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Thermodynamic Aspects of TiAl and $TiSi_2$ Oxidation: The Al–Ti–O and Si–Ti–O Phase Diagrams

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Thermodynamic data from the literature were used to calculate the activity variations of Ti and Al in the Ti-Al system at 700, 900, and 1100°C and of Ti and Si in the Ti-Si system at 800, 1000, and 1300°C. The activity data were then applied to estimate the stable oxide phase in equilibrium with the metal phase, assuming that the activity of the oxide phase was unity. It was found that in the Ti-Al-O system the stable oxide changed from TiO to Al_2O_3 in the existence region of the TiAl phase, while in the Ti-Si-O system a comparable change from Ti-oxide to SiO_2 occurred in the existence region of the Ti_5Si_3 phase. The significance of these results to the oxidation of intermetallics in the Ti-Al and Ti-Si systems is discussed briefly.

KEY WORDS: metal activity variation; Ti-Al system; Ti-Si system; Ti-Al-O phase diagram; Ti-Si-O phase diagram.

INTRODUCTION

Metallic materials can be protected against high-temperature oxidation only by the formation of scales consisting of Cr_2O_3, Al_2O_3, or SiO_2, because only these oxides have a sufficiently slow growth rate. Cr_2O_3 undergoes evaporation by forming gaseous CrO_3 at high temperatures so that materials with such scales can be used only up to temperatures of approximately 1000°C. For even higher temperatures only the oxides Al_2O_3 and SiO_2 remain as scale-forming compounds.

One necessary, but not sufficient, prerequisite for the formation of a dense and continuous scale of Al_2O_3 or SiO_2 on the surface of an alloy is

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that this oxide be the most stable of all possible oxides, otherwise it would be reduced by the base metal or other components of the alloy. Thermodynamic calculations of the oxide stabilities have to take into account the activities of the various components of the alloy, and, if necessary, those of the oxide, too. Fortunately, the oxides Al_2O_3 and SiO_2 are among the most stable oxides, otherwise their slow growth rate could not be used to protect alloys.

Al_2O_3 and SiO_2 scale formation on the present Fe-, Ni-, and Co-base high-temperature materials does not generally cause difficulties from the thermodynamic point of view, because the oxygen equilibrium pressures of the pure metal/oxide equilibria of Al and Si are many orders of magnitude lower than those of Fe, Ni, and Co, (Fig. 1). Moreover, the activities do not depart significantly from the atom fraction in solid solutions.

The situation is distinctly different if intermetallic phases with titanium as one of the main components are considered. Two aspects are important:

- The oxygen equilibrium pressures of Al/Al_2O_3 and Ti/TiO are very

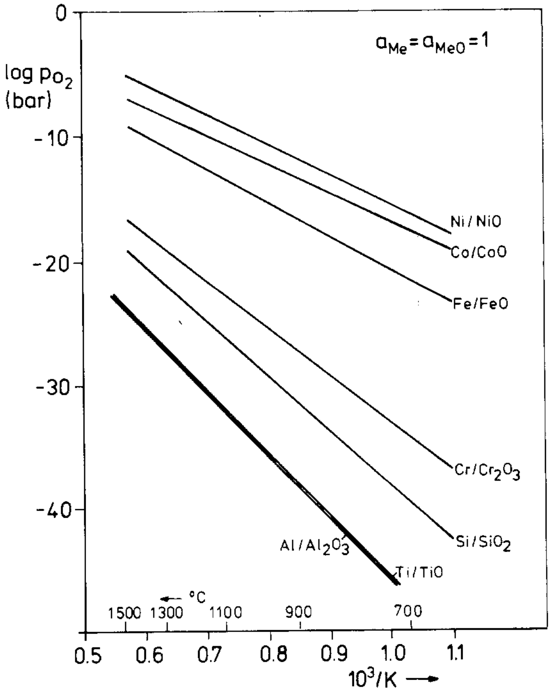

Fig. 1. Oxygen equilibrium pressures of selected pure metal/oxide systems.

similar, whereas the Si/SiO$_2$ equilibrium pressure is several orders of magnitude higher than that of Ti/TiO (Fig. 2). SiO$_2$ could be reduced by titanium if all activities are unity. Thus, it would be unstable as a protective scale.

- The activities of metals in systems with intermetallic phases can depart strongly from ideal (Raoultian) behavior, as for example, in the Ni–Al system.[1,2] This, again, strongly affects the oxygen pressure of the metal/oxide equilibria, as will be shown in the following.

From this brief introduction it follows that correct statements on the stability of oxides on intermetallics can be made only if the activity variation of the metals in the system under consideration is known.

The activities of Ti and Al in the binary Ti–Al system and of Ti and Si in the Ti–Si system have been calculated using existing thermodynamic data. Thus, the essential prerequisites for estimating oxide stabilities in these two systems are available.

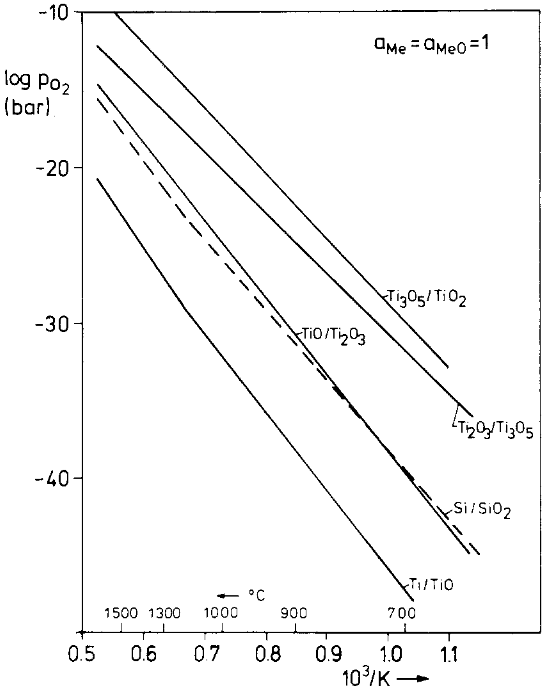

Fig. 2. Oxygen equilibrium pressures in the Si–O and Ti–O systems.

THE Ti–Al–O SYSTEM

Metal/Oxygen Equilibrium Pressures

The activity variation of Al and Ti in the Ti–Al system at 700, 900, and 1100°C is shown in Fig. 3. These values are based on data in Ref. 3. Very large deviations from ideal behavior exist, which increase with decreasing temperature. This is to be expected because the binding forces in the intermetallics increase with decreasing temperature. The activities remain constant in two-phase regions. Greater changes occur in the stability ranges of the various single phases. The exact activity behavior in a single-phase region has not been estimated, because it did not appear to be critical for the following considerations.

The oxygen equilibrium pressure of a metal/oxide mixture can be calculated from the free energy of formation, ΔG, of the corresponding reaction of oxide formation. For the formation of Al_2O_3

$$2Al + \tfrac{3}{2}O_2 = Al_2O_3 \tag{1}$$

$$\Delta G_1 = RT \ln K_1 \tag{2}$$

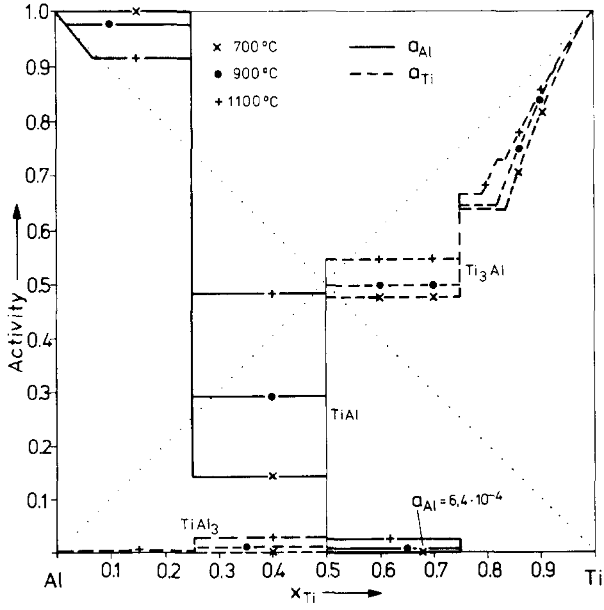

Fig. 3. Variation of the activity of Al and Ti in the Ti–Al system Reference state: Ti: 700°C hex; 900, 1000°C, bcc; Al: liquid-Al-activity at $x_{Al} = 0.1$; 700°C, $a_{Al} = 5.3$ E−5; 900°C, $a_{Al} = 4.7$ E−4; 1100°C, $a_{Al} = 3.0$ E−3.

with the equilibrium constant

$$K_1 = \frac{a_{Al_2O_3}}{a_{Al}^2 P_{O_2}^{3/2}} \tag{3}$$

To form a pure oxide from a pure metal (i.e., for $a_{Al} = a_{Al_2O_3} = 1$), it follows from Eqs. (2) and (3)

$$\ln P_{O_2}(Al/Al_2O_3) = \frac{2\Delta G_1}{3RT} \tag{4}$$

In an analogous manner, for an equilibrium between two oxides of one metal (e.g., TiO and Ti_2O_3), according to the reaction

$$2TiO + \tfrac{1}{2}O_2 = Ti_2O_3 \tag{5}$$

and the equilibrium constant

$$K_5 = \frac{a_{Ti_2O_3}}{a_{TiO}^2 P_{O_2}^{1/2}} \tag{6}$$

$$\ln P_{O_2}(TiO/Ti_2O_3) = \frac{2\Delta G_5}{RT} \tag{7}$$

The oxygen equilibrium pressures calculated by this method are given in Figs. 1 and 2 for selected metal/oxide and oxide/oxide equilibria as functions of the reciprocal absolute temperature. For these calculations, data from the thermodynamic databank THERDAS* were used and the activities of metal and oxide were set to one.

For the following calculations of the equilibrium pressures of Al/Al_2O_3 and Ti/TiO across the Ti-Al system, the assumption was made that TiO and Al_2O_3 exist as pure oxides (i.e., $a_{TiO} = a_{Al_2O_3} = 1$). It then follows from eq. (3) that

$$\log P_{O_2} = \tfrac{2}{3}\log K_1 - \tfrac{3}{4}\log a_{Al} \tag{8}$$

In an analogous manner for the reaction

$$Ti + \tfrac{1}{2}O_2 = TiO \tag{9}$$

with

$$K_9 = \frac{a_{TiO}}{a_{Ti} P_{O_2}^{1/2}} \tag{10}$$

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*THERDAS (Thermodynamische Datenbank für Anorganische Stoffe) is a project of the Lehrstuhl für Theoretische Hüttenkunde und Metallurgie der Kernbrennstoffe of the Technische Hochschule Aachen. Access to the data and advisary service of THERDAS can be obtained via GTT, Mies van der Rohestraße 25, D-5100 Aachen, Tel. 0241/870174 it follows that

$$\log P_{O_2} = -2 \log K_9 - 2 \log a_{Ti} \tag{11}$$

If the corresponding data for K and a_{Al} or a_{Ti} are introduced into Eqs. (8) and (11), the result is the data summarized in Table I. The exact variation in the α-Ti and β-Ti phases has been neglected, because it was not important for the ensuing considerations. A graphical representation is given in Fig. 4 for 900°C. The course is very similar at 700 and 1100°C, thus a graphical presentation at these temperatures has been omitted.

From Table 1 and Fig. 4 it follows that:

- In the two-phase regions Al/$TiAl_3$ and TiAl/$TiAl_3$, the oxygen pressure of Al/Al_2O_3 is several orders of magnitude below that of Ti/TiO. Here Al_2O_3 is the most stable oxide.
- In the existence range of the TiAl phase, the oxygen pressure of Al/Al_2O_3 increases, that of Ti/TiO decreases dramatically, so that both pressures intersect. Consequently, in the two-phase region Ti_3Al/TiAl, the oxide TiO is more stable than Al_2O_3.
- The difference in the oxygen pressures of Ti/TiO and Al/Al_2O_3 increases within the Ti_3Al phase, and then even more within both α-Ti and β-Ti.

Table I. Activities in the Ti-Al System and Metal/Oxide Equilibrium Pressures

Phases	Temp. (°C)	a_{Al}	$P_{O_2}(Al/Al_2O_3)$ (bar)	a_{Ti}	$P_{O_2}(Ti/TiO)$ (bar)
Ti ($x_{Ti} = 0.9$)	700	5.3 E−5	5.0 E−43	0.815	7.5 E−48
	900	4.7 E−4	7.9 E−35	0.890	7.1 E−39
	1100	3.0 E−3	1.7 E−26	0.905	7.7 E−33
Ti + Ti_3Al	700			0.634	1.2 E−47
	900			0.645	7.9 E−39
	1100			0.665	1.4 E−32
Ti_3Al + TiAl	700	6.4 E−4	1.8 E−44	0.475	2.2 E−47
	900	5.0 E−3	3.5 E−36	0.495	2.0 E−38
	1100	0.02	1.4 E−27	0.545	2.2 E−32
TiAl + $TiAl_3$	700	0.14	1.4 E−47	0.002	2.5 E−45
	900	0.29	1.5 E−38	0.010	5.0 E−35
	1100	0.48	1.9 E−29	0.025	1.0 E−29
$TiAl_3$ + Al	700	0.915	1.1 E−48		
	900	0.980	3.0 E−39		
	1100	0.995	7.4 E−30		

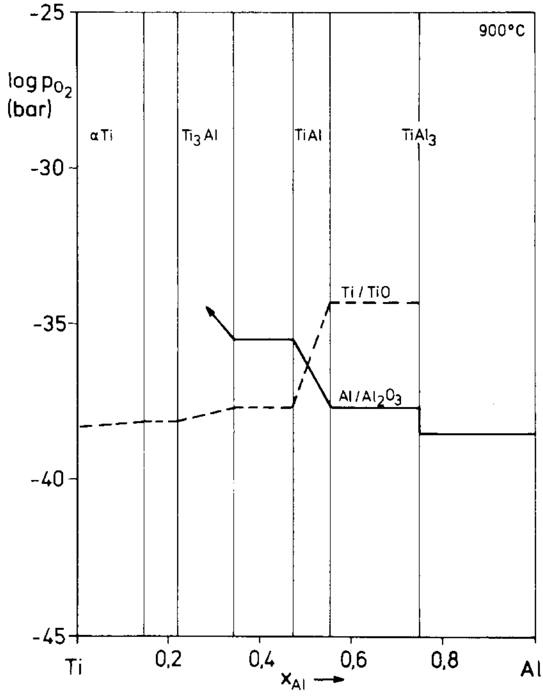

Fig. 4. Variation of the metal/oxide equilibrium pressures in the Ti–Al–O system at 900°C.

The Ti–Al–O Phase Diagram

A simplified Ti–Al–O phase diagram, compiled by using the existing thermodynamic data, is shown in Fig. 5 for 900°C. The phases Ti_3Al, TiAl, and $TiAl_3$ are treated as line compounds, although, in particular, Ti_3Al and TiAl have a significant existence range.[4] At this temperature only the binary oxides of the Ti–O and Al–O system are stable. At temperatures above approximately 1010°C the ternary oxide $TiAl_2O_5$ becomes stable as follows from Fig. 6. The data stored in THERDAS for this compound have been slightly modified to give a decomposition temperature close to 1000°C.

Consequences for the Oxidation of TiAl

The formation of a continuous Al_2O_3 scale is not to be expected if the composition of the alloy is in the two-phase region Ti_3Al/TiAl. This corresponds with our own experimental observations.[5] During the oxidation experiment, a Ti_3Al zone was often formed underneath the scale, which further favors TiO stability. The kinetics of TiO formation were clearly not

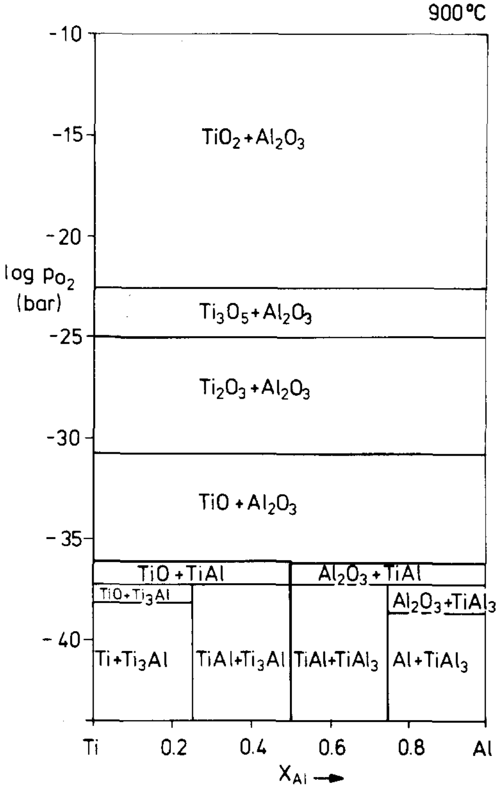

Fig. 5. Simplified Ti-Al-O phase diagram. Isothermal section at 900°C (phases Ti_3Al, TiAl, and $TiAl_3$ treated as line compounds).

investigated in detail. From studies of the oxidation of titanium it is known, however, that the main reaction product is TiO_2, and that TiO, Ti_2O_3, and the Magneli phases, with the general formula Ti_xO_{2x-1}, are oxidized rapidly to TiO_2, or that the formation of these oxides is retarded due to slow phase-boundary reactions.[6] The same appears to apply to the oxidation of TiAl, because according to the literature[7-10] and our own observations[5] TiO_2 and Al_2O_3 are the reaction products observed.

The formation of a continuous protective Al_2O_3 scale should be favored by:

a. Increase in the Al content up to or even above the TiAl/$TiAl_3$ equilibrium composition, because the alloy is then in equilibrium with Al_2O_3. The selective oxidation of Al to form the protective

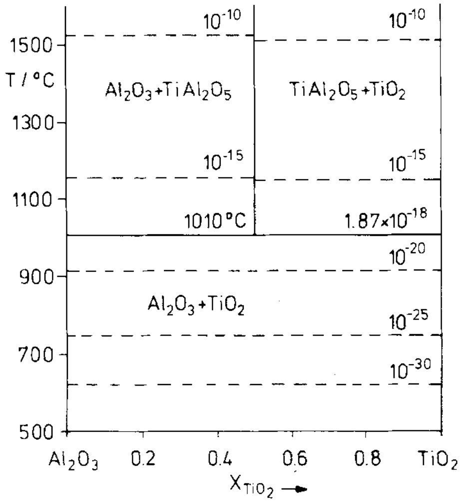

Fig. 6. Calculated Al_2O_3-TiO_2 phase diagram showing iso-P_{O_2} values (bar) across the system.

scale can nevertheless decrease the Al content in the subsurface zone below the critical value of Al_2O_3 stability.

b. Alloying of TiAl with components which decrease the Ti activity and increase the Al activity. Concrete proposals cannot be made, because the activities in Ti–Al–X systems have not been calculated as yet.

According to Perkins *et al.*[9,10] the diffusion of Al in β-titanium is about two orders of magnitude higher than in α-titanium. Such a statement is not consistent with the data critically reviewed by Kubaschewski.[11] According to that study, the diffusion of Al at 1250°C in β-Ti is only four times greater than in α-Ti. For the ratio D_{Ti}/D_{Al} the value is between 7.7–8.5 in Ti_3Al and 0.37 for TiAl.[11] These ratios are rather independent of temperature. However, the faster Al diffusion in the β-Ti phase can hardly be used, because if the Al depletion in the subsurface zone is so high that the Ti phase is formed, Al_2O_3 is in any case no longer the stable oxide.

THE Ti–Si–O SYSTEM

Influence of Titanium Activity on the Stability of Titanium Oxides

From Eq. (10) and (11), respectively, it follows that the oxygen pressure of the Ti/TiO equilibrium increases with decreasing Ti activity, and this decrease can be described by Eq. (11) for the condition $a_{TiO}=1$. TiO can be oxidized to Ti_2O_3 according to

$$2TiO+\tfrac{1}{2}O_2=Ti_2O_3 \tag{12}$$

with the equilibrium constant

$$K_{12}=\frac{a_{Ti_2O_3}}{a^2_{TiO}P^{1/2}_{O_2}} \tag{13}$$

The oxygen pressure of this equilibrium is independent of the activity of Ti metal. The oxygen pressure of Ti/TiO, given in eq. (10) or (11), therefore, becomes for a defined a_{Ti} value and the condition $a_{TiO}=a_{Ti_2O_3}$ equal to the oxygen pressure of the equilibrium TiO/Ti_2O_3 given in Eq. (13). Under this condition, the three solid phases (Ti, TiO, and Ti_2O_3) are in equilibrium. Below this critical Ti activity, TiO is no longer stable. In the case of the $Ti/TiO/Ti_2O_3$ equilibrium, it follows from Eqs. (10) and (13), by setting the oxygen pressures equal,

$$a_{Ti}(Ti/TiO/Ti_2O_3)=\frac{a^3_{TiO}K_{12}}{a_{Ti_2O_3}K_9} \tag{14}$$

and for the condition $a_{TiO}=a_{Ti_2O_3}=1$

$$a_{Ti}(Ti/TiO/Ti_2O_3)=\frac{K_{12}}{K_9} \tag{15}$$

A further decrease in the Ti activity leads to instability of Ti_2O_3, and Ti metal is then in equilibrium with the oxide Ti_3O_5. For the equilibrium $Ti/Ti_2O_3/Ti_3O_5$, it follows in an analogous manner with the reactions

$$2Ti+\tfrac{3}{2}O_2=Ti_2O_3 \tag{16}$$

with

$$K_{16}=\frac{a_{Ti_2O_3}}{a^2_{Ti}P^{3/2}_{O_2}} \tag{17}$$

and

$$3Ti_2O_3+\tfrac{1}{2}O_2=2Ti_3O_5 \tag{18}$$

with

$$K_{18}=\frac{a^2_{Ti_3O_5}}{a^3_{Ti_2O_3}P^{1/2}_{O_2}} \tag{19}$$

and by again setting the oxygen pressures equal and for the condition

$$a_{Ti_2O_3} = a_{Ti_3O_5} = 1$$

$$a_{Ti}(Ti/Ti_2O_3/Ti_3O_5) = \frac{K_{18}^{3/2}}{K_{16}^{1/2}} \tag{20}$$

If the so-called Magneli phases with the general formula Ti_xO_{2x-1} existing between Ti_3O_5 and TiO_2 are ignored (and for which thermodynamic data are in any case not available), the Ti activity for the $Ti/Ti_3O_5/TiO_2$ equilibrium can be calculated. For this the reactions

$$3Ti + \tfrac{5}{2}O_2 = Ti_3O_5 \tag{21}$$

with

$$K_{21} = \frac{a_{Ti_3O_5}}{a_{Ti}^3 P_{O_2}^{5/2}} \tag{22}$$

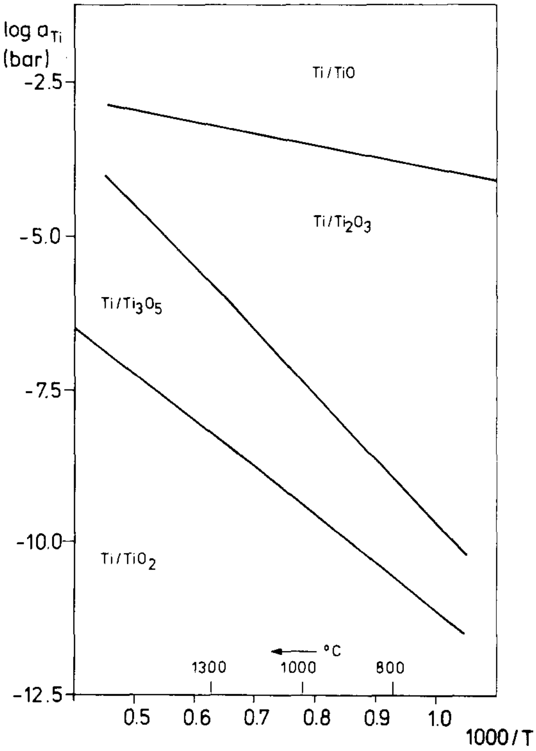

Fig. 7. Stability fields of titanium oxides as a function of Ti activity and reciprocal absolute temperature.

and

$$Ti_3O_5+\tfrac{1}{2}O_2=3TiO_2 \tag{23}$$

with

$$K_{23}=\frac{a^3_{TiO_2}}{a_{Ti_3O_5}P^{1/2}_{O_2}} \tag{24}$$

must be used. Again, setting the oxygen pressures of both equilibria equal and $a_{Ti_3O_5}=a_{TiO_2}=1$, it follows that

$$a_{Ti}(Ti/Ti_3O_5/TiO_2)=\frac{K^{5/3}_{23}}{K^{1/3}_{21}} \tag{25}$$

If the corresponding numbers are introduced into Eqs. (15), (20), and (25), the Ti activities of the three equilibria discussed can be calculated. The results of such calculations are summarized in Fig. 7, where the stability fields of the Ti oxides as a function of Ti activity and the reciprocal absolute temperature are presented.

In the following calculations of the oxygen partial pressures in the Ti-Si system, it has to be taken into account that, depending on the Ti activity, the correct Ti/oxide equilibrium has to be selected. This was not necessary in the Ti-Al system, because the stability region of the TiO phase was not departed from.

Metal/Oxygen Equilibrium Pressures

The activities of Ti and Si in the two-phase regions in the Ti-Si system at 800, 1000, and 1300°C are summarized in Table II. They were calculated from the thermodynamic data published in Ref. 12. These data were evaluated in conjunction with the then available phase diagram information presented by Hansen[13] and Elliott[14], which did not include the subsequently reported Ti_3Si phase. The inclusion of the Ti_3Si phase in the present work would not necessitate important changes to the discussed effect. The oxygen pressures of the equilibria Ti/TiO, Ti/Ti_2O_3, and Si/SiO_2, calculated with the help of these activity data, are also presented in Table II. These calculations are based on the assumption $a_{TiO}=a_{Ti_2O_3}=a_{SiO_2}=1$. The possible formation of a ternary oxide phase has also been ignored. A graphical presentation of the data at 1000°C is shown in Fig. 8. The behavior is very similar at the other two temperatures.

From Table II and Fig. 8 it follows that:

- SiO_2 is the stable oxide between pure Si and the equilibrium $TiSi/Ti_5Si_3$. Within the existence field of the Ti_5Si_3 phase, the oxide stability inverts, and TiO is then the stable oxide.

Table II. Activities in the Ti-Si System and Metal/Oxide Equilibrium Pressures[a]

Phases	Temp. (°C)	a_{Si}	$P_{O_2}(Si/SiO_2)$ (bar)	a_{Ti}	P_{O_2}(Ti/Oxid) (bar)
$Ti + Ti_5Si_3$	800	3.5 E−11	2.24 E−25	0.995	6.31 E−43 (++)
	1000	1.39 E−9	2.88 E−20	0.973	7.94 E−36 (++)
	1300	6.81 E−8	1.55 E−13	0.913	2.51 E−27 (++)
$Ti_5Si_3 + TiSi$	800	0.013	6.03 E−34	7.36 E−6	1.29 E−33 (+)
	1000	0.019	2.13 E−27	5.09 E−5	7.08 E−27 (+)
	1300	0.029	3.47 E−20	3.82 E−4	2.63 E−20 (+)
$TiSi + TiSi_2$	800	0.080	9.77 E−35	1.16 E−6	1.35 E−32 (+)
	1000	0.095	4.17 E−28	1.02 E−5	6.16 E−26 (+)
	1300	0.114	8.91 E−21	9.79 E−5	1.62 E−19 (+)
$TiSi_2 + Si$	800	1.0	7.94 E−36	7.28 E−9	1.32 E−29 (+)
	1000	1.0	4.17 E−28	9.12 E−8	3.31 E−23 (+)
$TiSi_2 + Si$ (liquid)	1300	0.884	1.13 E−21	1.61 E−6	3.93 E−17 (+)
$TiSi_2 + Si$ (liquid suppressed)	1300	1.0	1.0 E−21	1.26 E−6	5.37 E−17 (+)

[a] Reference state: Si solid/Ti hex (800°C); bcc (1000, 1300°C); + = equilibrium Ti/Ti_2O_3; ++ = equilibrium Ti/TiO.

- In the range between $TiSi_2/Si$ and $Ti_5Si_3/TiSi$, Ti is in equilibrium with Ti_2O_3, and TiO is unstable. Only within the Ti_5Si_3 phase does the Ti activity exceed the critical value for TiO formation.
- The formation of a continuous SiO_2 scale, at least at $T > 1200°C$, is observed on $TiSi_2$,[5] which agrees with the thermodynamic data developed in this paper. Ti oxides are only stable within or above the SiO_2 scale. Due to the selective oxidation of silicon even Si depletion in the subsurface zone down to the equilibrium $Ti_5Si_3/TiSi$ does not endanger the SiO_2 stability.

The Ti–Si–O Phase Diagram

Figure 9 shows the isothermal section at 900°C of the Ti-Si-O phase diagram, compiled by using the existing thermodynamic data. In addition to the binary oxides, the ternary compound $3Ti_2O_3 \cdot 2SiO_2$ has been included. Such a compound exists according to Ref. 15. The estimated data for $3Ti_2O_3 \cdot 2SiO_2$ are based partly on information for $3Al_2O_3 \cdot 2SiO_2$ and partly on the estimated data for the hypothetical compound $TiSiO_3$. According to electron microprobe analysis of precipitates in the SiO_2 scale on $TiSi_2$, a further compound $Ti_2O_3 \cdot 5SiO_2$ may exist.[5] Such a compound has been neglected in Fig. 9, because its existence needs further confirmation.

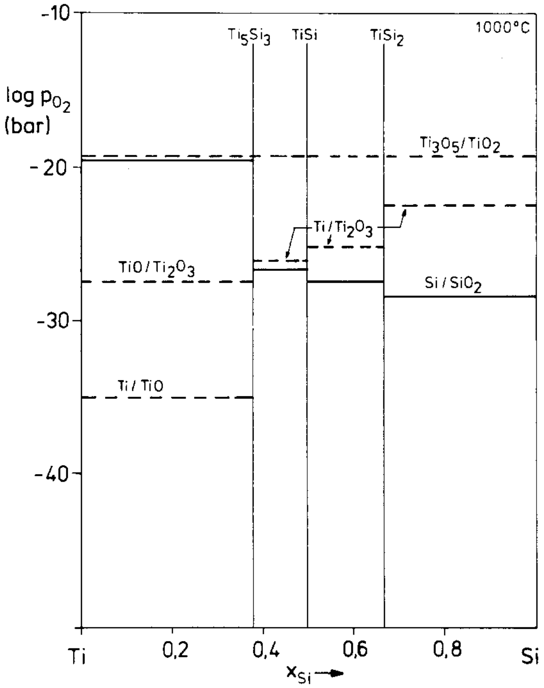

Fig. 8. Variation of the metal/oxide equilibrium pressures in the Ti-Si-O system at 1100°C.

CONCLUSIONS

The thermodynamic calculations presented in this paper demonstrate that a knowledge of the activity variations within the metal system in which intermetallic phases exist is necessary to calculate the oxide stabilities correctly. This is because the activities in the metal phases can differ by orders of magnitude from ideal behavior.

It may be interesting to compare the stability of the oxides in equilibrium with the metal phase in the Ti-Al-O and Ti-Si-O systems. Certainly, the TiAl and TiSi phases, each containing 50 at.% titanium, can be compared. Within the TiAl phase, the stability changes from Al_2O_3 to TiO; whereas within the entire range of the TiSi phase, SiO_2 is the stable oxide. This may be surprising, because the oxygen pressure of the pure phases Si/SiO_2 is several orders of magnitude higher than that of Ti/TiO, while the oxygen pressures of the pure phases Al/Al_2O_3 and Ti/TiO are close together (Figs. 1 and 2). The stability of SiO_2 on TiSi is caused by the much greater decrease in Ti activity in the Ti-Si system compared with its decrease in the Ti-Al system (see Tables I and II).

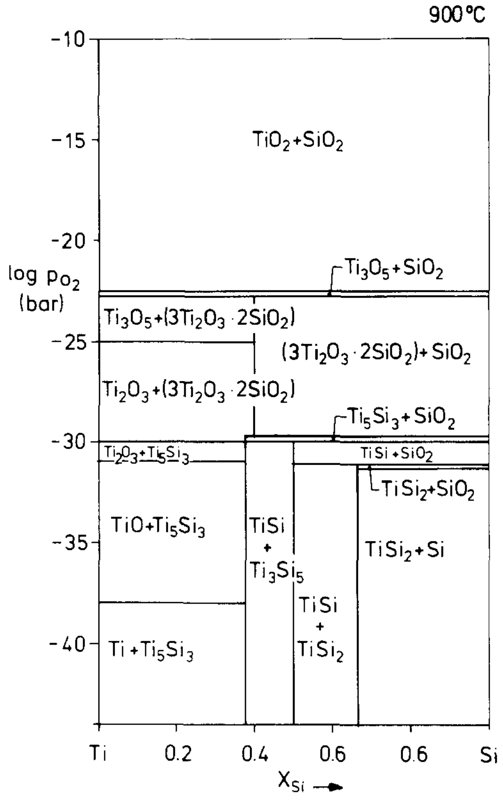

Fig. 9. Calculated Ti–Si–O phase diagram at 900°C (estimated data for $3Ti_2O_3 \cdot 2SiO_2$).

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REFERENCES

1. A. Steiner and K. L. Komarek, *Trans. Met. Soc. AIME* **230**, 786 (1964).
2. N. C. Oforka and B. B. Argent, *J. Less-Common Metals* **114**, 97 (1985).
3. L. Kaufmann and H. Nesor, *CALPHAD* **2**, 326 (1978).
4. T. B. Massalsk *et al.*, *Binary Alloy Phase Diagrams*, Vol. 1, (Amer. Soc. Metals, 1986), p. 173.
5. S. Becker, A. Rahmel, and M. Schütze (to be published).
6. P. Kofstad, *High Temperature Corrosion* (Elsevier, New York, 1988).
7. Y. Umakoshi, M. Yamagushi, T. Sakagami, and T. Yamani, *J. Mater. Sci.* **24**, 1599 (1989).

8. E. U. Lee and J. Waldman, *Scripta Metall.* **22**, 1389 (1988).
9. R. A. Perkins, K. T. Chiang, and G. H. Meier, *Scripta Metall.* **21**, 1505 (1987).
10. R. A. Perkins, K. T. Chiang, G. H. Meier, and R. Miller, in *Oxidation of High Temperature Intermetallics*, T. Grobstein and J. Doychak, eds. (The Mineral, Metals and Materials Society 1989), S. 157.
11. O. Kubaschewski, in *Atomic Energy Review* (Special Issue No. 9, International Atomic Energy Agency, Vienna, 1983, S. 441 ff).
12. L. Kaufmann and H. Nesor, *CALPHAD* **3**, 45 (1979).
13. M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).
14. R. P. Elliott, *Constitution of Binary Alloys* (First Supplement, 1965).
15. E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagrams for Ceramists* (The American Ceramic Society, 1964), p. 69.