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THERMO-CHEMISTRY CALCULATIONS IN MOLTEN Ti-Al ALLOY

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Abstract

The results of thermo-chemistry calculations in molten Ti-Al alloy were shown that the ceramics crucible stability in contact with molten titanium-aluminum alloys depend on temperature and compositions of alloys. The compatibility of ceramics with Ti-Al alloy will depend on their thermodynamic stability as a function of temperature, titanium concentration, and oxygen concentration. The ceramics crucibles, which have positive free energy of reaction in Ti-Al at 1873K indicates that these oxides do not dissolve. They are compatible with Ti-Al alloy and can be successfully used for their melting.

***Keywords**: thermo-chemistry, Ti-Al alloy, ceramics crucibles*

1. INTRODUCTION

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 [1,2], in this paper will be presented the results of predicting thermodynamic calculations with the aim to determine the ceramics crucible oxide stability in contact with molten Ti-Al alloy.

This research will try to help shed some light on problems connected with interaction between ceramics crucibles and titanium-aluminum alloys and give the answer can crucible oxides be used for melting titanium alloys.

2. RESULTS AND DISCUSSION

To assess the stability of crucible oxides in Ti-Al alloy, the activity of titanium and aluminum as a function of temperature should be calculated. The activity of titanium and aluminum in Ti-Al alloy is calculated using the FactSage thermochemical software and databases [3].

The activity-temperature relationship can be expressed as:

$$\ln aTi = A+B/T \quad (1)$$

The coefficients A and B are determined by FactSage, as well as the activity-temperature relationship in titanium-aluminum alloys for titanium composition. The activity of titanium and aluminum 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 Figure 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.

This activity-temperature-composition relationship is used for further thermodynamic calculations.

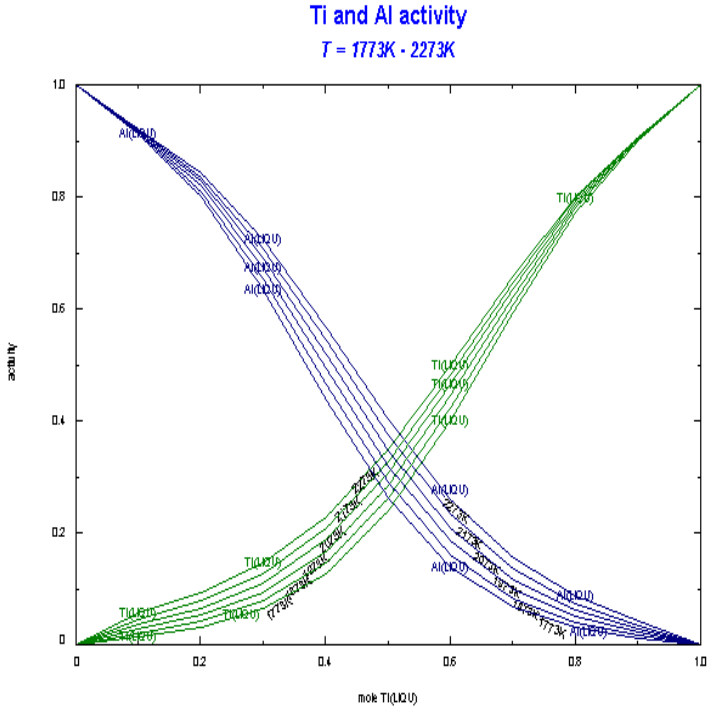


Figure 1. *Titanium and aluminum activity in the liquid phase as function of mole fraction at 1773K - 2273K*

The compatibility of crucible ceramics with Ti-Al alloy will depend on their thermodynamic stability (ΔGr, free energy of reaction) as a function of temperature, titanium concentration, and oxygen concentration. To evolutes ΔGr, the activity of oxygen must be known, which depend on the standard free energy of formation, ΔGf_0, of the corresponding oxides.

The standard energy of formation of the selected oxides is calculated by use of the FactSage.

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 alloys melting.

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	$-542{,}95+0{,}1005T-3\cdot10^{-6}T^2-6\cdot10^{-10}T^3$	273-1973
Ti_2O_3	$-1523{,}1+0{,}3099T-3\cdot10^{-5}T^2+7\cdot10^{-9}T^3$	273-2073
TiO_2	$-945{,}42+0{,}1908T-1\cdot10^{-5}T^2+3\cdot10^{-9}T^3$	273-2073
CaO	$-629{,}57+0{,}0959T-6\cdot10^{-6}T^2+8\cdot10^{-9}T^3$	273-2773
Y_2O_3	$-1906{,}7+0{,}3021T-1\cdot10^{-5}T^2+4\cdot10^{-9}T^3$	273-3073
ZrO_2	$-1099{,}3+0{,}2031T-1\cdot10^{-5}T^2+3\cdot10^{-9}T^3$	273-2873
MgO	$-570{,}73+0{,}0027T+8\cdot10^{-5}T^2-1\cdot10^{-8}T^3$	273-3073
Al_2O_3	$-1670{,}4+0{,}2904T+3\cdot10^{-5}T^2-6\cdot10^{-9}T^3$	273-2273
SiO_2	$-917{,}37+0{,}213T-4\cdot10^{-5}T^2+1\cdot10^{-8}T^3$	273-1973

The reduction reaction of an oxide ceramic (M_xO_y) in molten titanium-aluminum alloy can be expressed by the following equation:

$$M_xO_y \xrightarrow{liquid\,Ti\text{-}Al} yO(Ti-Al)+xM \tag{2}$$

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

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

where $G_O(Ti\text{-}Al)$ is the solute free energy in titanium-aluminum alloy, in this case of oxygen.

The equation (3) represents a relative equilibrium state between the oxygen solute free energy and the Gibbs free energy of the metal oxide formation, which is the thermodynamic driving force ΔG_r.

For a smaller ΔG_r relative to $G_O(Ti\text{-}Al)$ the oxide is more stable than the oxygen in solution with titanium-aluminum. This would indicate that the ceramic would be thermodynamically compatible with titanium-aluminum alloys.

In order to model the 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 must be evaluated using solubility data:

$$\begin{aligned} G_O(Ti-Al) &= RT\ln a_O = RT\ln a_O^* + RT\ln(x_O/x_O^*) = \\ &= \Delta G_f^0(TiO) - G_{Ti}(Ti) + RT\ln(x_O/x_O^*) \end{aligned} \tag{4}$$

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} $(=RTlna_{Ti})$ is the partial free energy of 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:

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

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

$$\Delta G_r = 1/x \cdot \left\{ y\left[\Delta G_f^0(TiO) - G_{Ti}(Ti-Al)\cdot 0.01\right] - \Delta G_f^0(M_xO_y)\right\} \quad (6)$$

According to equation (6), the activity-temperature ($0,1<X_{Ti}<0,9$) relationships for selected crucible oxides in the temperature range between 1273K and 1973K are calculated.

After calculating and summarizing the free energy change of reactions of selected ceramics, it is compared their relative stability for Ti-Al alloy at temperature 1873K and obtained that the most stable ceramics are Y_2O_3, followed by ZrO_2, and then the CaO.

3. CONCLUSION

The results of thermodynamic calculations and interactions were shown that the stability of ceramics crucible in contact with molten titanium-aluminum alloy depend on temperature and compositions of alloys.

CaO, Y_2O_3, ZrO_2 and Al_2O_3 have positive ΔGr values in Ti-Al alloy in the temperature range 1273K-1973K for all compositions of titanium-aluminum, which indicates that these oxides do not dissolve. They are compatible with Ti-Al alloy and can be used as materials for crucibles.

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