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THERMODYNAMICS, SOLUBILITY, AND DIFFUSIVITY OF OXYGEN IN TITANIUM AND Ti-Al ALLOYS

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Titanium aluminides and titanium aluminide-based composites are attractive candidate materials for high-temperature structural applications. As these materials may be exposed to oxidizing environments during their use at elevated temperatures, it is essential that they possess a good oxidation resistance. Previous studies (ref. 1) have shown that the oxidation resistance of Al-rich alloys in the Ti-Al system is superior to that of the Ti-rich alloys. The scales formed on the surface of the Al-rich and Ti-rich alloys have been reported (ref. 1) to be predominantly Al_2O_3 and TiO_2, respectively. Since the relative stabilities of the oxides of Al and Ti at various temperatures and oxygen pressures can be assessed from their thermodynamic data, it is possible, with the help of thermodynamic calculations, to determine the compositions of the alloys which would form scales of Al_2O_3, TiO_x or a ternary oxide such as $TiAl_2O_5$ during oxidation at a given temperature. The thermodynamic calculations require reliable activity data for the Ti-Al system. These data have not been determined for the entire composition and temperture range of interest. Using the data available in the literature, Rahmel and Spencer (ref. 2) recently performed thermodynamic calculations and concluded that the stable oxide changed from TiO to Al_2O_3 in the existence region of the TiAl phase.

In the case of titanium aluminide-based composites, another major concern is the mutual chemical compatibility of the matrix material with the reinforcement phase. Fibers of SiC, TiB_2 and Al_2O_3 are currently being investigated for reinforcement of titanium aluminide matrices. Recent studies (ref. 3) have shown that SiC is incompatible with Ti_3Al. No detectable reaction has been observed between TiB_2 and Ti-43 at.% Al ($\alpha_2+\gamma$) alloy at 1473K (ref. 4). γ-TiAl has been reported to be compatible with Al_2O_3. However, in a recent study by Misra (ref. 5), a chemical reaction between Al_2O_3 and titanium aluminides containing less than 50 at.% Al has been observed. Misra (ref. 5) has found that the reaction between a Ti-Al alloy, (with < 50 at.% Al) and Al_2O_3 is that of the dissolution of Al and atomic oxygen from Al_2O_3:

$$Al_2O_3 = 2\underline{Al} + 3\underline{O} \qquad (1)$$

The above reaction results in an increase in the concentration of Al in the surface of the Ti-Al alloy. The formation of γ-TiAl phase thus takes place. Diffusion of Al and atomic oxygen away from the interface causes the reaction to proceed further.

For reaction (1) to be feasible the product $\{a^3_{\underline{O}} \cdot a^2_{\underline{Al}}\}$ (where $a_{\underline{Al}}$ is the activity of Al and $a_{\underline{O}}$ is the activity of oxygen in the alloy), should be less than the equilibrium constant, K_1, for reaction (1). At high values of $a_{\underline{Ti}}$ and/or $a_{\underline{O}}$ in the alloy, the following reaction may also take place:

$$\underline{Ti} + \underline{O} = TiO \qquad (2)$$

Thus, the feasibility and the extent of reactions between a Ti-Al alloy and Al_2O_3 are influenced by the thermodynamic activities of various species in the alloy. As there is little information available on the thermodynamics, solubility and diffusivity of oxygen in Ti-Al alloys, it is important to investigate the Ti-Al-O system.

The thermodynamics of the Ti-O system has been studied by Kubaschevski and Dench (ref. 6), and Miyazaki, et. al (ref. 7). The solubility of oxygen at partial pressures of oxygen established by Ca-CaO and Mg-MgO equilibria has also been determined in these studies. The phase diagram for the system shows that the maximum solubility of oxygen in β-Ti is about 8 at.% and that in α-Ti is 31.9 at.%. The diffusivity of oxygen in titanium has been estimated from oxidation and internal friction studies. The activation energy for the diffusion process has been reported (ref. 8) to be about 203 kJ/mole for α-Ti and about 246 kJ/mole for β-Ti.

It has been reported (ref. 9) that the additions of Al to Ti result in a decreased solubility of oxygen. However, the information on the thermodynamics, solubility and diffusivity of oxygen in Ti-Al alloys is very limited. Attempts are therefore being made to investigate the thermodynamics, solubility and diffusivity of oxygen in Ti-Al alloys using electrochemical cells with yttria-doped thoria as a solid electrolyte. High reactivity of these alloys with oxygen is, however, a problem in these measurements. Other approaches, such as oxidation kinetics studies, may also therefore have to be tried to determine the solubility and diffusivity of oxygen in Ti-Al alloys of various compositions.

Acknowledgement

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OBJECTIVES

- THERMODYNAMIC STUDY OF TI-AL-O ALLOYS
- DETERMINE THE SOLUBILITY OF OXYGEN IN TI-AL ALLOYS

RATIONALE FOR WORK

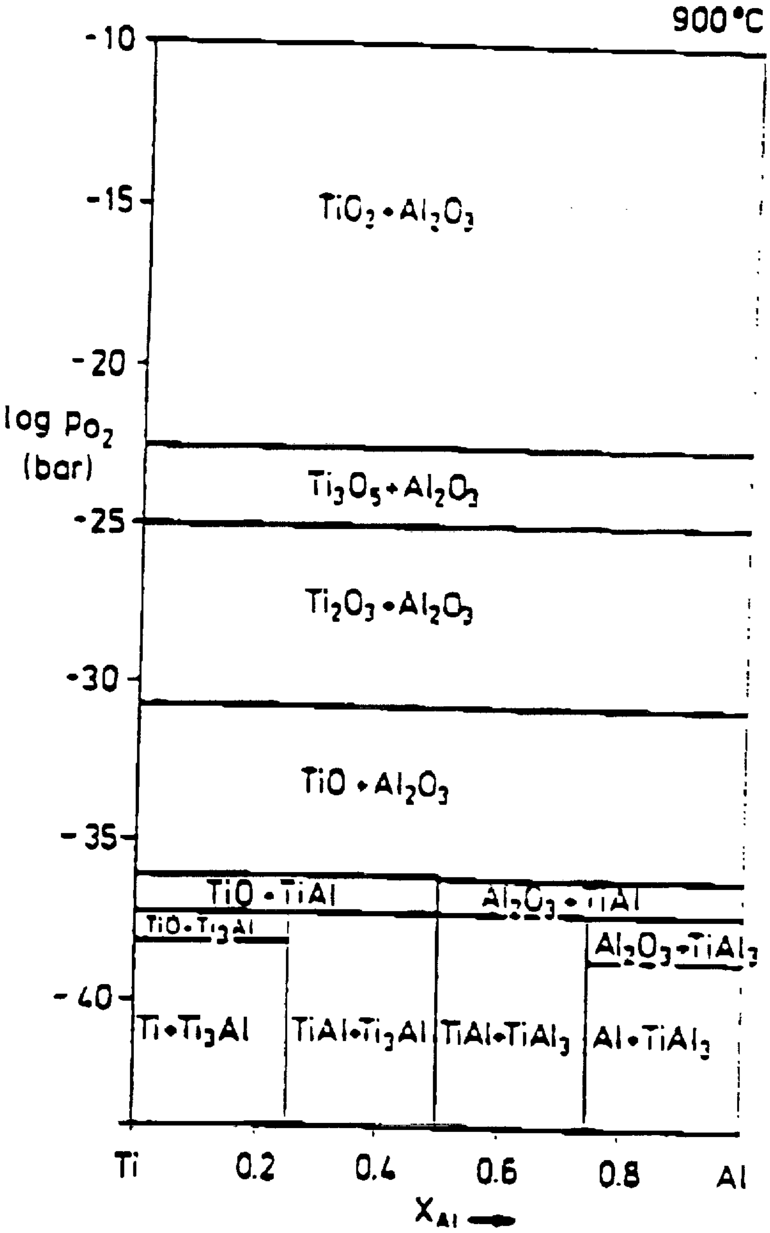
- THERMODYNAMIC DATA ON TI-AL-O SYSTEM USEFUL IN PREDICTING THE PHASES FORMED DURING OXIDATION
- CHEMICAL COMPATIBILITY OF AL_2O_3 REINFORCEMENT PHASE WITH TITANIUM ALUMINIDE MATRICES

$$AL_2O_3 = 2\underline{AL} + 3\underline{O} \quad \text{(MISRA)}$$

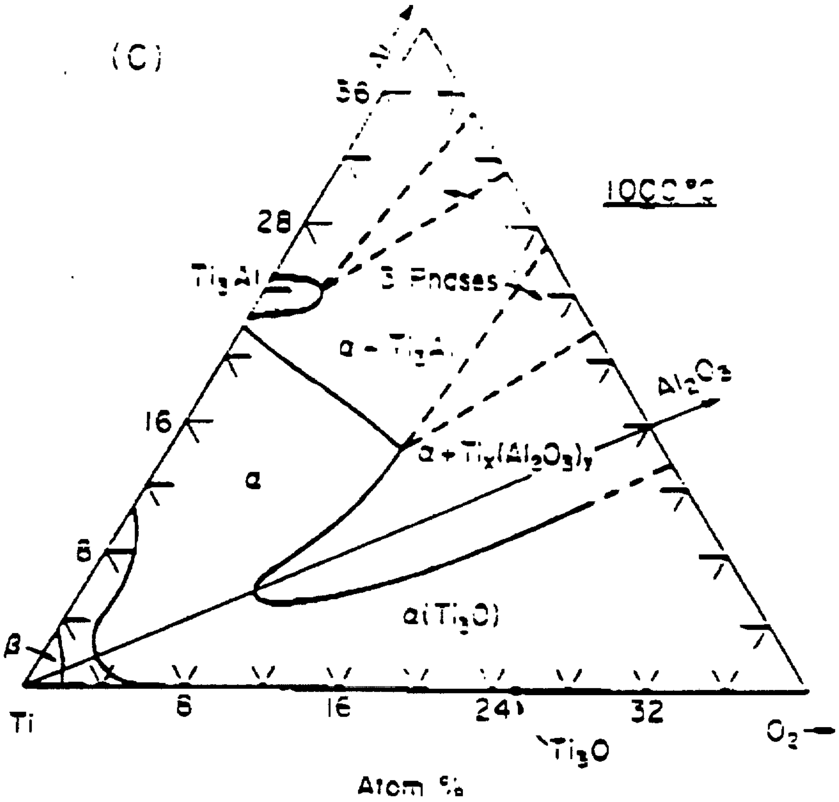
$$\underline{TI} + \underline{O} = TIO$$

APPROACH

- ELECTROCHEMICAL MEASUREMENTS USING YTTRIA-DOPED THORIA AS SOLID ELECTROLYTE
- OXIDATION STUDIES



SIMPLIFIED TI-AL-O PHASE DIAGRAM. ISOTHERMAL SECTION AT 1173 K. (FROM RAHMEL AND SPENCER)

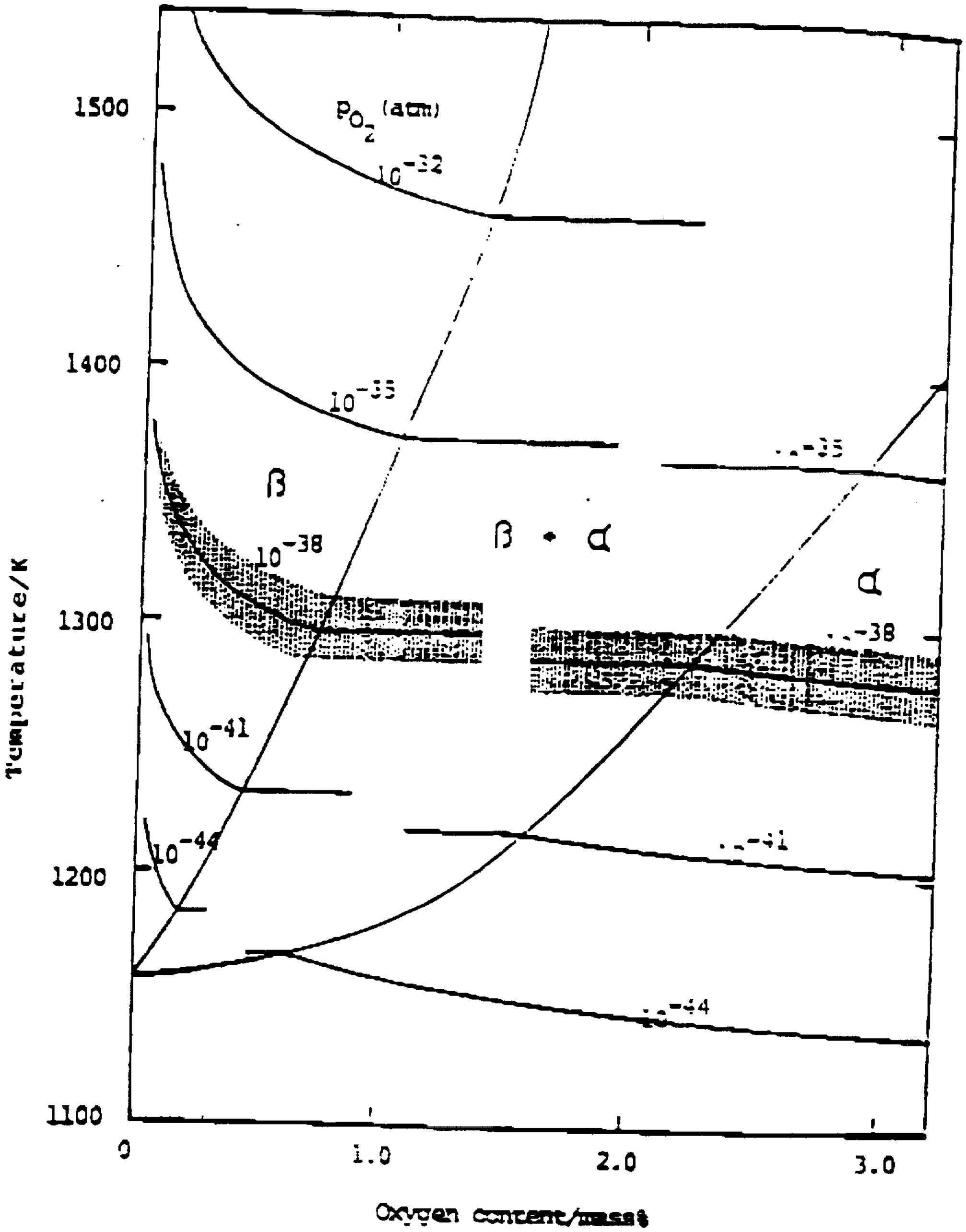


Phase Diagram for the System Ti-Al-O. Isothermal Section at 1273 K. (From Glazova)

SOLUBILITY OF OXYGEN IN TITANIUM

MATERIALS	OXYGEN SOLUBILITY (AT %)
α - TI	0-31.9
β - TI	0-4

- AL AND SI LOWER THE SOLUBILITY OF OXYGEN (CHAZE AND CODDET)
    - AT 700°C, IN THE PRESENCE OF AL, THE SOLUBILITY OF OXYGEN DECREASES FROM 31.9 AT% TO 0.3 AT%
- CR HAS NEGLIGIBLE EFFECT ON THE OXYGEN SOLUBILITY



SOLUBILITY OF OXYGEN IN TITANIUM AS A FUNCTION OF TEMPERATURE AND OXYGEN PRESSURE. (FROM MIYAZAKI, ET AL.)

SOLUBILITY OF OXYGEN IN TITANIUM AS A FUNCTION OF TEMPERATURE AND OXYGEN PARTIAL PRESSURE*

T(°C)	EQUILIBRIUM PO_2 ESTABLISHED BY	PO_2(ATM)	O IN TI(AT%)
800	CA - CAO	1.2×10^{-51}	0.04
	MG - MGO	1.9×10^{-50}	0.16
1000	CAO - CAO	6.4×10^{-42}	0.05
	MG - MGO	2.7×10^{-39}	0.98
1200	CA - CAO	8.7×10^{-35}	0.08
	MG - MGO	3.7×10^{-31}	5.34
	TI - TIO	1.7×10^{-29}	36.2

ALPHA: $\frac{1}{2} \ln PO_2 = \ln(\% \underline{O}) + 10.3 - \frac{70,500}{T}$ (1150-1340K)

BETA: $\frac{1}{2} \ln PO_2 = \ln(\% \underline{O}) + 12.1 - \frac{71,900}{T}$ (1150-1600K)

* MIYAZAKI, ET AL.

DIFFUSIVITY OF OXYGEN IN TITANIUM

QUACH-KAMIMURA, ET AL.

$$D = 0.45 \text{ EXP} \left(\frac{-200 \text{ KJ/MOLE}}{RT} \right) \quad \text{CM}^2\text{S}^{-1}$$

ROSA

$$\begin{cases} D_\alpha = 0.778 \text{ EXP} \left(\frac{-48,600 \text{ CAL/MOLE}}{RT} \quad \text{CM}^2\text{S}^{-1} \right) & (932\text{-}1142^\circ\text{C}) \\ D_\beta = 3.3 \times 10^2 \text{ EXP} \left(\frac{-58,800 \text{ CAL/MOLE}}{RT} \right) & (932\text{-}1142^\circ\text{C}) \end{cases}$$

DECHAMPS

$$D_o = 0.408 \text{ EXP} \left(\frac{-47,040 \text{ CAL/MOLE}}{RT} \right)$$

$\alpha \rightarrow \beta$ TRANSITION AT 882°C

TEMP. (°C)	QUACH-KAMIMURA D_o	ROSA D_α	ROSA D_β	DECHAMPS D_o
700°C	8.24×10^{-12}	-	-	1.11×10^{-11}
800	8.25×10^{-11}	-	-	1.07×10^{-10}
900	5.58×10^{-10}	6.84×10^{-10}	3.65×10^{-9}	1.72×10^{-9}
1000	2.79×10^{-9}	3.52×10^{-9}	2.65×10^{-8}	3.42×10^{-9}

ELECTROCHEMICAL MEASUREMENTS

- THE CELL SCHEME USED TO CHECK THE PROPER FUNCTIONING OF THE GALVANIC CELL:

$$\text{Ta} + \text{Ta}_2\text{O}_5 \mid \begin{array}{c}\text{Yttria-Doped}\\ \text{Thoria}\end{array} \mid \text{Nb} + \text{NbO}$$

- THE VIRTUAL CELL REACTION IS:

$$2\text{Nb} + 2/5\,\text{Ta}_2\text{O}_5 = 2\text{NbO} + 4/5\,\text{Ta}$$

FOR WHICH

$$\Delta G^0 = 2\Delta G^0_{\text{NbO}} - 2/5\,\Delta G^0_{\text{Ta}_2\text{O}_5}$$

$$= -nE^0F$$

WHERE E^0 = CELL EMF
F = FARADAY'S CONSTANT
n = NUMBER OF ELECTRONS TRANSFERRED IN THE REACTION (4 FOR THE ABOVE REACTION)

- USING THE THERMODYNAMIC DATA FROM JANAF TABLES, THE EXPECTED VALUES OF CELL EMF ARE:

TEMP. (K)	E^0 (mV)
1000	39.1
1100	37.1
1200	34.9
1300	32.8

SUMMARY

- RECENT STUDIES SHOW THAT AL_2O_3 REACTS WITH TI-AL ALLOYS CONTAINING LESS THAN 50 AT. % AL AND THAT THE REACTION MECHANISM INVOLVES THE DISSOLUTION OF AL AND ATOMIC OXYGEN FROM AL_2O_3.

- LITERATURE SURVEY REVEALS THAT THE SOLUBILITY AND DIFFUSIVITY OF OXYGEN IN TI-AL ALLOYS ARE VERY DIFFERENT FROM THOSE IN TI. HOWEVER, THE INFORMATION IS VERY LIMITED.

- ATTEMPTS TO STUDY THE TI-AL-O SYSTEM USING AN ELECTROCHEMICAL TECHNIQUE AND OXIDATION STUDIES ARE UNDERWAY.