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Thermochemical Calculations of the Stability of Ti_2AlC in Various Atmospheres

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Abstract

The thermochemical stability of the MAX phase Ti_2AlC under vacuum, inert Ar, pure O_2 and N_2 and a reactive air atmosphere was explored based on thermochemical equilibrium calculations. A dataset on the enthalpy of formation, standard molar entropy and the temperature variation of the heat capacities of Ti_2AlC and $TiC_{0.5}$ was derived from thermochemical properties given in the literature and implemented in the software package HSC Chemistry. In inert atmosphere Ti_2AlC decomposes peritectically into solid $TiC_{0.5}$ and a liquid Al-rich phase at approximately 1673 °C whereas in vacuum (1 mPa) dissociation into solid $TiC_{0.5}$ and an Al gas phase is observed at a significantly lower temperature of 984 °C. When Ti_2AlC is exposed to air as well as pure O_2, solid Al_2O_3 and TiO_2 will form with the carbon being oxidized to gaseous CO and CO_2. At very low air content, however, the calculations show $TiC_{0.5}$ and AlN as the prevailing reaction products with small fractions of Al_2O_3. In a pure nitrogen atmosphere Ti_2AlC is nitrided to AlN, TiN and residual carbon.

Keywords: MAX phase, thermochemical calculations, atmosphere stability

I. Introduction

Ternary $M_{n+1}AX_n$ phases (abbreviated as MAX phases) of hexagonal crystal symmetry are distinguished by a unique alteration of metal-bonded A-layers (A = A group element) and XM_6-octahedra layers (M = early transition metal and X = C, N) differing in stacking sequence, e.g. n = 1,2, to 6 [1]. Due to their nano-laminate structure, MAX phase materials may exhibit superior fracture toughness and thermal shock resistance as well as high thermal and electrical conductivity [2]. Ti_2AlC was reported to offer excellent mechanical properties and machinability combined with a superior oxidation stability [3]. The oxidation stability of Ti_2AlC was attributed to the formation of a protective Al_2O_3 scale on the material surface [4]. This is surprising since Ti-Al intermetallic phases, such as Ti_3Al and TiAl, do not form a protective oxide scale during high-temperature oxidation [5]. Although less Al is present in the MAX phase Ti_2AlC, the high mobility of Al along the (0001) basal plane gives rise to a thin Al-depleted layer near the oxide scale/substrate interface and facilitates selective oxidation of Al [6].Its high-temperature stability, however, is still a matter of controversial discussion. While in vacuum Ti_2AlC was reported to decompose at temperatures ranging from 700 °C [7] to 1400 °C [8], melting was reported to occur at atmospheric pressure in inert gas at a temperature from 900 °C [7] to 1625 °C [9]. On the other hand, MAX phases M_2AC with M = Ti, V, and A = Al, Si, Cr recently gained interest on account of their ability to heal surface cracks based on an oxidation reaction (with O_2 or N_2) at temperatures exceeding 1000 °C [10]. Filling of the open crack space with solid products of the oxidation reaction, however, is strongly dependent on the local oxygen (or nitrogen) activity in the surface crack, which may differ from the environmental partial pressure in air near the surface from that at great distance from the surface [11]. Since the environment is thought to strongly affect the stability of Ti_2AlC at elevated temperatures, it is of great interest to analyze the thermochemical limitations for applying this MAX phase ceramic in different atmospheres and at elevated temperatures.

It is the aim of the present work to describe the thermochemical stability of Ti_2AlC under various environmental atmospheric conditions by means of thermochemical equilibria calculations. The results of the stability calculations were validated with literature data, and phase stability diagrams were constructed for a variety of scenarios relevant for applications at elevated temperatures. Since thermochemical data for Ti_2AlC (and $TiC_{0.5}$) were not yet implemented in the thermochemical software, coefficients of the temperature-dependent polynomial of heat capacity were derived from literature data.

II. Thermochemical Calculations

A standard thermochemical software package (HSC Chemistry 8.1.4, Outotec Oyj, Pori, Finland) was applied to derive equilibrium phase composition by calculating the minimum of total Gibbs energy for a system of four components (Ti, Al, C + gas phase) by means of the GIBBS solver. The software allows for efficient thermodynamic

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equilibrium calculations of complex multicomponent systems and gives access to an extensive database for thermodynamic data especially for ceramics. The phase stability of Ti_2AlC in vacuum, inert (Ar) as well as reactive atmospheres (O_2, N_2) was calculated for the reactions 1 a,b and 2 a,b at different temperatures up to a maximum temperature of 2000 °C. The amount of gas phase was varied by changing the compositional variable *x*. Because the calculations were used to determine equilibria at ambient and low pressure, the gas phase was treated as an ideal mixture. Decomposition:

$$Ti_2AlC(s) \rightarrow 2\ TiC_{0.5}(s) + Al(l,g) \quad (1a)$$

$$Ti_2AlC(s) \rightarrow TiC(s) + Ti(l,g) + Al(l,g) \quad (1b)$$

Oxidation:

$$Ti_2AlC(s) + x\ O_2(g) \rightarrow 2\ TiO_2(s) + 0.5\ Al_2O_3(s) + CO_2(g) \quad (2a)$$

with = 0…4 (x = 3.75 stoichiometric reaction)

$$Ti_2AlC(s) + x\ N_2(g) \rightarrow 2\ TiN(s) + AlN(s) + C(s) \quad (2b)$$

with x = 0…2 (x = 1.5 stoichiometric reaction)

While the thermochemical data of the major condensed and gaseous species involved in the reaction scenarios presented above (Al(l,g), Ti(l,g), C(s), TiC(s), TiO_2(s), TiO(s), Al_2O_3(s), Al_2TiO_5(s), TiN(s), AlN(s), O_2(g), N_2(g), CO(g), CO_2(g)) could be taken from the existing data source included in the HSC software package, the thermochemical data for Ti_2AlC(s) and $TiC_{0.5}$(s) had to be acquired from other sources and then implemented.

The heat of formation ΔH_f^0 and the standard molar entropy S_m^0 for solid hexagonal Ti_2AlC were taken from *ab-initio* calculations [12]. The Kelley-polynomial equation was applied to express the temperature dependence of measured heat capacity values c_p over a wide temperature range.

$$c_p(T) = A + BT \cdot 10^{-3} + CT^{-2} \cdot 10^5 + DT^2 \cdot 10^{-6} \quad (3)$$

The coefficients *A*,*B*,*C* and *D* were determined from experimentally measured c_p values by combining two different sources covering the low temperature regime from 0 to 260 K [13] and the high temperature regime from 300 to 1600 K [14], Fig. 1.

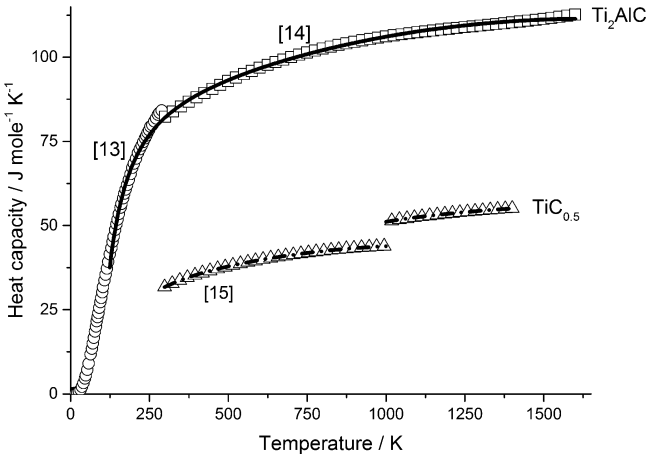

Fig. 1: Heat capacity c_p data determined experimentally for the MAX phase Ti_2AlC [13, 14] and $TiC_{0.5}$ [15]. The coefficients *A*, *B*, *C*, and *D* for Eq. (2) were derived from regression analysis of the experimentally measured c_p data in the temperature interval 124 K to 1600 K for Ti_2AlC (solid line) and in the temperature interval 298 K to 1400 K for $TiC_{0.5}$ (dash-dot line).

Thermochemical data for $TiC_{0.5}$ were separated into a cubic phase from 298.15 up to 1000 K and a disordered phase from 1000 to 1400 K [15]. The values of ΔH_f^0 and S_m^0 were derived from *ab-initio* calculations [16]. Experimental c_p-data measured on $TiC_{0.54}$ were taken to derive the coefficients of Eq. (3). Table 1 summarizes the thermochemical data for Ti_2AlC and $TiC_{0.5}$ used in the thermochemical calculations.

Table 1: Thermochemical data for Ti_2AlC and $TiC_{0.5}$ implemented in the thermochemical calculation package.

Species	**Ti_2AlC**	**$TiC_{0.5}$**	
Crystal system	hexagonal	Cubic	disordered
T_{min} (K)	124.00	298.15	1000.00
T_{max} (K)	1600.00	1000.00	1400.00
Phase	solid	Solid	solid
ΔH_f^0 kJ/mol	-258.36 [13]	-113.24 [17]	1.50 [16]
S_m^0 J/(mol·K)	78.10 [14]	22.43 [17]	0.00
C_p coefficient A J/(mol·K)	79.22	28.38	45.87
C_p coefficient B J/(mol·K^2)	39.66	27.56	13.48
C_p coefficient C J/(mol·K^{-1})	-7.14	-3.38	-44.32
C_p coefficient D J/(mol·K^3)	-12.10	-11.71	-3.77
Density g/cm^3	4.11	4.91	4.91

III. Results and Discussion

(1) Thermally induced decomposition

The stability of the Ti_2AlC MAX phase was calculated for an inert Ar atmosphere of ambient pressure and for vacuum (1 mPa), Fig. 2. In inert atmosphere Ti_2AlC is likely to decompose peritectically into solid $TiC_{0.5}$ and a liquid Al-rich phase at approximately 1673 °C, which is in reasonable agreement with literature data reporting peritectic decomposition reactions at 1600 °C [17], 1625 °C [9] and 1740 °C [18], respectively. It should be mentioned that the resulting Al(l) phase is supposedly not pure like that calculated here under ideal conditions, but may dissolve carbon from the substoichiometric $TiC_{0.5}$ depending on the temperature. When Ti_2AlC is heated in vacuum, dissociation into solid $TiC_{0.5}$ and an Al gas phase is supposed to occur at a significantly lower temperature of 984 °C. Experimentally a slightly lower temperature of 900 °C was presented in literature for the complete decomposition of Ti_2AlC thin films [19].

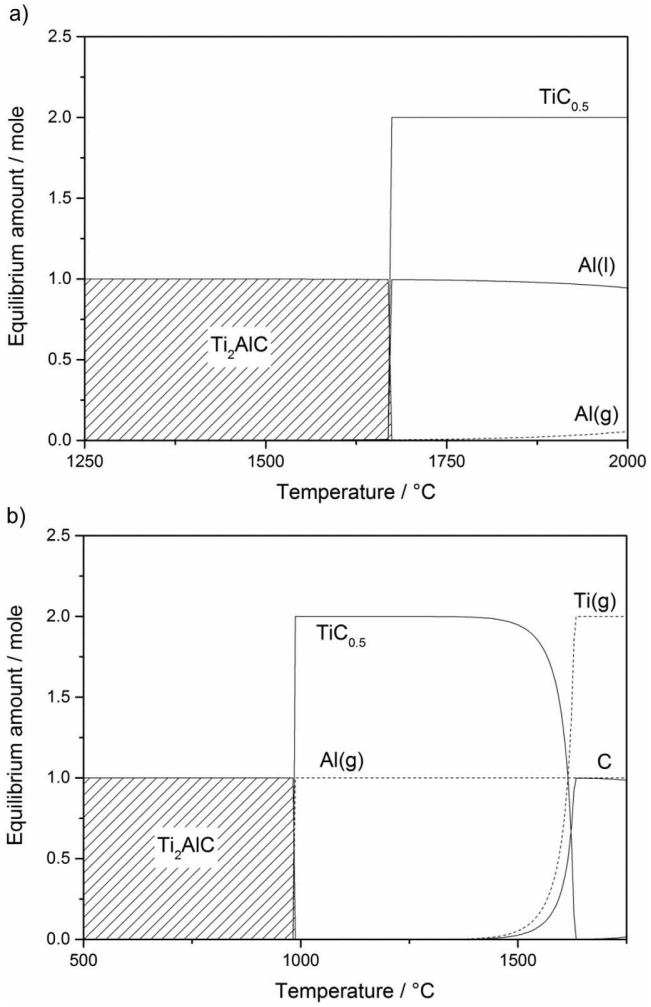

Fig. 2: Equilibrium calculation for the peritectic decomposition of Ti_2AlC at ambient pressure in inert gas Ar(g) (a) and in vacuum (1 mPa) (b).

(2) Oxidation in air

The reaction of Ti_2AlC with oxygen is of great importance for long-term operation of Ti_2AlC components in air as well as for oxidation-induced healing of surface cracks [3, 11]. The oxidation of Ti_2AlC was calculated in pure $O_2(g)$ and pure $N_2(g)$ atmosphere and for engineering-relevant conditions in dry air at a constant temperature of 700 °C. The change in Gibbs free energy for the stoichiometric addition of pure $O_2(g)$ and $N_2(g)$ in Eq. (2a) and (2b) at 700 °C was calculated to be - 2376.39 kJ/mol and - 466.66 kJ/mol respectively, indicating a highly exothermic reaction in oxygenated atmospheres. The different stages of the oxidation and nitridation behavior in pure $O_2(g)$ and $N_2(g)$ were determined with equilibrium calculations for increasing additions of gas phase, Fig. 3.

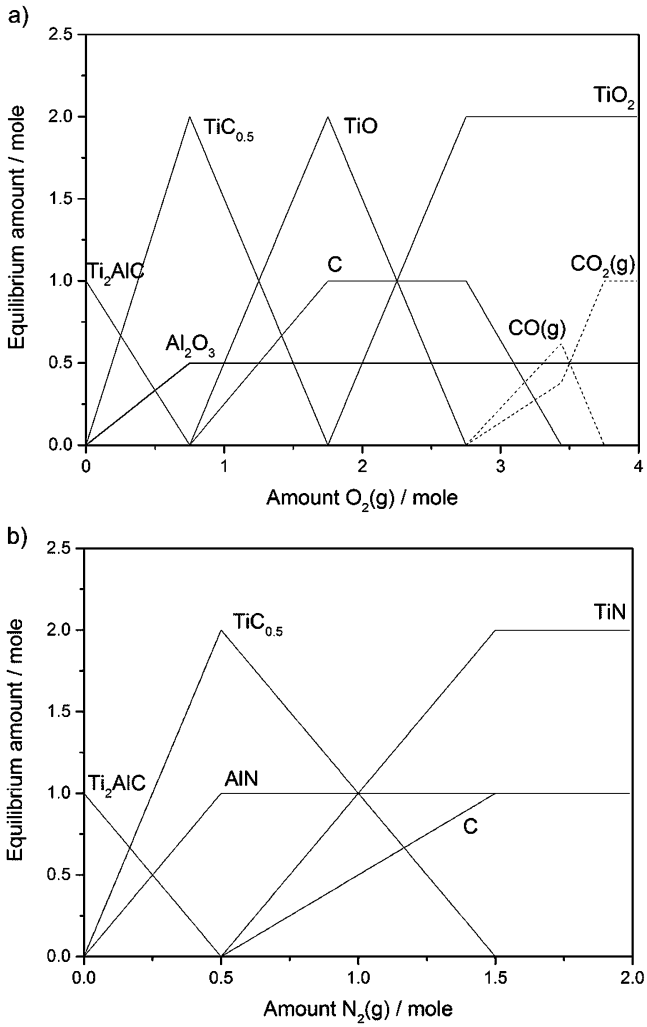

Fig. 3: Equilibrium calculation for the oxidation and nitridation of Ti_2AlC at 700 °C in pure $O_2(g)$ (a) and pure $N_2(g)$ (b).

The addition of a high amount of $O_2(g)$ to Ti_2AlC leads to the formation of the thermodynamically most stable products TiO_2, Al_2O_3 and CO_2 as described by Eq. (2a). Already at small additions of oxygen, Al_2O_3 is forming, which has been described as the primary product responsible for the long-term oxidation stability of Ti_2AlC [4]. While the Al is preferentially oxidized, a substoichiometric carbide $TiC_{0.5}$ is formed which is oxidized at a higher oxygen content of $x = 0.75$ mole to TiO and subsequently to TiO_2.

For small additions of $N_2(g)$ to Ti_2AlC, aluminum nitride AlN and the substoichiometric titanium carbide $TiC_{0.5}$ are the reaction products. For increasing additions of nitrogen above $x = 0.5$ mol $N_2(g)$ $TiC_{0.5}$ is also nitrided

to TiN. The final products at a stoichiometric addition of x = 1.5 mol N_2(g) are TiN, AlN and residual carbon. Plasma nitridation experiments with Ti_2AlC at 800 °C revealed the formation of a nitride surface layer composed mostly of TiN with smaller fraction of AlN [20].

Instead of pure oxygen and nitrogen displayed in Eq. (2a) and (2b), respectively, the composition of air (78.084 % N_2(g), 20.942 % O_2(g), 0.934 % Ar(g), 0.040 % trace gases) was also applied to calculate the phase evolution as a function of the air content at a constant temperature of 700 °C. Two regimes of air concentration were considered: i. a large amount of air with $x > 2$ mole simulating long-term oxidation of Ti_2AlC surface in excess of the oxidant gas and ii. a small amount with $x < 2$ mole which is of interest for confined oxidation reactions that may occur on the surface of cracks (crack healing), Fig. 4.

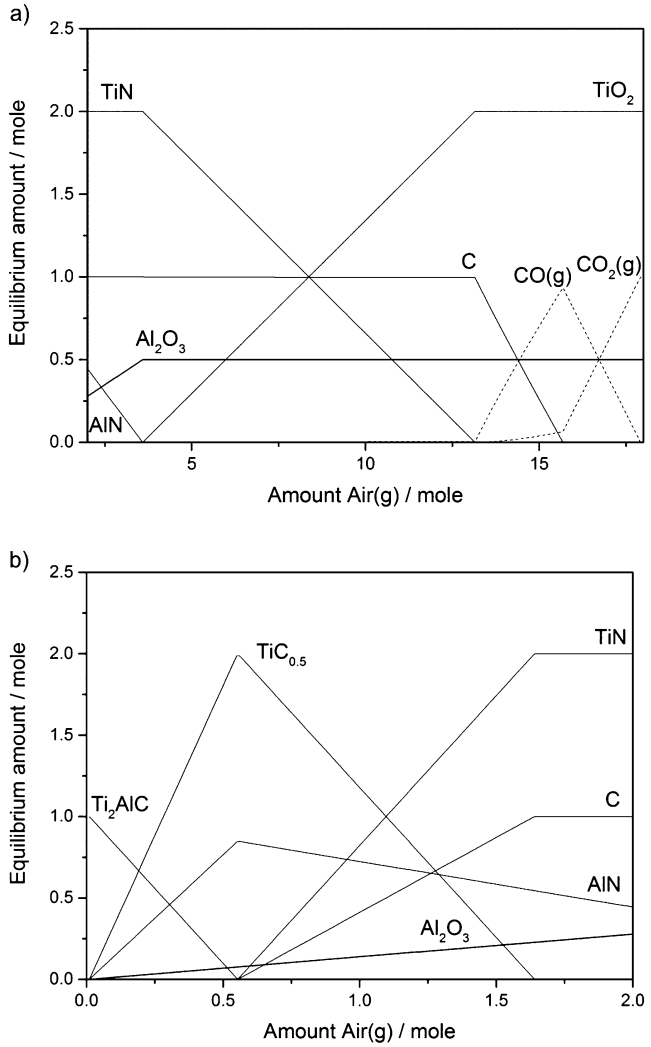

Fig. 4: Equilibrium calculation for the oxidation of Ti_2AlC in dry air at 700 °C for the case of excessive air (a) and for deficiency of air (b).

At a high amount of air, the oxidation reaction of Ti_2AlC finally results in the formation of Al_2O_3 and TiO_2 with the carbon being oxidized to gaseous CO and CO_2. This overall reaction as described by Eq. (2a) was confirmed by a number of experimental reports which show Al_2O_3 and TiO_2 as the dominating reaction products [3, 10]. At elevated temperatures Al_2TiO_5 is likely to form following the reaction of Al_2O_3 with TiO_2 as was observed at 1400 °C [21].

At a very low air content, which may be the case at the front of a crack far from the surface [11], the calculations show $TiC_{0.5}$ and AlN as the prevailing reaction products with small fractions of Al_2O_3. Above an air content of 0.6 mole, $TiC_{0.5}$ will undergo a nitridation reaction forming TiN and residual C. Owing to the high solubility of titanium nitrides in carbides, as described by Duwez [22], $TiC_{0.5}$ and TiN will likely form a carbonitride. In the calculation, this system is simplified to only account for the end members owing to the lack of thermodynamic data for $TiC_{0.5}N_{0.5}$. Simultaneously the amount of AlN decreases until all Al is oxidized to Al_2O_3 at approximately x = 2.7 mole, at which point TiN starts to react with O_2(g) to form TiO_2 (for simplification suboxides TiO_n with n = 1, 5/3, and 3/2 were not considered in the calculation).

IV. Conclusions

Thermochemical data for Ti_2AlC and $TiC_{0.5}$ were derived from literature data and implemented in a thermochemical software package. It was successfully demonstrated that the stability and reaction behavior of the MAX phase Ti_2AlC at different temperatures and in an air and pure O_2(g) and N_2(g) atmosphere could be calculated in agreement with the experimental reports.

The benefit of these thermodynamic calculations are detailed information on thermal stability and partial vapor pressure, which e.g. may influence the sintering behavior. Higher temperatures and smaller particle sizes (higher surface curvature) lead to a higher vapor pressure and thus increase the vapor phase transport. Besides this, sintering is also heavily influenced by surface, grain boundary and lattice diffusion. which require an additional kinetic investigation.

It might be of interest to extend these calculations to different environmental atmosphere conditions to evaluate the potential applications of Ti_2AlC phases in harsh environments including reducing atmospheres like H_2(g), NH_3(g), CH_4(g) and aggressive environments like H_2S(g) and Cl_2(g).

Acknowledgments

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