A Mass Spectrometric Study of Vaporization of Refractory Metal- Al_2O_3 Systems in Elevated Temperature

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(Received February 16, 1978)

Vaporization of several refractory metal- Al_2O_3 systems have been investigated by mass spectrometry in order to assess compatibility of these systems in elevated temperature. Nearly neutral conditions are reached in both tungsten- and molybdenum- Al_2O_3 system. In these systems, vapor species and their partial pressures have been in good agreement with previous works. While, some reactions have been observed in both tantalum- and niobium- Al_2O_3 systems. The main components of the gaseous phase in these systems were Al, and some metal oxide molecules.

The partial pressures of them were nearly one order higher than in tungsten- Al_2O_3 system. The compatibility of these reducible refractory metals have been discussed relating with their oxygen solubility, free energy of formation of oxides and production of oxide solution.

1. Introduction

In high temperature technology, stability and compatibility of materials are one of the most important subjects of investigation. From mass spectrometric studies of vaporization of high temperature materials, various thermodynamical data of them have been obtained and a number of new chemical vapor species have been indentified.

Recrystallized alumina (Al_2O_3) is a popular refractory oxide and widely used for vaporization and melting experiments. The vaporization of solid and molten Al_2O_3 has been studied by numerous investigators¹⁻⁵⁾.

In these investigations, both equilibrium technique, which used a Knudsen effusion cell^{2,3)}, and non equilibrium free evaporation method^{4,5)} have been used with a mass spectrometer to identify the vapor species and obtain their partial pressures.

In these neutral or nearly neutral conditions, it has been known that Al_2O_3 vaporizes mainly as atomic molecules, Al and O. Furthermore, AlO and Al_2O molecules are rather important components of the vapor. However, contrary to these neutral condition experiments, in more reducible conditions which are encountered frequently for practical caces in high

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temperature technology, the vaporization behavior of Al_2O_3 may show rather different aspects by some oxide-metal reaction.

This work is undertaken to investigate the reaction of Al_2O_3 to various refractory metals and discuss the compatibility of these systems.

2. Experimental

The recrystallized Al_2O_3 used was obtained from NIPPON CHEMICAL CERAMICS Co.. Impurities in this specimen were Mg and Ca less than 0.5 %. The sintered tungsten rod which was obtained from NIPPON TUNGSTEN Co. was used as Knudsen cell material. Other refractory metals, such as molybdenum, tantalum and niobium, are obtained from electron beam melting.

The Knudsen cell assembly used in this experiment is shown in Fig. 1. This has two parts, one being an inner effusion cell which is fabricated from above various refractory metals and another being an outer cell supporter machined from tungsten block, in which side two upper and lower

Fig. 1. Knudsen cell assembly.

black body holes were drilled in order to measure cell temperatures by sighting them with an optical pyrometer.

Other characteristics of the apparatus and procedure have been reported previously⁶⁾, and resemble to conventional experiments. Briefly, the Knudsen cell assembly is heated up to experimental temperature by electron bombarding. A vaporized molecular beam enters the ionization chamber of a sector type single focussing mass spectrometer (HITACHI) and is ionized by a electron beam accelerated to 30 eV. A dinode type SEM is used as a detector and its gains for various ions are experimentally determined comparing with Faraday cup method. The gains of Al^+ and Al_2O^+ were directly measured and those of rather smaller peak ions were estimated from interpolating a calibration curve which was obtained by relating the gains of SEM for several high intensity peak ions to roots of their molecular weight. Absolute partial pressures of vapor species are estimated from silver calibration method, in which a known amount of silver was vaporized prior to vapor pressure measurement, and the intensities of silver and vapor species were compared.

The relative ionization cross sections were cited from Mann⁷⁾ and assumed as a simple summation for non uni-atomic molecules.

In order to detect non condensable vapor species, such as O, O_2 and N_2 successfully, a slight modification was done to the shutter, as shown in Fig. 2, Which discriminates vapor species from back ground gaseous molecules presented mainly in the ionization source chamber. The structure and mechanism of this shutter is

Fig. 2. Improved molecular beam shutter.
K cell: Knudsen cell
SS Block: Stainless steel Block

as follows. A stainless steel block which has two holes crossing at right angle each other, is installed with a screw nut at the center of the partition which is located between the ion source chamber and the Knudsen cell chamber. Through the vertical hole, (2.0 mm dia.) molecular beams vaporized enter from the lower Knudsen cell chamber into the upper ion source chamber. On the other hand, through the horizontal hole, (4.0 mm dia.) a rod-like shutter fabricated from a tantalum sheet goes in and out by outer operation. Since the clearance of the rod-like shutter and the stainless steel block is less than 0.1 mm, the penetration of non condensable gases could be interrupted sufficiently. Therefore the shutter effect for these species are very improved.

3. Results

3.1. Composition of the vapor

The ions of vapor species were identified

by their masses, isotopic distributions, appearance potentials and shutter effect. The appearance potentials found for the species were 6.0 ± 0.5 eV for Al, 9.5 ± 0.5 eV for AlO and 8.7 ± 0.5 eV for Al_2O which are in good agreement with the literature²⁾. In order to detect O^+ ion effectively, ionizing electron energy of 30 eV was used, but the appearance potential of O^+ ion could not be measured with sufficient accuracy because of a pressure of a background, probably CH_4^+ .

The observed atomic and molecular ions characterized by tungsten- and molybdenum- Al_2O_3 systems were O^+ , Al^+ , AlO^+ , Al_2O^+ and some ions of cell metal oxides which were WO , WO_2 , WO_3 and Mo , MoO and MoO_2 , respectively. O_2 was scarcely observed due to presence of rather high back ground. From the estimated decomposition equilibrium constant, the partial pressures of O_2 were about one order smaller than those of O atom. No other vapor species could be found, the search being made up to mass 300. While in tantalum and niobium cells, the observed vapor species were Al and Al_2O as major components. AlO ion was rather small. On the other hand, comparatively high metal and metal oxide ions were identified, which were Ta, TaO, TaO_2 and Nb, NbO, and NbO_2 . O and O_2 vapor species could not be observed in these cases.

3.2. Pressure data

Pressure data for the tungsten- Al_2O_3 system are presented in Fig. 3 with the reference^{2,6)}. Four sets of plots are corresponded to O, Al, AlO and Al_2O in order of intensity respectively. Other vapor species

of tungsten oxides are plotted together in Fig. 3. As shown from the figure, slightly higher values of vapor pressures for Al and O are obtained in this work, while

those of AlO indicate rather low values.

However, the slopes of these Clausius-Clapeyron plots, which are $\log P$ against $1/T$, are in roughly agreement with the

Fig. 3. Partial pressures (atm) of the vapor species in the W-Al₂O₃ system as a function of $1/T \times 10^4 \text{ K}^{-1}$.

reference^{2,3}). Moreover, pressures of WO , WO_2 and WO_3 are fairly in agreement with those of previous work²). Consequently it can be mentioned that the reduction of

Al_2O_3 by tungsten in this work are not remarkable.

Pressure data for the molybdenum- Al_2O_3 system are presented in Fig. 4 with

Fig. 4. Partial pressures (atm) of the vapor species in the Mo- Al_2O_3 system as a function of $1/T \times 10^4 \text{ K}^{-1}$.

the previous work²⁾. For the partial pressures of Al, AlO and Al₂O, the values obtained in this work were lower than those of the reference, while for O and

molybdenum oxides higher values were obtained. Slopes of the Clausius-Clapeyron plots of these vapor species are different, but not so widely, each other. The partial

Fig. 5. Partial pressures (atm) of the vapor species in the Ta-Al₂O₃ system as a function of $1/T \times 10^4 \text{ K}^{-1}$.

pressures of Al and O for molybdenum cell are slightly higher than those for tungsten. Consequently, it could be mentioned that the reduction of Al_2O_3 by molybdenum are

more appreciable than the tungsten.

Pressure data for tantalum- and niobium- Al_2O_3 systems are presented in Fig. 5 and 6. As shown from these figures,

Fig. 6. Partial pressures (atm) of the vapor species in the Nb- Al_2O_3 system as a function of $1/T \times 10^4 \text{ K}^{-1}$.

some fairly distinct aspects of vaporization or reactions of Al_2O_3 with cell metals are observed. The major species were Al and Al_2O . Contrary, AlO was minor and O or O_2 were scarcely observed. The metal oxides species were considerable high, so that they constituted major gaseous components in these cases. Furthermore, some distinct stages of reaction could be observable. At lower temperature region, the partial pressures of Al and Al_2O in both tantalum and niobium cells are about one order higher than in tungsten or molybdenum cells. However, the ion intensities were fairly stable with time, and did not show so large increasing when the cell temperature rised. When the temperature of the cell reached at a level (1950 K for Ta and 2000 K for Nb), rapid increasing of those pressures were started and after several minutes elapsed keeping the cell temperature at a constant, they decreased gradually with time. The maximum pressures observed in this way are plotted in the "reaction region" in Fig. 5 and 6, which are connected with broken lines.

At the temperature (2083 K for Ta and 2045 K for Nb), the cells was kept on this constant temperature for about two hours until the pressures revealed comparatively stable values. The decrease of pressures were shown with arrow marks in Fig. 5 and 6.

Measurements of pressures on the next stage were started at these comparatively stable states. The temperature of the cell was rised again and sometimes downed. In this higher temperature region, fairly stable values of pressures were obtained in both tantalum and niobium cells with

reasonable increasing or decreasing when the cell temperature changed. These values were plotted with real lines in Fig. 5 and 6. When the real lines are extrapolated toward lower temperature region, it could be shown that these lines are in good agreement with that of lower temperature region. However, the characteristics of vaporization in these region are probably different from each other.

In the niobium cell, rapid increase of vapor pressures were revealed again at the cell temperature 2155 K. It shows that certain higher oxidation of Nb occurred. Vapor species of niobium oxides at this condition were yet unchanged but the values of partial pressures of them increased rapidly. While in the tantalum cell, such rapid reaction could not be observed in corresponding temperature range.

4. Discussion

4.1. Partial pressures and some thermodynamic data for nealry neutral condition

The partial pressures of Al and O obtained using tungsten cells in this work are in good agreement with those of the reference^{2,3)} within error factor. These errors are considered mainly due to some errors for silver calibration, temperature distribution and ion currents measurements. Perhaps, a possible slight reduction by tungsten did not contributed mainly to this error, since the ratios of P_{O} to P_{Al} were about 1.0 over tungsten cell. If a neutral condition and congruently evaporation was reached the ratio was estimated to be 1.15. By a non equilibrium method, the ratio being 1.4 was reported⁵⁾, but by the equilib-

rium condition previously reported²³ which was similar to this work, this ratio was smaller than 1.0.

The error of silver calibration is estimated to be within $\pm 20\%$ which is owing to ion currents and multiplier gain measurements and uncertainty of ionization cross sections. The error due to temperature distribution is similarly estimated to be within $\pm 20\%$. Another error due to ion currents measurements is also estimated to be within $\pm 10\%$. Consequently the error of this work is totally within 50% , this is shown in Fig. 3 by an error bar.

Some thermodynamic data were obtained from the values for the tungsten cells. Three equilibrium relations were considered as follows.

Table 1. Third-law reaction enthalpy for reaction (1)

T	$-10 \log K_p$	$-\Delta f_{\text{ef}}$ (cal K ⁻¹ mole ⁻¹)	ΔH°_{298} (Kcal mole ⁻¹)
2413	26.93	180.15	732.1
2413	27.91	180.15	742.9
2433	27.02	180.12	739.1
2388	26.99	180.18	725.2
2363	27.92	180.22	727.8
2333	28.96	180.27	729.7
2313	30.24	180.30	737.1
2283	31.09	180.36	736.6
2248	31.13	180.38	725.7
Average			732.9

The equilibrium constant K_p and the third law ΔH_{298} for these reaction shown

in Table 1 were obtained on combining the partial pressures and the free energy function change referenced in JANAF data²⁴. The average ΔH_{298} from the third law for this reaction is 732.9 ± 10 Kcal/mole, which is in good agreement with the reference value 739.2 Kcal/mole²⁵. For the reaction (2) the ΔH_{298} obtained is -111.9 ± 6 Kcal/mole whose reference data is -121.1 Kcal/mole²⁶ and for the reaction (3) the $\Delta H_{298} = 134.4 \pm 6$ Kcal/mole is obtained which corresponds to the literature value 128.2 Kcal/mole²⁷. These discrepancies are mainly deduced from difference between AlO partial pressure data. The partial pressures of AlO and Al₂O obtained in this work are in good agreement with those of J. Drowart et al., but not so good with Farber et al. Consequently, the smaller values of AlO partial pressures may be characteristic in the tungsten-Al₂O₃ system.

The vapor species such as Al₂O₂ or AlO₂ were reported by previous experiments^{2,3}. However, we could not detect such species. Probably, in this experiment, these species may be hidden by background ions. Moreover the presence of AlO₂, which was found by Farber et al²⁸, and not observed by Paul²⁹, could not be confirmed. Nevertheless the reported Al₂O₂ and AlO₂ partial pressures were quite small, the absence of such vapor species will have a small effect upon the total pressures of Al₂O₃-metal systems.

4.2. Compatibility of refractory metal-Al₂O₃ systems

It is suggested from the Fig. 5 and 6 that Nb and Ta are more reducible to Al₂IO₃ at high temperature comparing with

W and Mo. The effect of these metals on the Al_2O_3 vaporization is considered as follows.

At lower temperature region below

about 2000 K in the Fig. 5 and 6 solubility of oxygen in niobium and tantalum is more higher than tungsten and molibdenum. As an example it is known that at about 1900

Fig. 7. Pressures of Al (atm) over various metal- Al_2O_3 systems at 1920 K versus the free energy of formation of metal oxides, assuming those to be formed by reduction of Al_2O_3 in the cells. The dotted line is a rough approximation.

K under one atm of O_2 , oxygen dissolves in niobium and tantalum to an extent of several at. %. While in tungsten and molybdenum the solubility is less than 0.1 at. %. Such oxygen dissolution may promote decomposition of Al_2O_3 since the oxygen partial pressure is lowered in those metal cells. Consequently higher pressures of Al and lower pressures of O could be attained.

To evaluate an effect of metal-oxygen bonding on the decomposition pressures of Al_2O_3 , we considered a relation which combined the partial pressures Al to the free energy of formation of various metal oxides presumed. The presumed oxides are WO_3 for W, MoO_2 for Mo, Ta_2O_5 for Ta and NbO for Nb, but such selections of composition of oxides are speculative. However, a somewhat linear relation could be obtained as shown in Fig. 7.

When the temperature of the cell had risen to about 2000 K, Nb and Ta were set up to react directly with Al_2O_3 to produce some metal oxides and their aluminates. In this temperature region, partial pressures of Al and others were rapidly increased with time. It is appeared that such reaction occurred from the abrupt dissolution and diffusion of Nb and Ta into Al_2O_3 and proceeded a formation of aluminates, which composition were proceeding conceivably toward to $AlNbO_4$ and $AlTaO_4$ ⁹⁾. Contrary, since for Mo and W metal oxides have comparatively high vapor pressures and the solubility of these metals into Al_2O_3 may be very small, it seems that the aluminate formation reaction has not been occurred for W and Mo.

Consequently above 2000 K, the partial

pressures of Al and others are governed by such reactions and metal-aluminate solution rather than Al_2O_3 itself. Then for compatibility of Nb and Ta to Al_2O_3 , it could be concluded that at comparatively low temperature region, the reduction of Al_2O_3 by such metals is affected by their oxygen solubility, but not so serious, while above 2000 K the formation of various metal aluminates strongly governed the compatibility between them. For the latter condition compatibilities of them are not good, especially comparing with Mo and W.

Acknowledgements

The authors are grateful to Prof. T. Kirihaara.

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Keywords

Vaporization
Knudsen cell
Refractory metal
 Al_2O_3
Compatibility