - 0.0244 \cdot T$
0.7	$\Delta G_r = 254.74 - 0.1086 \cdot T$	$\Delta G_r = 149.22 - 0.0271 \cdot T$	$\Delta G_r = -10.861 + 0.0012 \cdot T$
0.8	$\Delta G_r = 208.57 - 0.104 \cdot T$	$\Delta G_r = 75.464 - 0.0202 \cdot T$	$\Delta G_r = -109.2 + 0.0103 \cdot T$
0.9	$\Delta G_r = 199.01 - 0.1092 \cdot T$	$\Delta G_r = 61.134 - 0.028 \cdot T$	$\Delta G_r = -128.31 - 1 \cdot 10^{-5} \cdot T$
X_{Ti}	CaOAl ₂ O ₃	CaO6Al ₂ O ₃	CaOAl ₂ O ₃ 2SiO ₂
0.1	$\Delta G_r = 2474.5 - 0.4089 \cdot T$	$\Delta G_r = 2497.1 - 0.4225 \cdot T$	$\Delta G_r = 4125.9 - 0.7149 \cdot T$
0.2	$\Delta G_r = 1838.5 - 0.2873 \cdot T$	$\Delta G_r = 1839.9 - 0.2969 \cdot T$	$\Delta G_r = 3113.9 - 0.5215 \cdot T$
0.3	$\Delta G_r = 1221.9 - 0.1689 \cdot T$	$\Delta G_r = 1202.7 - 0.1746 \cdot T$	$\Delta G_r = 2132.7 - 0.333 \cdot T$
0.4	$\Delta G_r = 646.77 - 0.0593 \cdot T$	$\Delta G_r = 608.31 - 0.0613 \cdot T$	$\Delta G_r = 1217.6 - 0.1586 \cdot T$
0.5	$\Delta G_r = 135.19 + 0.0358 \cdot T$	$\Delta G_r = 79.622 + 0.037 \cdot T$	$\Delta G_r = 403.49 - 0.0072 \cdot T$
0.6	$\Delta G_r = -290.77 + 0.1108 \cdot T$	$\Delta G_r = -360.58 + 0.1145 \cdot T$	$\Delta G_r = -274.34 + 0.112 \cdot T$
0.7	$\Delta G_r = -609.04 + 0.1598 \cdot T$	$\Delta G_r = -689.48 + 0.1652 \cdot T$	$\Delta G_r = -780.78 + 0.1901 \cdot T$
0.8	$\Delta G_r = -797.53 + 0.1773 \cdot T$	$\Delta G_r = -884.26 + 0.1832 \cdot T$	$\Delta G_r = -1080.7 + 0.2179 \cdot T$
0.9	$\Delta G_r = -834.17 + 0.1576 \cdot T$	$\Delta G_r = -922.11 + 0.1628 \cdot T$	$\Delta G_r = -1139 + 0.1864 \cdot T$

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:

$$G_O(Ti-Al) = \Delta G_r^0(TiO) - G_{Ti}(Ti) \cdot 0.01 \quad (5)$$

Using equations (3) and (5) the free energy change of reaction for oxide ceramic materials can be evaluated by:

$$\Delta G_r = 1/x \cdot \{y[\Delta G_f^\circ(\text{TiO}) - G_{\text{Ti}}(\text{Ti-Al}) \cdot 0.01] - \Delta G_f^\circ(M_xO_y)\} \quad (6)$$

According to equation (6), the activity-temperature ($0.1 < X_{\text{Ti}} < 0.9$) relationships for selected crucible oxides in the temperature range between 1273K and 1973K are calculating and the results are shown in Table 2.

The thermodynamic stability of ceramic materials was modeled based on the free energy of changes of reactions between various oxides. After calculating and summarizing the free energy change of reactions of selected ceramics at Figs. 3-5 are shown a bar-chart representation of their relative stability for Ti-Al alloys and Ti composition ($0.1 < X_{\text{Ti}} < 0.9$) at temperature range 1673K-1873K.

Based on this analysis the most stable ceramics are Y_2O_3 , followed by ZrO_2 , and then the CaO .

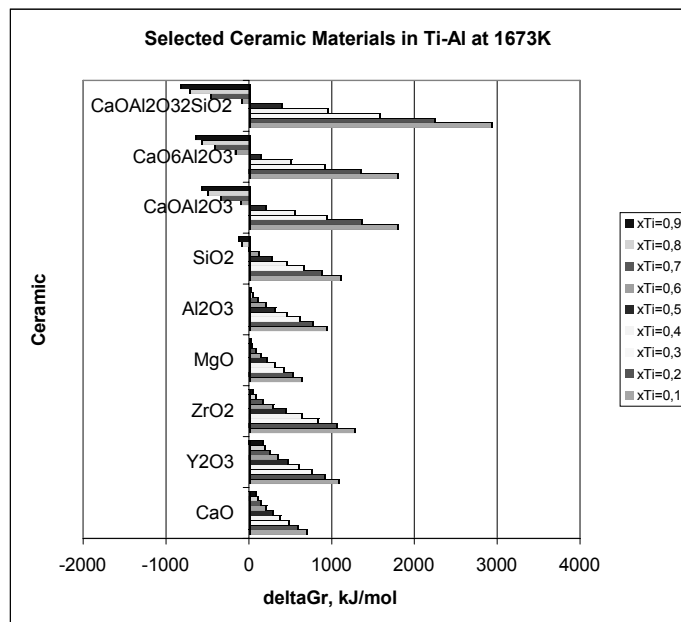


Fig.3. Estimated ΔG_r of selected ceramics in Ti-Al alloys ($0.1 < X_{\text{Ti}} < 0.9$) at 1673K

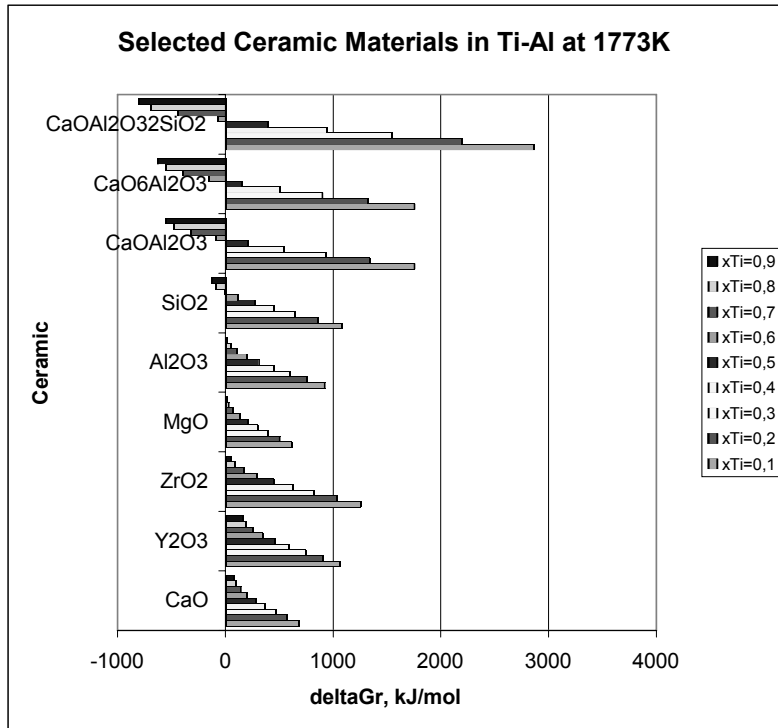


Fig.4. Estimated ΔG_r of selected ceramics in Ti-Al alloys ($0.1 < X_{Ti} < 0.9$) at 1773K

Conclusions

The results of thermo-chemistry analysis was shown that the crucible oxide stability in contact with molten titanium and titanium-aluminum alloys depend of temperature and compositions of alloys.

CaO, Y₂O₃, ZrO₂ and Al₂O₃ have positive ΔG_r values in Ti-Al in the temperature range 1273K-1973K 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.

SiO₂ has a negative ΔG_r value in liquid Ti-Al at 1273K-1973K for compositions of Ti-Al equal $X_{Ti} = 0.7 - 1$, 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 SiO_2 would not be stable.

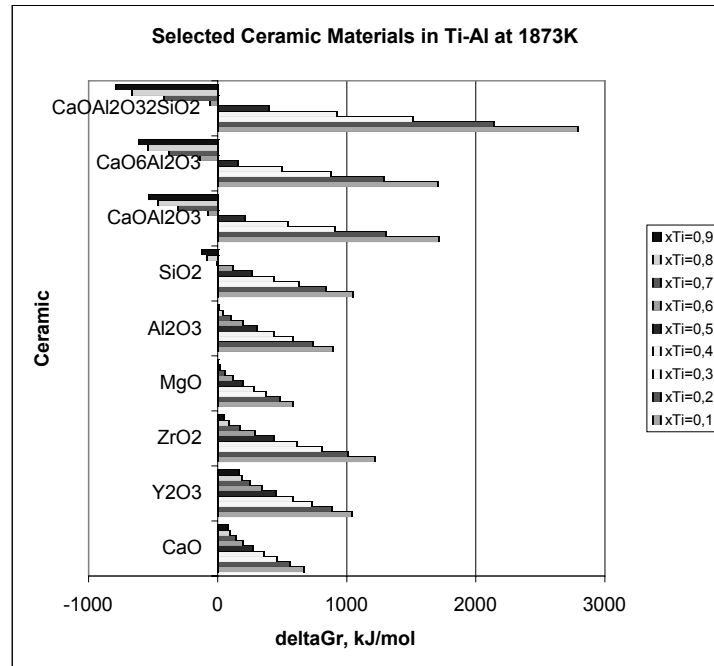


Fig.5. Estimated ΔG_r of selected ceramics in Ti-Al alloys ($0.1 < X_{\text{Ti}} < 0.9$) at 1873K

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

Also, it can be noticed that standard free energy of formation of chosen combination oxides-based ceramics is very low, which indicate those crucible materials are not very stable for titanium and titanium alloys melting and can be used for melting very selected materials based on 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.

The crucible oxides Y_2O_3 , ZrO_2 , CaO and Al_2O_3 can be successfully used for melting titanium and its alloys, while MgO and SiO_2 can be used only for some alloys, but not for titanium.

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