JOURNAL OF MATERIALS SCIENCE 26 (1991) 2421–2430

Thermal stability of refractory materials for high-temperature composite applications

H. WIEDEMEIER, M. SINGH
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

A computational thermodynamic analysis of the stability of group IV, V, and VI transition metal borides, carbides, nitrides, and oxides is presented. The results of these computations can be employed to assess the stability and decomposition of these materials at high temperatures under different ambient conditions. The thermodynamic stabilities of group IV, V, and VI compounds increase with atomic number of the metal in the same group and decrease with atomic number in the same period. Based on the equilibrium computations of the decomposition reactions considered, V_3B_4, HfC, HfN and Ti_3O_5 are the most stable compounds in each class. In general, the refractory oxides are the most stable compounds followed by the borides, carbides and nitrides.

1. Introduction

In recent years, considerable attention has been focused on the development of high-temperature structural composite materials, which might serve as replacements for superalloys in high-temperature and aerospace applications. These materials should have high melting points, good oxidation resistance, low density, and superior high-temperature creep and other mechanical properties. The thermochemical behaviour and properties of refractory borides, carbides, nitrides, silicides and oxides are being investigated for the above purposes. One of the major requirements for the efficient design and operation of high-temperature components and processes is reliable data about the thermodynamic stabilities, decomposition and oxidation behaviour under different conditions. These data are very useful in estimating the vaporization losses and predicting the lifetime of such materials.

Despite continuing research efforts and the use of advanced experimental techniques, there are still many gaps in the knowledge and understanding of the high-temperature properties of these refractory materials. The considerable lack of reliable experimental data concerning the stability and oxidation under different conditions at elevated temperatures has encouraged us to estimate these properties using thermodynamic data.

The present investigation deals with the stability relative to decomposition (vaporization) of borides, carbides, nitrides and oxides of group IV (titanium, zirconium and hafnium), group V (vanadium, niobium and tantalum), and group VI (chromium, molybdenum and tungsten) metals. Several of these compounds are of current interest for high-temperature structural applications. Hillig [1] discussed various problems and prospects for several of these compounds as constituents (fibre/matrix/coating) for high-temperature composites. Titanium diboride reinforcements are reported to be compatible with and to improve the mechanical properties of intermetallic (aluminides) and of some ceramic (oxide) matrix composites [2–4]. Pure and partially stabilized zirconia (PSZ) are found to be quite attractive and effective as thermal barrier coatings for high-temperature applications [5]. A number of compounds of this class, i.e. TiC, TiN, TiO_2, TaC, Cr_3C_2 and Cr_2O_3 are widely used for different applications in heat engines [6]. In addition, studies [7] indicate that TiC and TiB_2 are also promising materials for use as limiters (the part of a fusion reactor nearest to the plasma). Other applications of materials containing refractory metal carbides, nitrides and borides include their use as effective wear-resistant materials for cutting tools [8–10]. A number of composite systems containing these compounds as reinforcements (whiskers, particulates and fibres), matrices, and coatings are reported in the literature. The main objectives of this investigation are to evaluate the thermal stabilities of these materials at high temperatures and to provide a data base for further computations. Other more specific analyses of the high-temperature applications and properties of these materials are part of a continuing effort and are being reported elsewhere [11–13].

2. Thermodynamic considerations

Thermodynamic equilibrium calculations represent a powerful tool to assess the chemical reactivities of materials, in particular at elevated temperatures. The free energies of reactions provide guidelines with respect to the dominant direction and extent of processes. However, thermodynamically favourable reactions may not occur owing to reaction kinetics. In such cases the actual physical state of the material, e.g. texture, porosity, stress and strain, may become very important. The rate of a reaction is also affected by the surface area available which, in turn, is related to the porosity of the material. Reactions may be inhibited

0022-2461/91 $03.00 + .12

by the formation of protective layers. The latter case is of particular interest for the application of many composite materials at high temperatures, where the partial pressures of gaseous reactant or product species may stabilize or destabilize the system.

One of the main problems encountered in the thermochemical analysis of the refractory materials is the lack of reliable thermodynamic data for compounds at high temperatures. In such cases, the estimation of data is required. For the analysis of the decomposition behaviour of a given material, various reactions are considered which may occur in a particular system. Using the available and estimated data, equilibrium thermodynamic computations are performed for all reactions. For a meaningful application and interpretation of thermochemical computations a brief review of the basic relationships and conventions may be desirable.

The equation for chemical equilibrium can be intuitively expressed in terms of activities, namely

$$\mu_i(T, p, \text{comp.}) \equiv \mu_i^0 + RT \ln a_i(T, p, \text{comp.}) \quad (1)$$

where μ_i^0 is the chemical potential of a substance in its standard state in a particular phase. The choice of standard states for a substance is a matter of convenience. Conventionally, the standard state of a component in a gaseous phase is that of unit fugacity, i.e. the pure gas in the hypothetical ideal condition at temperature T and 1 atm pressure. Thus $a_i \to p_i$ as $\rho_i \to 0$. For a pure solid or liquid or for a solid or liquid solution, the most convenient standard state is the pure solid or liquid (or pure solvent) at temperature T and 1 atm pressure. For such a substance, $a_1 \to x_1$ as $x_1 \to 1$ if the pressure is 1 atm. Unless the pressure is very high, the pressure dependence of μ_i of condensed phases can be neglected because of the small molar volume in the term $v_i \mathrm{d}p$ of the modified Gibbs–Duhem equation.

With Equation 1 the change in Gibbs free energy for a chemical reaction is defined as

$$\Delta G \equiv \sum_i \nu_i \mu_i \equiv \sum_i \nu_i \mu_i^0 + RT \sum_i \nu_i \ln a_i, \quad (2)$$

where the stoichiometric coefficients ν_i are negative for reactants and positive for products. Introducing the quantity ΔG^0 for $\sum_i \nu_i \mu_i^0$, Equation 2 can be written in the form

$$\Delta G \equiv \Delta G^0 + RT \ln \prod_i a_i^{\nu_i}. \quad (3)$$

It is useful to recall that ΔG^0 is the change in Gibbs free energy for a process starting with the stoichiometric number of moles of reactants in their standard states, and ending with the stoichiometric number of moles of products in their standard states. The second term in Equation 3 is the product of activities and/or partial pressures of reactants and products. When the process is at equilibrium, $\Delta G \equiv 0$ and Equation 3 takes the form

$$\Delta G \equiv 0 \equiv \Delta G^0 + RT \ln K_{\mathrm{eq}}, \quad (4)$$

where $K_{\mathrm{eq}} = \Pi_i a_i^{\nu_i}$ and is the equilibrium constant of the reaction. When gaseous species are involved in the reaction, the symbol K_{p} is frequently used for K_{eq}. The equilibrium condition is commonly expressed by the equation

$$\Delta G^0 = -RT \ln K_{\mathrm{eq}}. \quad (5)$$

The quantity ΔG^0 is related to the reaction enthalpies and entropies of substances in their standard states by the expression

$$\Delta G_T^0 = \Delta H_T^0 - T \Delta S_T^0 \quad (6)$$

For computational purposes Equation 6 can be expanded to

$$\Delta G_T^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta C_{\mathrm{p}}^0 \,\mathrm{d}T - T\Delta S_{298}^0 - T \int_{298}^{T} \frac{\Delta C_{\mathrm{p}}^0}{T} \mathrm{d}T \quad (7)$$

where ΔH_{298}^0 and ΔS_{298}^0 are enthalpy and entropy changes, respectively, of reaction at 298 K. Thus, ΔG^0 can be computed for any reaction and at any temperature for which thermodynamic data (heats of formation, absolute entropies, heat capacities) of reactants and products are available. Assuming that the reaction process involves at least one reactant or product substance in the gaseous state and that the others are in the condensed state, then based on the above definition of ΔG^0 and at equilibrium, the activities of the substances in the condensed phase are unity and of those in the gaseous state are equal to their equilibrium partial pressures.

Under these conditions, the sign of ΔG^0 indicates the endo- or exo-thermicity (direction) of the reaction as written. The magnitude of ΔG^0 is related to the magnitude of the partial pressure(s) of gaseous species present, which, in turn, is related to the amount(s) of gaseous substances in the reaction system. On the other hand, the activity of a pure condensed phase (at 1 atm) is unity by definition and independent of the amount of substance present. Thus, for a process in which only reactants and products in the condensed phase participate, ΔG^0 indicates the direction of a process, but not the "extent" of the reaction. If $\Delta G^0 < 0$, then eventually all reactants must disappear; if $\Delta G^0 > 0$, eventually all products must disappear. Only at one particular temperature is $\Delta G^0 = 0$, and the ratio of activities is unity for condensed-phase reactions. Therefore, generally it is not meaningful to compute equilibrium constants from thermodynamic data for reactions involving only condensed-phase substances. The computation of ΔG^0 values for such reactions provides an indication whether the reaction as written is thermodynamically favourable or not. As indicated above, kinetic factors may have a considerable influence on the actual behaviour of a process under given conditions of temperature, pressure, and of the physical state of the materials involved.

A computer program has been developed to calculate ΔG^0 values for all individual reactions considered in this work over wide temperature ranges. The majority of the chemical reactions employed in the thermodynamic analysis of the different systems contain one or more gaseous reactant(s) and/or product(s). For these condensed-gas phase reactions, based on the

TABLE I Sources of thermochemical data for substances considered in equilibrium calculations of this work

Substance	Ref.	Substance	Ref.	Substance	Ref.	Substance	Ref.
B(s, l)	17	Ta(g)	16	ZrC(s)	17	CrN(s)	18
B(g)	17	Cr(s, l)	15	HfC(s)	14	Cr_2N(s)	18
C(s)	19	Cr(g)	16	VC(s, l)	15	TiO(s, l)	14
C(g)	19	Mo(s, l)	15	V_2C(s, l)	14	TiO(g)	14
C_2(g)	17	Mo(g)	18	NbC(s)	18	TiO_2(s, l)	14
C_3(g)	17	W(s)	14	Nb_2C(s)	14	Ti_2O_3(s, l)	14
N(g)	19	TiB(s, l)	17	TaC(s)	15	Ti_3O_5(s, l)	14
N_2(g)	19	TiB_2(s)	17	Ta_2C(s)	15	ZrO(g)	14
O(g)	19	ZrB_2(s)	17	Cr_3C_2(s)	18	ZrO_2(s, l)	14
O_2(g)	19	HfB_2(s)[a]	17	Cr_7C_3(s)	18	HfO_2(s, l)	14
Ti(s, l)	17	V_3B_2(s)	15	Mo_2C(s)[a]	14	VO_2(s, l)	14
Ti(g)	17	VB(s)	15	WC(s)	14	V_2O_5(s, l)	14
Zr(s, l)	17	V_3B_4(s)	15	W_2C(s)	15	NbO(s, l)	14
Zr(g)	17	V_2B_3(s)	15	TiN(s)	17	NbO_2(s, l)	14
Hf(s, l)	14	V_5B_6(s)	15	ZrN(s)	17	Nb_2O_5(s, l)	14
Hf(g)	16	VB_2(s)	15	HfN(s)[a]	14	Ta_2O_5(s, l)	14
V(s, l)	15	NbB_2(s)	14	VN(s, l)	18	Cr_2O_3(s, l)	18
V(g)	18	TaB_2(s)	14	NbN(s, l)	14	MoO_2(s)	18
Nb(s, l)	14	CrB(s)[a]	–	Nb_2N(s)	14	MoO_3(s, l)	18
Nb(g)	18	CrB_2(s)[a]	–	TaN(s)	15	WO_2(s, l)	18
Ta(s)	14	TiC(s)	17	Ta_2N(s)	15	WO_3(s, l)	18

[a] Extrapolated to higher temperatures.

stoichiometry of the reaction and on Equation 5, equilibrium constants (K_p) for individual reactions and equilibrium partial pressures of different gaseous species are computed. For those reactions containing only substances in the condensed phase, ΔG^0 values are reported. For the representative compound of a given class of materials, the equilibrium constants of individual reactions are given as a function of temperature in graphical representation. In the interest of numerical accuracy and for the convenience of the user, the ΔG^0 and equilibrium constant values of all individual reactions are expressed in the form of linear, two-term equations. The numerical constants a and b of these equations are listed in tables. In this way, the results provided can be used for specific reactions alone, and in combination with other reactions of the same and of other systems.

The sources of the thermochemical values of the elements and compounds used in the present computations are listed in Table I. The heat capacity and entropy values of HfN and HfB_2 are given in the literature [14] only up to 1500 and 1700 K, respectively. Thermochemical data for the molybdenum and tungsten borides and nitrides are not readily available. There are various sources of thermochemical data in the literature for a given material. The selection of the sources used in this work is based on a critical analysis of literature data and on a comparative evaluation of theoretical predictions and experimental evidence.

3. Results and discussion

Among the important criteria for the assessment of thermochemical properties and for the application of composite materials at high temperatures is the stability of their constituents with respect to decomposition (volatilization) and their "inertness" with respect to chemical reactivity. Based on common experience and on available literature [1], some stability criteria of these materials have been established. Vapour pressures or dissociation pressures of about 10^{-6} atm or less present no long-term stability problems. However, vapour pressures of about 10^{-3} atm or higher are considered excessive and may cause serious damage and failure of components of a system. Thus, vapour pressures of about 10^{-5} atm may be taken as an upper-bound safety limit.

These criteria are, of course, qualitative guidelines, and individual materials have to be evaluated under actual conditions. Detailed analyses of the decomposition behaviour of these materials involve specific assumptions about the reaction mechanisms. Thermodynamic analyses of individual chemical reactions have been carried out to estimate their relative importance and that of different vapour species participating in the decomposition process. The chemical stabilities of the refractory borides, carbides, nitrides and oxides will be discussed in separate sections below.

3.1. Stability of metal borides

The decomposition reactions of the refractory metal borides presently considered to yield different product species are represented by the following generalized equations:

$$MB_x(s, l) = M(s, l) + xB(s, l) \qquad (8)$$

$$MB_x(s, l) = M(g) + xB(s, l) \qquad (9)$$

$$MB_x(s, l) = M(s, l) + xB(g) \qquad (10)$$

$$MB_x(s, l) = M(g) + xB(g) \qquad (11)$$

where M is a refractory metal of group IV, V, and VI elements and x is the number of boron atoms per metal atom. Because of the large number of compounds and reactions involved, a detailed representation of the K_p values against reciprocal temperature

TABLE II Values of a and b in the relation $\log K_p = a + (10^4 b/T)$ for different decomposition reactions of refractory borides; the headings indicate the type of reaction products, but not in all cases the stoichiometry

Compound[a]	M(s, l) + B(s, l)[b]	M(s, l) + B(g)	M(g) + B(s, l)	M(g) + B(g)
TiB	$a = 30.86$ $b = 0.4414$	$a = 8.273$ $b = -3.762$	$a = 7.926$ $b = -3.308$	$a = 15.358$ $b = -6.191$
TiB_2	$a = 50.89$ $b = 0.8353$	$a = 16.595$ $b = -7.283$	$a = 8.348$ $b = -3.919$	$a = 23.689$ $b = -9.711$
ZrB_2	$a = 59.20$ $b = 0.955$	$a = 16.746$ $b = -7.515$	$a = 8.481$ $b = -4.942$	$a = 23.82$ $b = -10.73$
HfB_2	$a = 70.48$ $b = 0.4847$	$a = 16.088$ $b = -7.554$	$a = 7.678$ $b = -5.405$	$a = 23.01$ $b = -11.20$
V_3B_2[a]	$a = 64.56$ $b = 0.3745$	$a = 16.187$ $b = -7.395$	$a = 23.857$ $b = -9.620$	$a = 39.34$ $b = -15.42$
VB[a]	$a = 29.42$ $b = 0.1689$	$a = 8.065$ $b = -3.627$	$a = 7.933$ $b = -3.394$	$a = 15.781$ $b = -6.302$
V_3B_4[a]	$a = 102.2$ $b = 0.6417$	$a = 32.20$ $b = -14.15$	$a = 24.39$ $b = -10.58$	$a = 55.35$ $b = -22.18$
V_2B_3[a]	$a = 72.10$ $b = 0.4717$	$a = 24.09$ $b = -10.51$	$a = 16.35$ $b = -7.159$	$a = 39.58$ $b = -15.86$
V_5B_6[a]	$a = 118.5$ $b = 2.846$	$a = 52.04$ $b = -21.41$	$a = 44.18$ $b = -17.38$	$a = 90.62$ $b = -34.78$
VB_2[a]	$a = 41.98$ $b = 0.3029$	$a = 16.066$ $b = -6.868$	$a = 8.293$ $b = -3.741$	$a = 23.786$ $b = -9.544$
NbB_2	$a = 36.09$ $b = 0.2555$	$a = 15.766$ $b = -6.701$	$a = 8.304$ $b = -4.738$	$a = 23.64$ $b = -10.53$
TaB_2	$a = 43.31$ $b = 0.325$	$a = 15.862$ $b = -6.889$	$a = 7.860$ $b = -5.172$	$a = 23.18$ $b = -10.96$
CrB[a]	$a = 17.21$ $b = 0.0179$	$a = 7.753$ $b = -3.284$	$a = 7.274$ $b = -2.427$	$a = 15.017$ $b = -5.328$
CrB_2[a]	$a = 18.25$ $b = 0.1705$	$a = 15.843$ $b = -6.288$	$a = 7.609$ $b = -2.529$	$a = 23.145$ $b = -8.330$

[a] All K_p values are for the temperature range 500 to 3000 K, except for those compounds marked ([a]) which are for the temperature range 500 to 2500 K.

[b] ΔG^0 values from $\Delta G^0 = a + (10^4 b/T)$ are given in kcal mol^{-1} for the reactions in this column only (1 cal = 4.19 J).

for the individual solid–gas phase reactions of TiB and TiB_2 is given in Fig. 1. The temperature dependence of the equilibrium constants of the other group IV, V, and VI borides is represented by the a and b terms of the corresponding linear equations listed in Table II.

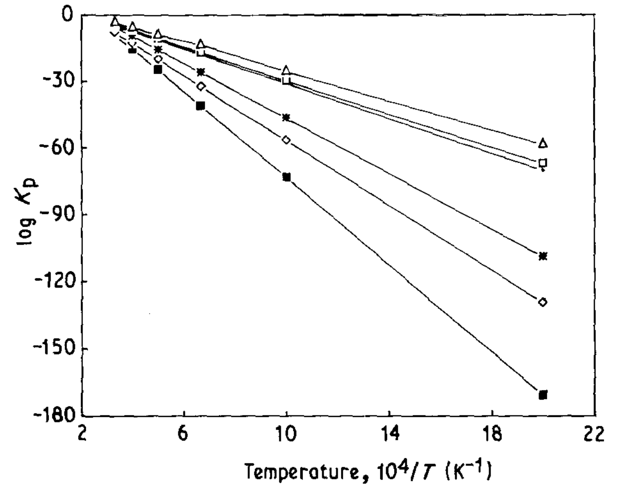

Figure 1 Equilibrium constants as a function of reciprocal temperature for the main solid–gas phase decomposition reactions of TiB(s) and TiB_2(s). (△) TiB(s) = Ti(g) + B(s, l); (□) TiB(s) = Ti(s, l) + B(g); (*) TiB(s) = Ti(g) + B(g); (●) TiB_2(s) = Ti(g) + 2B(s, l); (◇) TiB_2(s) = Ti(s, l) + 2B(g); (■) TiB_2(s) = Ti(g) + 2B(g).

No reliable thermochemical data for the borides of molybdenum and tungsten are presently available. Therefore, these compounds are not included in the present investigation.

It is evident from Fig. 1 that at lower temperatures the reactions yielding gaseous species are rather insignificant with respect to decomposition of TiB and TiB_2. But with increasing temperature and owing to the increasing dominance of the entropy contribution, these reactions may become important for the stability evaluation of the materials. If the gaseous molecules can escape from the reaction interface, even a minor reaction may become critical and become a "runaway reaction". It is also apparent from Fig. 1 that TiB is less stable with respect to decomposition than TiB_2. It is intuitively obvious that the decomposition reactions of a given compound yielding condensed-phase products require less energy than those leading to gaseous products. Thus, under given temperature and pressure conditions, the former reactions are more critical with respect to thermal stability of the compound than the latter.

In an attempt to compare the relative thermodynamic stabilities of the metal borides investigated here, the lowest ΔG^0 values at 2000 K, corresponding to the decomposition of a given compound to condensed-phase products, are graphically represented in the

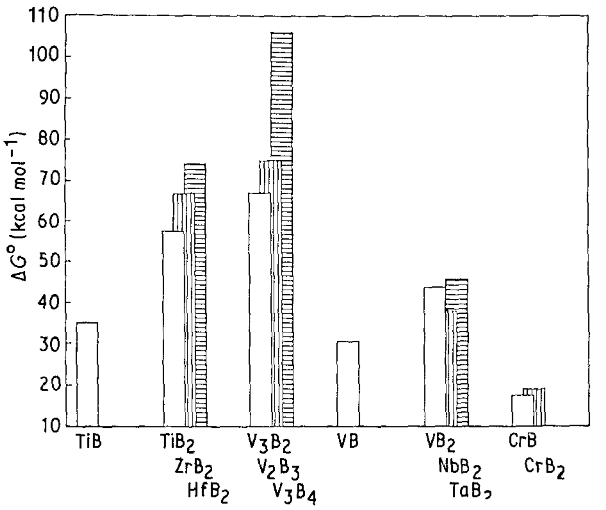

Figure 2 Standard Gibbs free energy changes of the thermodynamically most favourable condensed-phase decomposition reactions of metal borides at 2000 K (1 cal = 4.19 J).

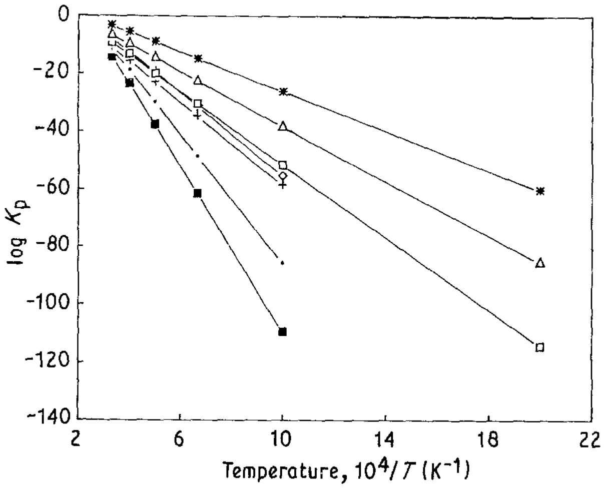

Figure 3 Equilibrium constants as a function of reciprocal temperature for the main solid–gas phase decomposition reactions of TiC(s). (∗) $TiC(s) = Ti(g) + C(s)$; (△) $TiC(s) = Ti(s, l) + C(g)$; (□) $2TiC(s) = 2Ti(s, l) + C_2(g)$; (◇) $TiC(s) = Ti(g) + C(g)$; (+) $3TiC(s) = 3Ti(s, l) + C_3(g)$; (●) $2TiC(s) = 2Ti(g) + C_2(g)$; (■) $3TiC(s) = 3Ti(g) + C_3(g)$.

form of a bar diagram in Fig. 2. In other words, the Gibbs free energy changes (under standard conditions) of the thermodynamically most favourable decomposition reactions of these metal borides are given. Within the constraints of the definition of ΔG^0 and of the meaning of activities for condensed-phase reactions, and assuming that all other conditions (e.g. kinetic limitations) are the same for different compounds, the heights of the bars in Fig. 2 provide a qualitative guideline for the relative stability of the compounds. A larger ΔG^0 value indicates a more stable compound. Apparently, with increasing atomic number of the metal atom, the stabilities of the borides increase within the same group and decrease within the same period of the periodic table for compounds of the same metal to non-metal ratio. In view of the above constraints, a further interpretation of Fig. 2 is not justified. Bolgar *et al.* [19] measured high-temperature thermodynamic properties (enthalpy and heat capacity) of transition metal refractory borides and has shown that with increasing number of boron atoms per metal atom in the compound, the bond strength of the compounds increases. The same trend is predicted in Fig. 2, based on independent thermochemical computations. These computations suggest that V_3B_4 is the most stable boride followed by V_2B_3 and HfB_2.

3.2. Stability of metal carbides

High-temperature applications of metal carbides require resistance to decomposition and to chemical attack at a free surface. The high melting points and low vapour pressures of group IV, V and VI transition-metal carbides provide the stability in vacuum and inert atmospheres of these materials. For most metal carbides, decomposition occurs by vaporization which may be congruent or incongruent. For some decomposition reactions, product species containing metal–carbon bonds have been reported. The following decomposition reactions of the above metal carbides are considered for the computational analysis:

$$MC(s,l) = M(s,l) + C(s) \tag{12}$$

$$MC(s,l) = M(g) + C(s) \tag{13}$$

$$MC(s,l) = M(s,l) + C(g) \tag{14}$$

$$2MC(s,l) = 2M(s,l) + C_2(g) \tag{15}$$

$$MC(s,l) = M(g) + C(g) \tag{16}$$

$$3MC(s,l) = 3M(s,l) + C_3(g) \tag{17}$$

$$2MC(s,l) = 2M(g) + C_2(g) \tag{18}$$

$$3MC(s,l) = 3M(g) + C_3(g) \tag{19}$$

where M is the same as above. The equilibrium constants as a function of $1/T$ for the most important solid–gas phase decomposition reactions of TiC are graphically represented in Fig. 3. The overall trend of the temperature dependence of the different decomposition reactions and the interpretation are very similar to those of TiB. Again, reactions involving gaseous products can become rather critical at elevated temperatures and seriously affect the stability of the material. The *a* and *b* values of the linear equations for the above thermodynamic functions of the other metal carbide decomposition reactions are given in Table III. Reliable thermodynamic data for MoC are presently not available. Drowart *et al.* [20] reported that at temperatures of about 2500 K and higher, TiC evaporates predominantly as Ti(g) and $C_n(g)$. The different slopes of the decomposition reactions in Fig. 3 are consistent with these observations. For HfC and TaC, Engelke *et al.* [21] reported that a vapour pressure of carbon higher than that of the metal leads to a loss of carbon at temperatures close to the melting point. A more comprehensive review of the properties of refractory carbides is given by Storms [22] and by Toth [23].

Analogous with the borides, the decomposition reactions of the metal carbides yielding exclusively condensed-phase products are more favourable than

TABLE III Values of a and b in the relation $\log K_p = a + (10^4 b/T)$ for different decomposition reactions of refractory carbides; the headings indicate the type of reaction products, but not in all cases the stoichiometry.

Compounds[a]	M(s, l) + C(s)[‡]	M(g) + C(s)	M(s, l) + C(g)	M(s, l) + C_2(g)	M(s, l) + C_3(g)	M(g) + C(g)	M(g) + C_2(g)	M(g) + C_3(g)
TiC	$a = 33.94$	$a = 7.844$	$a = 9.017$	$a = 11.639$	$a = 12.400$	$a = 16.126$	$a = 26.21$	$a = 34.42$
	$b = 0.5072$	$b = -3.401$	$b = -4.727$	$b = -6.300$	$b = -7.051$	$b = -7.147$	$b = -11.25$	$b = -14.44$
ZrC	$a = 39.48$	$a = 7.645$	$a = 8.801$	$a = 11.587$	$a = 12.491$	$a = 15.889$	$a = 25.73$	$a = 33.71$
	$b = 0.3668$	$b = -4.248$	$b = -4.784$	$b = -6.505$	$b = -7.328$	$b = -7.994$	$b = -12.94$	$b = -16.99$
HfC	$a = 48.50$	$a = 7.417$	$a = 8.731$	$a = 11.422$	$a = 12.231$	$a = 15.661$	$a = 25.28$	$a = 33.01$
	$b = 0.3271$	$b = -4.850$	$b = -4.953$	$b = -6.861$	$b = -7.860$	$b = -8.596$	$b = -14.15$	$b = -18.79$
VC[a]	$a = 18.06$	$a = 8.259$	$a = 8.811$	$a = 11.670$	$a = 12.523$	$a = 16.521$	$a = 27.09$	$a = 35.58$
	$b = 0.2933$	$b = -3.212$	$b = -4.293$	$b = -5.529$	$b = -5.857$	$b = -6.968$	$b = -10.88$	$b = -13.87$
V_2C[b]	$a = 33.45$	$a = 15.79$	$a = 8.438$	$a = 11.06$	$a = 11.53$	$a = 24.06$	$a = 42.31$	$a = 58.40$
	$b = 0.0704$	$b = -6.132$	$b = -4.524$	$b = -6.001$	$b = -6.561$	$b = -9.889$	$b = -16.73$	$b = -22.65$
NbC	$a = 31.05$	$a = 8.003$	$a = 8.362$	$a = 10.685$	$a = 11.137$	$a = 16.241$	$a = 26.45$	$a = 34.77$
	$b = 0.0743$	$b = -4.542$	$b = -4.468$	$b = -5.874$	$b = -6.381$	$b = -8.297$	$b = -13.53$	$b = -17.87$
Nb_2C[b]	$a = 39.81$	$a = 16.55$	$a = 8.93$	$a = 12.09$	$a = 12.99$	$a = 24.82$	$a = 43.83$	$a = 60.68$
	$b = 0.2736$	$b = -8.681$	$b = -4.771$	$b = -6.497$	$b = -7.300$	$b = -12.44$	$b = -21.83$	$b = -30.30$
TaC	$a = 35.10$	$a = 7.226$	$a = 8.120$	$a = 10.209$	$a = 10.408$	$a = 15.463$	$a = 24.89$	$a = 32.43$
	$b = -0.0942$	$b = -4.804$	$b = -4.482$	$b = -5.902$	$b = -6.422$	$b = -8.558$	$b = -14.05$	$b = -18.65$
Ta_2C	$a = 47.95$	$a = 14.699$	$a = 8.326$	$a = 10.473$	$a = 10.796$	$a = 22.93$	$a = 39.82$	$a = 54.84$
	$b = -0.0101$	$b = -9.199$	$b = -4.814$	$b = -6.541$	$b = -7.379$	$b = -12.95$	$b = -22.84$	$b = -31.83$
Cr_3C_2[a]	$a = 27.83$	$a = 20.995$	$a = 15.755$	$a = 9.790$	$a = 19.44$	$a = 37.50$	$a = 31.55$	$a = 84.74$
	$b = -0.3679$	$b = -6.551$	$b = -7.934$	$b = -4.876$	$b = -9.755$	$b = -14.06$	$b = -11.01$	$b = -28.15$
Cr_7C_3	$a = 54.87$	$a = 49.20$	$a = 23.18$	$a = 14.251$	$a = 9.292$	$a = 73.97$	$a = 65.05$	$a = 60.08$
	$b = -0.7351$	$b = -15.12$	$b = -12.08$	$b = -7.501$	$b = -5.066$	$b = -26.39$	$b = -21.80$	$b = -19.37$
Mo_2C[a]	$a = 13.50$	$a = 14.921$	$a = 8.011$	$a = 10.08$	$a = 10.16$	$a = 23.19$	$a = 40.40$	$a = 55.64$
	$b = -0.0866$	$b = -7.084$	$b = -3.999$	$b = -4.943$	$b = -4.980$	$b = -10.84$	$b = -18.62$	$b = -25.50$
WC	$a = 7.653$	–	$a = 7.989$	$a = 10.84$	$a = 11.30$	–	–	–
	$b = 0.0678$	–	$b = -3.932$	$b = -4.858$	$b = -4.851$	–	–	–
W_2C	$a = 31.64$	–	$a = 6.037$	$a = 6.039$	$a = 4.163$	–	–	–
	$b = -1.397$	–	$b = -3.805$	$b = -4.548$	$b = -4.391$	–	–	–

[a] All K_p values are for the temperature range 500 to 3000 K, except ([a]) for 500 to 2500 K and ([b]) for 500 to 2000 K.
[‡] ΔG^0 values from $\Delta G^0 = a + (10^4 b/T)$ given in kcal mol^{-1} for the reactions in this column only (1 cal = 4.19 J).

those yielding gaseous products within a given temperature range. Thus, the thermal stability of the metal carbides is limited by the former reactions. Within the same constraints as discussed above for the metal borides, the relative stabilities of the metal carbides at 2000 K are compared in terms of the ΔG^0 values for the most favourable condensed-phase decomposition reactions in Fig. 4. Under these conditions, it is apparent from Fig. 4 that the stabilities of the monocarbides increase with atomic number of the metal in groups IV and V and for the di-metal carbides of group V at 2000 K.

For the chromium, molybdenum and tungsten carbides the trend is different owing to the molecularity effect. But on a per-atom basis, the trend is the same. Electronic band calculations for these carbides [24–26] suggest that electron transfer occurs from the metal to the interstitial carbon atoms upon bond formation in the above carbides. This direction of transfer would lead to the formation of a stronger C–M bond associated with a weakened M–M bond in MC relative to the pure metal. Shohoji [27] estimated the carbon–metal interactions in carbides and reported that the C–M bonds in group IV metal carbides tend to strengthen with increasing atomic number of the metal from titanium to hafnium. These theoretical considerations [27] are consistent with our thermochemical predictions concerning the relative stabilities of TiC, ZrC and HfC based on their decomposition reactions evaluated in this work (Fig. 4).

The metal–carbon bond energy ($E_{C\text{–}M}$) of the vanadium, niobium and tantalum carbides was also estimated by Shohoji [27]. The trend in the $E_{C\text{–}M}$ values is the same as that for the titanium, zirconium and hafnium carbides. But the $E_{C\text{–}M}$ values of group V

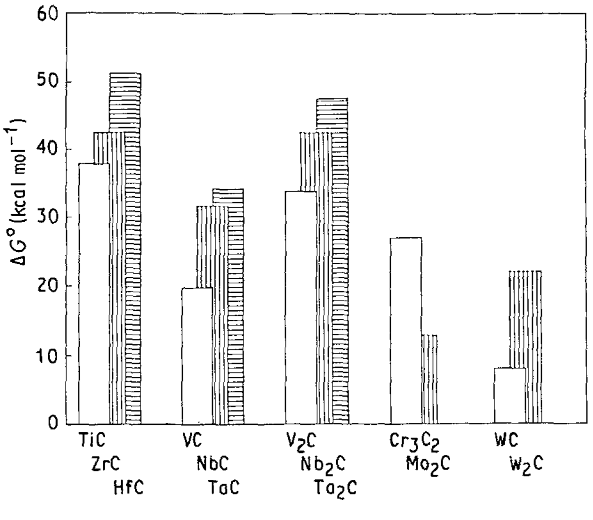

Figure 4 Standard Gibbs free energy changes of the thermodynamically most favourable condensed-phase decomposition reactions of metal carbides at 2000 K (1 cal = 4.19 J).

metal carbides are less negative (i.e. weaker C–M bond strength) than those of the group IV carbides. These trends are also reflected in our thermodynamic estimations. Our predictions are also supported by the suggestion of Storms [22], relating the increases in the melting points of group IV and V metal carbides relative to those of the pure group IV and V metals to the different C–M bond strengths in these metal carbides. Because the metal–carbon bonds in group IV (titanium, zirconium and hafnium) carbides are much stronger than the bonds in titanium, zirconium and hafnium metals, these carbides show a considerable increase in their melting points relative to those of the pure metals.

The corresponding differences in M–C and M–M bond energies in group V (vanadium, niobium and tantalum) carbides and metals, respectively, are less pronounced, which leads to the smaller increases in melting points of group V carbides relative to those of the pure metals. Samsonov *et al.* [28] presented a configurational model for these materials, according to which the degree of localization of valence electrons in stable configurations of titanium, zirconium and hafnium is not high. Thus, on forming carbides, these metals employ a greater part of their non-localized electrons for M–C bond formation. This leads to stabilization of the sp^3 configuration of carbon atoms, and titanium, zirconium and hafnium carbides are formed with strong metal–carbon bonds.

Based on our thermodynamic estimations, the stabilities of group IV, V and VI carbides are in the order of group IV > group V > group VI, and HfC is the most stable of these carbides.

3.3. Stability of metal nitrides

The main decomposition reactions of the metal nitrides considered in this work are given by the reactions

$$\mathrm{MN(s,l)} = \mathrm{M(s,l)} + \tfrac{1}{2}\mathrm{N_2(g)} \qquad (20)$$

$$\mathrm{MN(s,l)} = \mathrm{M(g)} + \tfrac{1}{2}\mathrm{N_2(g)} \qquad (21)$$

The temperature dependences of the equilibrium constants of the above decomposition reactions of titanium, zirconium and hafnium nitrides are given in Fig. 5. It is apparent from the results that at lower temperatures the reactions leading to M(g) are rather insignificant. At higher temperatures these reactions become increasingly more important, reflecting the increased dominance of the entropy contribution to the free energy of reaction. Combined with a continuous escape of the gaseous products under non-equilibrium conditions from the reaction interface, these reactions may cause catastrophic failure of the materials.

The *a* and *b* values of the linear $\log K_p$ against $1/T$ equations of the metal nitride reactions considered here are given in Table IV. The maximum $\log K_p$ values associated with the dominant reactions of group IV, V, and VI metal nitrides at 2000 K are graphically represented in Fig. 6. From this diagram it is evident that the stabilities of group IV and V metal nitrides increase with increasing atomic number of the metal within the same group and with increasing number of metal atoms in the compound. Reliable thermodynamic data for molybdenum and tungsten nitrides are not available. The relative thermodynamic stabilities of group IV, V and VI refractory nitrides are in the order group IV > group V > group VI.

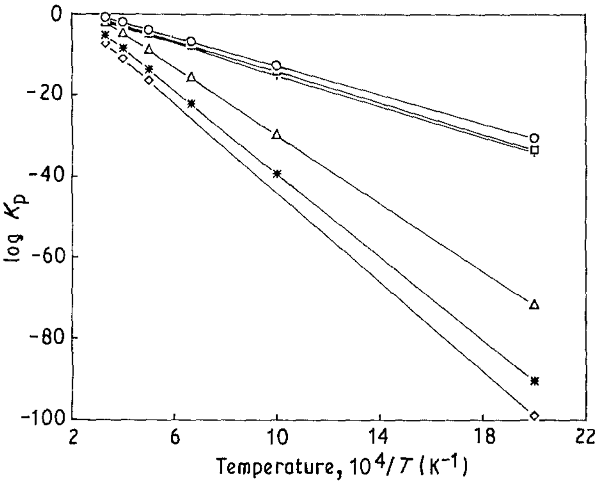

Figure 5 Equilibrium constants as a function of reciprocal temperature for the main solid–gas phase decomposition reactions of TiN(s), ZrN(s) and HfN(s). (○) $\mathrm{TiN(s)} = \mathrm{Ti(s,l)} + \tfrac{1}{2}\mathrm{N_2(g)}$; (△) $\mathrm{TiN(s)} = \mathrm{Ti(g)} + \tfrac{1}{2}\mathrm{N_2(g)}$; (□) $\mathrm{ZrN(s)} = \mathrm{Zr(s,l)} + \tfrac{1}{2}\mathrm{N_2(g)}$; (*) $\mathrm{ZrN(s)} = \mathrm{Zr(g)} + \tfrac{1}{2}\mathrm{N_2(g)}$; (●) $\mathrm{HfN(s)} = \mathrm{Hf(s,l)} + \tfrac{1}{2}\mathrm{N_2(g)}$; (◇) $\mathrm{HfN(s)} = \mathrm{Hf(g)} + \tfrac{1}{2}\mathrm{N_2(g)}$.

3.4. Stability of metal oxides

The decomposition reactions presently considered for the selected refractory metal oxides are

$$\mathrm{M}_x\mathrm{O}_y\mathrm{(s,l)} = x\mathrm{M(s,l)} + (y/2)\mathrm{O_2(g)} \qquad (22)$$

$$\mathrm{M}_x\mathrm{O}_y\mathrm{(s,l)} = x\mathrm{M(g)} + (y/2)\mathrm{O_2(g)} \qquad (23)$$

TABLE IV Values of *a* and *b* in the relation $\log K_p = a + (10^4 b/T)$ for the decomposition reactions of refractory metal nitrides; the headings indicate the type of reaction products, but not in all cases the stoichiometry

Compounds[a]	$\mathrm{M(s,l)} + \tfrac{1}{2}\mathrm{N_2(g)}$	$\mathrm{M(g)} + \tfrac{1}{2}\mathrm{N_2(g)}$
TiN	$a = 4.938$	$a = 12.031$
	$b = -1.762$	$b = -4.190$
ZrN	$a = 4.847$	$a = 11.936$
	$b = -1.091$	$b = -5.122$
HfN	$a = 4.409$	$a = 11.707$
	$b = -1.901$	$b = -5.508$
VN	$a = 4.305$	$a = 11.910$
	$b = -1.121$	$b = -3.789$
NbN	$a = 3.875$	$a = 11.753$
	$b = -1.194$	$b = -5.203$
Nb_2N[a]	$a = 4.110$	$a = 17.064$
	$b = -1.275$	$b = -9.069$
TaN	$a = 4.187$	$a = 11.491$
	$b = -1.272$	$b = -5.352$
Ta_2N	$a = 4.336$	$a = 19.199$
	$b = -1.364$	$b = -9.526$
CrN	$a = 3.847$	$a = 11.667$
	$b = -0.594$	$b = -2.669$
Cr_2N[a]	$a = 3.590$	$a = -18.104$
	$b = -0.632$	$b = -4.719$

[a] All K_p values are for the 500 to 3000 K temperature range except (a) which are for the 500 to 2500 K temperature range.

TABLE V Values of a and b in the relation $\log K_p = a + (10^4 b/T)$ for the decomposition reactions of refractory metal oxides; the headings indicate the type of reaction products, but not in all cases the stoichiometry

Compound[a]	$M(s, l) + O_2(g)$	$M(g) + O_2(g)$	$MO_2(s, l) + MO(s, l)$‡	$MO_2(s, l) + MO(g)$	$MO(s, l) + O_2(g)$	$MO(g) + O_2(g)$	$MO_2(s, l) + O_2(g)$
TiO	$a = 7.216$ $b = -5.350$	$a = 21.40$ $b = -10.21$	– –	– –	– –	– –	– –
TiO_2	$a = 9.159$ $b = -4.906$	$a = 16.254$ $b = -7.334$	– –	– –	$a = 11.102$ $b = -4.460$	$a = 27.030$ $b = -9.873$	– –
Ti_2O_3	$a = 25.96$ $b = -15.66$	$a = 54.34$ $b = -25.37$	$a = 8.724$ $b = 0.120$	$a = 8.180$ $b = -2.955$	$a = 5.774$ $b = -2.480$	$a = 21.70$ $b = -7.892$	– –
Ti_3O_5	$a = 21.35$ $b = -12.67$	$a = 42.63$ $b = -19.96$	$a = 15.96$[b] $b = -0.334$	$a = 7.466$ $b = -2.896$	$a = 10.51$ $b = -4.647$	$a = 34.40$ $b = -12.77$	– –
ZrO_2	$a = 9.629$ $b = -5.709$	$a = 16.684$ $b = -8.926$	– –	– –	– –	$a = 13.30$ $b = -5.973$	– –
HfO_2	$a = 8.958$ $b = -5.766$	$a = 15.891$ $b = -9.409$	– –	– –	– –	– –	– –
VO_2[a]	$a = 7.537$ $b = -3.653$	$a = 15.250$ $b = -6.329$	– –	– –	– –	– –	– –
V_2O_5	$a = 18.375$ $b = -7.887$	$a = 30.74$ $b = -12.70$	– –	– –	– –	– –	$a = 3.572$ $b = -0.599$
NbO	$a = 4.086$ $b = -2.104$	$a = 11.963$ $b = -5.932$	– –	– –	– –	– –	– –
NbO_2	$a = 8.439$ $b = -4.085$	$a = 16.321$ $b = -7.914$	– –	– –	$a = 4.357$ $b = -1.981$	– –	– –
Nb_2O_5	$a = 20.474$ $b = -9.770$	$a = 36.24$ $b = -17.43$	– –	– –	$a = 12.554$ $b = -5.579$	– –	$a = 3.697$ $b = -1.607$
Ta_2O_5	$a = 20.66$ $b = -10.52$	$a = 35.340$ $b = -18.67$	– –	– –	– –	– –	– –
Cr_2O_3	$a = 13.562$ $b = -5.898$	$a = 27.713$ $b = -9.961$	– –	– –	– –	– –	– –
MoO_2	$a = 8.687$ $b = -3.011$	$a = 16.195$ $b = -6.426$	– –	– –	– –	– –	– –
MoO_3[b]	$a = 12.035$ $b = -3.891$	$a = 19.679$ $b = -7.315$	– –	– –	– –	– –	– –
WO_2[a]	$a = 8.904$ $b = -3.034$	– –	– –	– –	– –	– –	– –
WO_3	$a = 12.463$ $b = -4.332$	– –	– –	– –	– –	– –	– –

[a] All K_p values are for the temperature range 500 to 3000 K, except ([a]) which are for 500 to 2500 K and ([b]) for 500 to 2000 K.

[b] ΔG^0 values from $\Delta G^0 = a + (10^4 b/T)$ are in kcal mol^{-1} for the reactions in this column only (1 cal = 4.19 J).

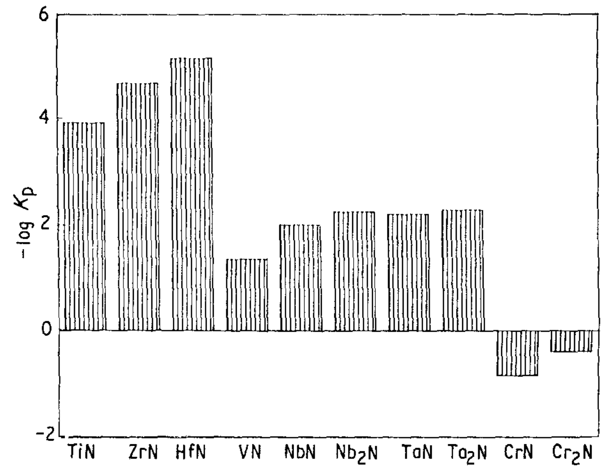

Figure 6 Equilibrium constants of the thermodynamically most favourable decomposition reactions of metal nitrides at 2000 K.

$$
\begin{aligned}
M_2O_3(s, l) &= MO_2(s, l) + MO(s, l) && (24)\\
M_2O_3(s, l) &= MO_2(s, l) + MO(g) && (25)\\
MO_2(s, l) &= MO(s, l) + \tfrac{1}{2}O_2(g) && (26)\\
MO_2(s, l) &= MO(g) + \tfrac{1}{2}O_2(g) && (27)\\
M_3O_5(s, l) &= 2MO_2(s, l) + MO(s, l) && (28)\\
M_3O_5(s, l) &= 2MO_2(s, l) + MO(g) && (29)\\
MO_3(s, l) &= MO_2(s, l) + \tfrac{1}{2}O_2(g) && (30)\\
M_2O_5(s, l) &= 2MO_2(s, l) + \tfrac{1}{2}O_2(g) && (31)
\end{aligned}
$$

The temperature dependences of the equilibrium constants for the TiO and TiO_2 decomposition reactions are shown in Fig. 7. The *a* and *b* values of the linear equations of the $\log K_p$ and ΔG^0 values of the refractory oxides are given in Table V. The maximum $\log K_p$ values associated with the dominant decomposition reactions of the different refractory oxides at 2000 K are shown in Fig. 8. It is apparent from Fig. 8 that for the same composition, the stabilities of group IV, V, and VI oxides increase with increasing atomic number of the metal within the same group. Also, the higher metal oxides are more stable than those of the lower oxidation states.

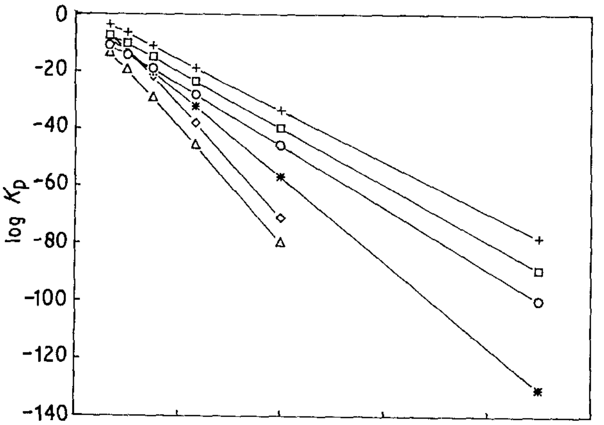

Figure 7 Equilibrium constants as a function of reciprocal temperature for the main solid–gas phase decomposition reactions of TiO(s) and TiO_2(s). (○) $2TiO(s) = 2Ti(s, l) + O_2(g)$; (△) $2TiO(s) = 2Ti(g) + O_2(g)$; (□) $TiO_2(s) = Ti(s, l) + O_2(g)$; (*) $TiO_2(s) = Ti(g) + O_2(g)$; (+) $2TiO_2(s) = 2TiO(s, l) + O_2(g)$; (◇) $2TiO_2(s) = 2TiO(g) + O_2(g)$.

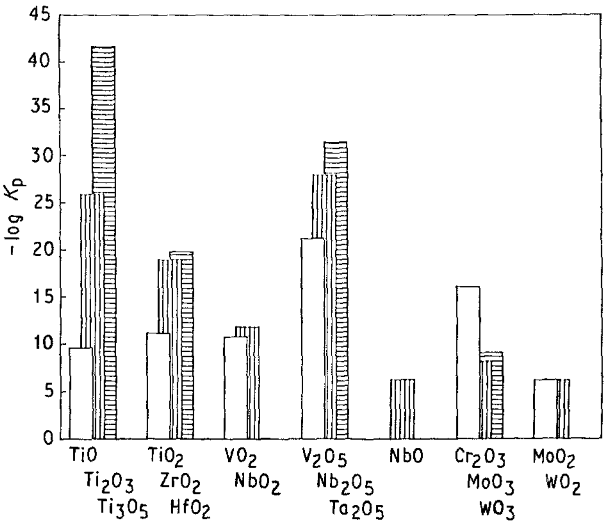

Figure 8 Equilibrium constants of the thermodynamically most favourable decomposition reactions of metal oxides at 2000 K.

4. Summary and conclusions

The equilibrium thermodynamic computations suggest that at 2000 K, V_3B_4 is the most stable boride followed by V_2B_3 and HfB_2. Of the refractory carbides and nitrides, HfC and HfN are predicted to be the most stable compounds. In the case of refractory oxides, Ti_3O_5 and Ta_2O_5 are the most stable ones with respect to decomposition at 2000 K. Based on the thermodynamic functions (ΔG^0, K_p), the stabilities of refractory metal borides, carbides, nitrides, and oxides are in the order

$$\text{oxides} > \text{borides} > \text{carbides} > \text{nitrides}$$

The predictions of our thermodynamic computations agree well with experimental observations and with other theoretical computations reported in the literature. The thermal stability of materials is one of the most important criteria for the selection of constituent materials for high-temperature composites. Other relevant considerations include mechanical properties, density, vaporization (mass loss), oxidation and thermal shock resistance.

The usefulness of our thermochemical computations is multifold. Based on the results obtained, work is in progress to estimate the vaporization (mass loss) rates of these materials under different conditions. In addition, the data produced in this work provide valuable guidelines for the selection of materials and for the prediction of their relative stabilities as constituents (fibre, matrix and coatings) in composite systems. Corresponding computations for selected systems are in progress in our laboratory. Most importantly, these theoretical considerations provide a scientific basis for a meaningful modification of present and design of new high-temperature materials.

Acknowledgements

The authors are pleased to acknowledge the support of this research by the Office of Naval Research–Defense Advanced Research Project Agency (ONR–DARPA) through the Center for High Temperature Advanced Structural Composites at Rensselaer.

References

1. W. B. HILLIG, in "Tailoring Multiphase and Composite Ceramics", Materials Science Research, Vol. 20, edited by R. E. Tressler, G. L. Messing, C. G. Pantano and R. E. Newnham (Plenum, New York, 1986) p. 697.
2. L. CHRISTODOULOU, P. A. PARISH and C. R. CROWE, *Mater. Res. Soc. Symp. Proc.* **120** (1988) 29.
3. R. K. VISWANADHAM, J. D. WHITTENBERGER, S. K. MANNAN AND B. SPRISSLER, *ibid.* **120** (1988) 89.
4. K. VEDULA, A. ABADA and W. S. WILLIAMS, *ibid.* **120** (1988) 61.
5. Proceedings of 2nd Conference on Advanced Materials for Alternative-Fuel-Capable Heat Engines, Monterey, California, August 1981, EPRI-RD-2369-ST (Electric Power Research Institute, Palo Alto, California, 1982).
6. W. J. LACKEY, D. P. STINTON, G. A. CERNY, A. C. SCHAFFHAUSER and L. L. FEHRENBACHER, *Adv. Ceram. Mater.* **2** (1) (1987) 24.
7. L. H. ROVNER and G. R. HOPKINS, *Nucl. Technol.* **29** (1976) 204.
8. K. SHOBU, T. WATANABE, Y. ENOMOTO, K. UMEDA and Y. TSUYA, *J. Amer. Ceram. Soc.* **70**(5) (1987) C-103.
9. B. L. MORDIKE, *Wear* **3** (1960) 374.
10. Y. G. TKACHENKO, S. S. ORDAN'YAN, D. Z. YURCHENKO, V. K. YULYUGIN and D. V. CHUPOV, *Sov. Powder Metall. Metal Ceram.* (English translation) **22**(1) (1983) 137.
11. M. SINGH and H. WIEDEMEIER, in "Interfacial Phenomena in Composite Materials, '89", edited by F. R. Jones (Butterworths, London, 1989) p. 303.
12. H. WIEDEMEIER and M. SINGH, in Symposium on "High Temperature Chemistry of Composite Materials", 176th Meeting of the Electrochemical Society, Hollywood, Florida (1989) p. 753.
13. *Idem*, in "Interfaces in Metal–Ceramics Composites", edited by R. Y. Lin, R. J. Arsenault, G. P. Martins and S. G. Fishman (The Minerals, Metals and Materials Society, Warrendale, PA, 1989) p. 125.
14. I. BARIN and O. KNACKE, "Thermochemical Properties of Inorganic Substances" (Springer, Berlin, 1973).
15. *Idem*, "Thermochemical Properties of Inorganic Substances", Supplement (Springer, Berlin, 1977).
16. D. R. STULL and H. PROPHET, "JANAF Thermochemical Tables", 2nd Edn (National Bureau of Standards, Washington, DC, 1971).
17. M. W. CHASE Jr, C. A. DAVIES, J. R. DOWNEY Jr., D. J. FRURIP, R. A. McDONALD and A. N. SYVERUD, "JANAF Thermochemical Tables", 3rd Edn (National Bureau of Standards, Washington, DC, 1985).
18. M. W. CHASE Jr, J. L. CURNUTT, R. A. McDONALD and A. N. SYVERUD, "JANAF Thermochemical Tables", Supplement (National Bureau of Standards, Washington, DC, 1978).
19. A. S. BOLGAR, A. B. LYASHCHENKO, L. A. KLOCHKOV, A. V. BLINDER, Y. B. MURATOV, M. I. SERBOVA and V. V. FESENKO, *J. Less-Common Met.* **117** (1986) 303.
20. J. DROWART, G. DEMARIA and M. G. INGHRAM, *J. Chem. Phys.* **29** (1958) 1015.
21. J. L. ENGELKE, F. A. HALDEN and E. F. FARLEY, US Air Force Report WADC-TR-59-654 (Stanford Research Institute, February 1960).
22. E. K. STORMS, "The Refractory Carbides" (Academic, New York, 1967).
23. L. TOTH, "Transition Metal Carbides and Nitrides" (Academic, New York, 1971).
24. T. HORI, H. ADACHI and S. IMATO, *Trans. Jpn Inst. Met.* **18** (1977) 31.
25. L. P. MOKHRACHEVA, V. A. TSKHAI and P. V. GELD, *Phys. Status Solidi* (*b*) **84** (1977) 465.
26. *Idem, ibid.* **87** (1978) 49.
27. N. SOHOJI, *Mater. Chem. Phys.* **17** (1981) 391.
28. G. V. SAMSONOV, A. S. BOLGAR, E. A. GUSEVA, L. A. KLOCHKOV, B. A. KOVENSKAYA, T. I. SEREBRYAKOVA, I. I. TIMOFEEVA, A. G. TURCHANIN and V. V. FRESENKO, *High Temp.–High Press.* **5** (1973) 29.

Received 5 December 1989
and accepted 2 August 1990