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THERMODYNAMICS OF CARBON DEOXIDATION AND
ALUMINIUM DEOXIDATION OF REFRACTORY METALS

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ABSTRACT

Carbon has been used for removing last traces of oxygen from many refractory metals by evaporation of CO at high temperature and vacuum. Similar purification can also be achieved employing aluminium deoxidation by evaporation of $\text{Al}_2\text{O}(g)$. In the present paper a theoretical thermodynamic approach has been attempted to evaluate the deoxidation tendencies of refractory metals of groups IV to VI by these two processes. Expressions have been theoretically derived, relating the concentration product of carbon and oxygen in the metal (which is a measure of the carbon deoxidation tendency of the metal) with temperature and pressure, for various M-C-O systems. Similarly the relative vapour pressure values of $\text{Al}_2\text{O}(g)$, $\text{Al}(g)$ and $\text{MO}(g)$ (suboxide of the metal) over various M-Al-O systems have been calculated as a function of aluminium and oxygen contents of the metal. From these analyses it has been shown that a substantial amount of oxygen can be removed from M-Al-O alloys by aluminium deoxidation. The estimated values are compared with the reported values based on experiment.

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1. INTRODUCTION

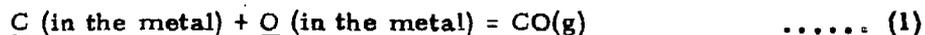
Carbon and aluminium are both used as reducing agents in the preparation of refractory metals of groups IV to VI by direct reduction of their oxides. In many cases, carbon can also be used as deoxidizing agent for removing last traces of residual oxygen from the refractory metals by vaporization of CO at high temperature and vacuum. In a few cases oxygen can be removed to some extent also by aluminium deoxidation with vaporization of aluminium suboxides Al_2O .

The present information about the two deoxidation processes is based mostly upon the experimental observations. The first theoretical explanation for the carbon deoxidation of refractory metals was given by Smith¹ in 1958. Very little is known about the thermodynamics of aluminium deoxidation of refractory metals.

In the present paper a theoretical approach has been attempted for examining further the deoxidation tendencies of refractory metals by these two processes. For carbon deoxidation, expressions have been theoretically derived relating concentration of oxygen and carbon in the metal as a function of temperature and pressure. Similar calculations have also been made for aluminium deoxidation of groups IV and V refractory metals. The calculated data are compared with the reported values based on the experimental observations.

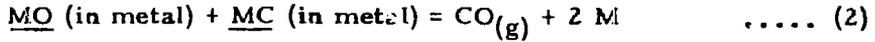
2. CARBON DEOXIDATION

Among the refractory metals niobium and tantalum are commercially produced by oxide-carbide reactions at high temperature and vacuum. There has been considerable research work during the past few years to extend the same process to the other metals of groups V and VI. The oxide-carbide reaction for any metal takes place in a number of steps depending upon the various phases of oxides and carbides present in the metal-carbon-oxygen system. During the last stages of this process, removal of carbon and oxygen by evolution of CO can be represented by the following reaction:



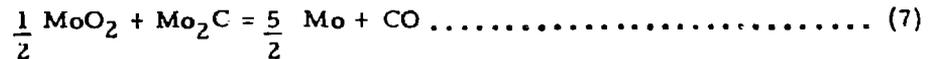
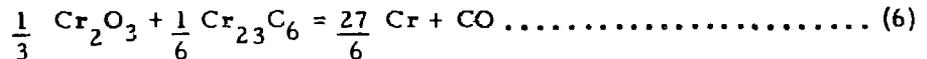
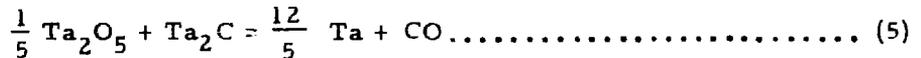
The equilibrium partial pressure of CO for the above reaction (1) will be a function of the activity of carbon and oxygen in the metal at any temperature. Assuming that equilibrium is attained during the last stages of pyrovacuum treatment, the concentration product of the residual carbon and oxygen contents of the metal is uniquely defined for any specific temperature and pressure. This concentration product can be taken as a measure of deoxidation tendency of carbon for the metal. A low value of the concentration product signifies higher carbon deoxidation tendency.

Smith¹ has calculated the concentration product values for various metals by assuming the concentration of oxygen and carbon as equivalent to the monoxide and monocarbide concentration in the metal. The reaction assumed for the carbon deoxidation was as follows :



The activities of MO and MC were taken as equal to their concentration in the metal. Based on these assumptions, the concentration product values were calculated for a particular temperature and pressure of CO. The values calculated by Smith could explain the carbon deoxidation tendencies of various metals qualitatively.

The present treatment is similar to that carried out by Smith, with this difference that the relevant carbide and oxide phases in reaction (2) are taken to be those that can exist in equilibrium with the pure metal (according to the phase diagram). For example, based on the constitution diagram for M-C-O systems^{2, 3}, Kruger and Warrel have reported that the last step of the carbothermic reduction of various metals can be represented as follows :



Considering the carbon deoxidation of niobium metal, the oxygen and carbon contents are thus expressed as the concentration of NbO and Nb₂C respectively in the range of solubility of oxygen and carbon in the metal. The equilibrium constant K for the reaction (4) under these conditions can be written as

$$K = P_{CO} / a_{Nb_2C} a_{NbO}$$

and thus

$$\begin{aligned} P_{CO} &= a_{Nb_2C} a_{NbO} \exp. (-\Delta G^0/RT) \\ &= a_{Nb_2C} a_{NbO} \exp. (-\Delta H^0/RT) \exp. (\Delta S^0/R) \end{aligned}$$

where ΔG^0 , ΔH^0 , and ΔS^0 are the standard free energy, enthalpy and entropy changes of reaction (4). Activities of the carbide and the oxide are assumed to be equal to their concentrations in the metal expressed in mole fractions. For sufficiently low carbon and oxygen contents they can be further equated with the mole fraction of carbon (N_C) and oxygen (N_O) respectively in the metal. Thus

$$P_{CO} = N_C N_O \exp. (-\Delta H^0/RT) \exp. (\Delta S^0/R) \quad \dots (9)$$

Introducing the ΔH^0 and ΔS^0 values as obtained from the literature⁴⁻⁶ and assuming them to be constant with respect to temperature, equation (9) can be written as

$$P_{CO(atm)} = N_C N_O 7.80 \times 10^8 \exp. (-104900/RT)$$

Converting p in torr and concentration in weight percentage carbon (W_C) and oxygen (W_O) the above equation gives

$$W_C W_O = 3.76 \times 10^{-10} P_{CO} \exp. (104900/RT) \quad \dots (10)$$

Equation (10), thus, gives the value of the concentration product ($W_C W_O$) as a function of equilibrium pressure and temperature. In deriving the above equation the loss of oxygen via suboxide evaporation has not been taken into account. Also, the equation is strictly valid for the equilibrium condition. Even with these limitations the above equation (10) can be a useful guide for calculating the concentration product at any

temperature and pressure. For example at 2273 K and 10^{-4} torr, $W_C W_O$ is equal to 4.6×10^{-4} . This means, theoretically, if the carbon content of niobium metal is 0.02 wt. % the oxygen content should be only 0.023 wt. % when the metal is vacuum sintered at 2273 K and 10^{-4} torr for sufficient time. Similar equations for other M-C-O systems have been calculated based on the reactions (3-8) and are given below :

V-C-O

$$W_C W_O = 1.76 \times 10^{-9} P_{CO} \exp. (108400/RT) \dots\dots\dots (11)$$

Ta-C-O

$$W_C W_O = 1.39 \times 10^{-10} P_{CO} \exp. (114100/RT) \dots\dots\dots (12)$$

Cr-C-O

$$W_C W_O = 1.61 \times 10^{-9} P_{CO} \exp. (78900/RT) \dots\dots\dots (13)$$

Mo-C-O

$$W_C W_O = 6.06 \times 10^{-10} P_{CC} \exp (54200/RT) \dots\dots\dots (14)$$

W-C-O

$$W_C W_C = 1.048 \times 10^{-10} P_{CO} \exp. (48690/RT) \dots\dots\dots (15)$$

$W_C W_O$ values as calculated from the above equations at 2273 K and 10^{-4} torr are given in Table I for a comparison of the carbon deoxidation tendencies of the various metals of groups V and VI.

Table II shows the comparative data for the concentration product in the metal as calculated from the equations (10) to (15) with the reported values based on the experimental observations. The values given in second and third column of the Table II correspond to the temperatures and pressures at which the final vacuum refining of the metals were carried

out. An interesting example for the comparison of the estimated values with the experimental values can be taken for those reported by Grala and Thyne¹¹. They have demonstrated successfully that carbon can be used as the deoxidizing agent for removing last traces of oxygen from niobium metal by vacuum sintering of the niobium powder at 2273 K and 5×10^{-4} torr. In a series of six experiments with niobium powder containing 0.35 wt. % oxygen the carbon content of the powder was varied from 0.01 to 0.17 wt. % by adding required amount of carbon in the charge. All the six compacts were treated at same temperature and pressure. The sintered compacts were then carefully analysed for their residual carbon and oxygen contents. From the reported values of oxygen and carbon contents, the concentration product have been calculated and found to be equal to 2.9, 1.5, 1.7, 1.8, 3.1, and 2.2×10^{-3} (wt %)². These values are practically constant and independent of initial or final carbon and oxygen contents of the charge. This has been anticipated in earlier discussion as the concentration product of carbon and oxygen in the metal is a function of temperature and pressure of CO. Only the average of the reported experimental values (2.2×10^{-3}) is shown in Table II. It can be seen from the Table II that this value is in excellent agreement with the estimated value (2.2×10^{-3}) calculated from equation (10) by substituting the values of temperature and pressure at which the vacuum sintering of the niobium powder was carried out. It can also be pointed out that under these conditions the removal of oxygen via sacrificial deoxidation would be negligible¹⁵ in comparison with carbon-deoxidation. This has also been confirmed by

Grala and Thyne during same investigations. In most of the other cases also, the estimated values and the reported values are in fair agreement within a factor of 10. This confirms the validity of the assumptions made in deriving equations(10) to (15). It can be seen from Table II, however, that the reported values based on the experimental observations are slightly lower than the estimated values in most of the cases. This can be explained from the fact that the solubility of carbon and oxygen in these metals are very low. Under these conditions the activity coefficients of carbide and oxide in the metal assumed to be unity in the derivations of equations(10) to (15) would in fact be higher. And, hence, the actual values of the concentration product would be slightly lower depending upon the activity coefficient values. In a few other cases, where the reported values are higher than the estimated values, the equilibrium conditions might not have been attained.

In general, for preparation of refractory metals by oxide carbide reactions, the ratio of carbon to oxygen content in the charge is an important factor for controlling the residual carbon and oxygen contents in the metal¹⁶. The concentration product values at any temperature and pressure can be used in selecting the optimum value of carbon to oxygen ratio in the charge.

The carbon deoxidation of the group IV metals is not feasible in view of the large affinity of oxygen for these metals compared to that for the group V metals. The equilibrium pressure of CO, in these cases, would be much lower even at very high temperature and also would be

comparable to the vapour pressure of the metal itself. The preparation of these metals by oxide-carbide reactions is not possible for the same reasons as has been reported by many workers^{17, 18}. The carbon deoxidation tendencies of these metals are hence not calculated.

3. ALUMINIUM DEOXIDATION

Aluminothermic reduction - also known as thermit reduction - has been successfully employed by many workers^{19, 22} for preparation of group V metals. The reaction is highly exothermic and once initiated spreads rapidly over the entire reaction charge. Similar investigations for aluminothermic reduction of group IV metal oxides have been attempted²³⁻²⁶, though the process is not as readily feasible as in the case of group V metals. In all cases, the metal thermit obtained from the reduction contains residual aluminium and oxygen which have to be removed by subsequent pyrovacuum treatment. During the pyrovacuum treatment, oxygen removal takes place both through a sacrificial deoxidation mechanism and through the evaporation of volatile aluminium suboxide Al_2O .

In the present discussion the thermodynamics of the aluminium deoxidation of the refractory metals of group IV and V has been investigated.

3.1 Aluminium Deoxidation of Group IV Metals

A thermodynamic analysis of the aluminium-deoxidation of group IV metals has been carried out by assuming the following reactions for removal of oxygen from the ternary M-Al-O system :



The activity of oxygen for both the above reactions is the same and hence

$$\log \frac{P_{Al_2O} a_M}{P_{MO} a_{Al}^2} = \frac{\Delta G_{MO(g)} - \Delta G_{Al_2O(g)}}{4.575 T} \quad \dots\dots\dots (18)$$

It is assumed here that the suboxide vapours do not interact in the gaseous phase. Introducing $\Delta G_{MO(g)}$ and $\Delta G_{Al_2O(g)}$ values as available from literature^{15, 27}, the above equation (18) gives at 2200 K for the Zr-Al-O system :

$$\frac{P_{Al_2O} a_{Zr}}{P_{ZrO} a_{Al}^2} = 1.2 \times 10^4 \quad \dots\dots\dots (19)$$

The above equation (19) indicates that the P_{Al_2O} will be much greater than P_{ZrO} as long as the activity of aluminium in the alloy is 10^{-2} or more. And, if any oxygen removal is possible from Zr-Al-O alloys it would be achieved mainly by evaporation of Al_2O , except for very low aluminium contents.

For Zr-Al-O alloys with low aluminium content it can be assumed that the oxygen activity in the alloy is closely comparable to that of a Zr-O alloy of the same oxygen content. In such cases the P_{ZrO} values can be calculated from the knowledge of activity of oxygen in the binary Zr-O system and $\Delta G_{ZrO(g)}$ values assuming reaction (16). The present authors have reported¹⁵ the calculated values of P_{ZrO} as a function of temperature for various compositions of Zr-C alloys. Using the calculated P_{ZrO} value of 2.3×10^{-5} torr for Zr-C alloy containing 10 atom

% oxygen at 2200 K and assuming the activity of zirconium in the alloy as unity, equation (19) gives

$$P_{Al_2O} = 2.8 \times 10^{-1} a_{Al}^2 \text{ torr} \dots\dots\dots (20)$$

The partial pressure of aluminium vapours can be represented by the following equation

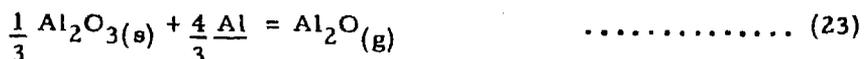
$$P_{Al} = a_{Al} 3.4 \times 10^1 \text{ torr} \dots\dots\dots (21)$$

where 3.4×10^1 torr is vapour pressure of pure aluminium at 2200 K as reported by Kubaschewski²⁸. Combining equations (20) and (21)

$$P_{Al_2O} / P_{Al} = 8.2 \times 10^{-3} a_{Al} \dots\dots\dots (22)$$

Equation (22) gives the aluminium deoxidation tendency of zirconium metal containing 10 atom % oxygen at 2200 K. It is evident from equation (22) that even for the aluminium content of the alloy corresponding to its activity value of 0.1, the P_{Al_2O} will be about 1000 times less than P_{Al} . The situation would be still worse as the aluminium and oxygen contents drop lower. The aluminium deoxidation of zirconium metal is, thus, not feasible for low aluminium contents when the most volatile species would be aluminium vapours instead of Al_2O .

When the zirconium content of the Al-Zr-O alloy is low (25 atom %), the activity of oxygen can be taken as corresponding to the Al-O system. In view of very low solubility of oxygen in aluminium, oxygen in Al-Zr-O alloys (with low zirconium contents) will be present as $Al_2O_3(s)$ and the deoxidation in such cases can be represented by the following reaction :



and thus

$$\log \frac{P_{Al_2O}}{a_{Al}^{4/3}} = \frac{\frac{1}{3} \Delta G_{Al_2O_3(s)} - \Delta G_{Al_2O(g)}}{4.575 T} \dots (24)$$

Substituting the reported²⁷ values of $\Delta G_{Al_2O_3(s)}$ and $\Delta G_{Al_2O(g)}$ at 1500 K the above equation (24) gives

$$P_{Al_2O} = 3.371 \times 10^{-3} \times a_{Al}^{4/3} \text{ torr} \dots (25)$$

From the reported²⁸ value of vapour pressure of pure aluminium at 1500 K, the partial pressure of aluminium over the alloy can be written as

$$P_{Al} = 1.67 \times 10^{-2} \times a_{Al} \text{ torr} \dots (26)$$

Combining equations (25) and (26)

$$P_{Al_2O} / P_{Al} = 2.0 \times 10^{-1} a_{Al}^{1/3} \dots (27)$$

Similarly at 2000 K

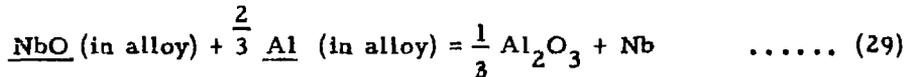
$$P_{Al_2O} / P_{Al} = 1.0 \times a_{Al}^{1/3} \dots (28)$$

As the $a_{Al}^{1/3}$ values will be nearly equal to unity for high aluminium content of Al-Zr-O alloy, the P_{Al_2O} will be nearly same as P_{Al} above 1500 K. This indicates feasibility of the aluminium deoxidation of Al-Zr-O alloy with considerable loss of aluminium. Gosse et al.²⁵ have observed during aluminothermic reduction of ZrO_2 that large excess of aluminium (about 3 times more than the stoichiometric requirement for the reduction) is required for complete removal of oxygen from the zirconium metal thermit.

The behaviour of the aluminium deoxidation of the other group IV metals would be more or less similar.

3.2 Aluminium Deoxidation of Group V Metals

Before proceeding to examine the aluminium deoxidation of group V metals it would be instructive to see the relationship between residual aluminium and oxygen contents of the metal thermit as experimentally observed in the thermit reduction tests. The final stage of the reduction for preparation of niobium metal, as in the case of oxide carbide reactions, can be represented according to following reaction



The overall reaction between Nb₂O₅ and Al is highly exothermic and an exact estimation of the final temperature of the charge under these conditions is difficult. However, as the metal thermit is obtained in well-separated massive form the final temperature of the reaction should exceed the melting point of niobium. Taking the activity of niobium and of Al₂O₃ as unity and assuming attainment of equilibrium, the following relationship can be derived for the reaction (29) at 2740 K (melting point of niobium) :

$$\left[a_{\text{NbO}} \right] \left[a_{\text{Al}}^{2/3} \right] = 3.68 \times 10^{-2} \quad \dots\dots\dots (30)$$

Wilhelm et al.²¹, and Kamat and Gupta²² have made extensive investigations on aluminothermic reduction of Nb₂O₅. The values of residual aluminium and oxygen contents of the as-reduced metal thermit, reported by them, are shown in Table III. These values are converted into mole fraction of aluminium (N_{Al}) and mole fraction of NbO (N_{NbO}), in the alloy respectively. The values of the product $\left[N_{\text{NbO}} \right] \left[N_{\text{Al}} \right]^{2/3}$ as calculated, are also shown in Table III. It can be seen that these

values are practically constant and are comparable with the value obtained by equation (30) assuming activities of NbO and aluminium as equal to their mole fractions. This would suggest that the activity coefficients of NbO and aluminium in the liquid Nb-Al-O alloys are not far different from unity. As the estimated value is in fact slightly higher (it will be still higher if actual temperature for the reaction (29) is more than the temperature assumed, or if the equilibrium conditions have not been attained), the indication is that the product of activity coefficient of NbO and aluminium in the liquid alloy would only be slightly more than unity. In the solid Nb-Al-O alloy this activity coefficient product would be still higher than in the liquid alloy as evident from the Nb-O and Nb-Al phase diagrams. Similar behaviour can be expected for the other group V metals.

The pyrovacuum treatment of the metal thermit is normally carried out between 2000 K - 2400 K. The oxygen is removed both by volatilization of $\text{NbO}_{(g)}$ and $\text{Al}_2\text{O}_{(g)}$ according to reaction (16) and (17). Substituting the reported values^{15, 27} for $\Delta G_{\text{NbO}(g)}$ and $\Delta G_{\text{Al}_2\text{O}(g)}$ in equation (18), following relationship is obtained at 2200 K for the Nb-Al-O system:

$$\frac{P_{\text{Al}_2\text{O}} \cdot a_{\text{Nb}}}{P_{\text{NbO}} \cdot a_{\text{Al}}^2} = 3.105 \times 10^5 \quad \dots\dots\dots (31)$$

The above equation (31) indicates that as in case of Zr-Al-O alloys, oxygen from Nb-Al-O alloys should be removed mainly by evaporation of Al_2O except for very low aluminium contents (corresponding to activity of aluminium $< 2 \times 10^{-3}$). It can be pointed out that the

equation (31) is valid whether oxygen is present in the form of solid solutions or as precipitated Al_2O_3 in the metal thermit. Similar equations for V-Al-O and Ta-Al-O systems at 2200 K can be represented as follows :

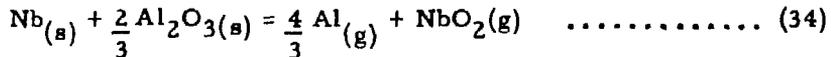
for V-Al-O

$$\frac{P_{Al_2O} a_V}{P_{VO} a_{Al}^2} = 9.02 \times 10^3 \dots\dots\dots (32)$$

and for Ta-Al-O

$$\frac{P_{Al_2O} a_{Ta}}{P_{TaO} a_{Al}^2} = 4.28 \times 10^7 \dots\dots\dots (33)$$

Wilhelm et al.²¹, however, have postulated that the removal of oxygen during the pyrovacuum treatment of niobium metal thermit takes place according to the following reaction :



They have attempted to verify this postulation from the material balance during pyrovacuum treatment of the metal thermit at 2273 K (the loss of niobium corresponded to the half the total loss of oxygen expressed in atom % as shown in Table IV). This analysis however does not hold good for the data reported by Kamat and Gupta. Their data (also shown in Table IV) indicate that the loss of oxygen (5.46 atom %) is much more than twice the niobium loss (1.71%) during pyrovacuum treatment for a similar niobium metal thermit.

Wilhelm, on the basis of a correlation between oxygen and niobium loss, has contended that de-oxidation of the niobium metal thermit takes place only by NbO_2 evaporation. On the other hand, it can be shown from

thermodynamic data, that for niobium metal with relatively low oxygen content, as in the case of Nb-Al-O metal thermit, $P_{\text{NbO}} \gg P_{\text{NbO}_2}$ even though $\Delta G_{\text{NbO}_2(\text{g})}^\circ$ is more negative than $\Delta G_{\text{NbO}(\text{g})}^\circ$ (Brewer²⁹ has also commented that in the sacrificial deoxidation of niobium, NbO will be the predominant oxide species in the vapour phase). Taking this into consideration the material balance has been again calculated here from the same analysis data reported by Wilhelm et al. and Kamat et al. as shown in Table IV. In the present calculation losses of oxygen through vaporization of CO and SiO have also been taken into account. The loss of oxygen as $\text{Al}_2\text{O}(\text{g})$ has been calculated by subtracting the losses of oxygen as NbO, CO, and SiO from the total loss of oxygen as observed.

The material balances as shown in Table IV for both the cases (Wilhelm & Kamat) indicate that about 40-55% of the total oxygen should have been initially removed as $\text{Al}_2\text{O}(\text{g})$ and as the aluminium content approached the equilibrium value for reaction (17), the remaining oxygen was then removed through vaporization of $\text{NbO}(\text{g})$.

The removal of aluminium during the pyrovacuum treatment takes place both by vaporization of $\text{Al}_2\text{O}(\text{g})$ and aluminium vapour. The relative vapour pressure values of $\text{Al}_2\text{O}(\text{g})$ and aluminium depends upon the oxygen and aluminium contents of the metal thermit and shall be discussed later in detail. At higher oxygen and aluminium contents $P_{\text{Al}_2\text{O}} > P_{\text{Al}}$ and most of the aluminium would be removed as $\text{Al}_2\text{O}(\text{g})$ only as is the case during the pyrovacuum treatment of the metal thermit carried out by Kamat and Gupta. It can be seen from Table IV that the loss of aluminium

as Al_2O (calculated value) is in excellent agreement with the total loss of aluminium as observed by them. On the other hand in case of pyro-vacuum treatment carried out by Wilhelm, since the oxygen content of the metal thermit was lower, some of the aluminium should have been removed as aluminium vapour also.

It is, thus, confirmed that a substantial amount of oxygen from Nb-Al-O alloys can be removed by aluminium deoxidation by pyrovacuum treatment of the metal thermit at 2000 K or more. Similar behaviour can be expected for the other group V metals thermits as is evident from equations (32) and (33).

The aluminium deoxidation of the group V metals has been analysed in a way similar to that for carbon deoxidation, as the activity data of oxygen in these metals are not available. For example, in the case of niobium metal thermit the deoxidation process has been assumed to occur according to following reactions:



From the available free energy data^{5, 27} of above reaction (35) at 2000 K, following expression is obtained:

$$P_{\text{Al}_2\text{O}} / a_{\text{Al}}^2 a_{\text{NbO}} = 5.7 \times 10^3 \text{ torr} \quad \dots\dots\dots (36)$$

The partial pressure of aluminium over the alloy can be expressed as

$$P_{\text{Al}} = 6.745 a_{\text{Al}} \text{ torr} \quad \dots\dots\dots (37)$$

where 6.745 torr is the vapour pressure of pure aluminium at 2000 K.

Equations (36) and (37) give

$$\frac{P_{Al_2O}}{P_{Al}} = 8.45 \times 10^2 \left[N_{NbO} \right] \left[N_{Al} \right] \gamma_{NbO} \gamma_{Al} \dots\dots (38)$$

N_{NbO} at lower oxygen concentrations can be equated to N_O . It has been discussed earlier that the product of the activity coefficient of NbO and aluminium ($\gamma_{NbO} \gamma_{Al}$) in the solid Nb-Al-O alloys is only more than unity and hence :

$$\frac{P_{Al_2O}}{P_{Al}} > 8.45 \times 10^2 \left[N_O \right] \left[N_{Al} \right] \dots\dots\dots (39)$$

The above equation (39) indicates that the P_{Al_2O} will be more than P_{Al} as long as the concentration product of oxygen and aluminium in the alloy is greater than 10^{-3} at 2000 K.

From similar thermodynamic treatment for V-Al-O and Ta-Al-O systems at 2000 K following expressions are obtained :

for V-Al-O system

$$\frac{P_{Al_2O}}{P_{Al}} > 4.8 \times 10^1 \left[N_O \right] \left[N_{Al} \right] \dots\dots\dots (40)$$

and for Ta-Al-O

$$\frac{P_{Al_2O}}{P_{Al}} > 4.5 \times 10^2 \left[N_O \right] \left[N_{Al} \right] \dots\dots\dots (41)$$

While equations (31-33) show the extent to which oxygen would be removed from the metal thermit by aluminium deoxidation instead of by sacrificial deoxidation, equation (39-41) give the relative values of the vapour pressure of Al_2O and aluminium as a function of aluminium and oxygen contents. For an appreciable deoxidation P_{Al_2O} should be

-18-

much greater than P_{MO} and at least comparable with P_{Al} . Further, during the deoxidation, loss of aluminium is invariably much more than that of oxygen (even when P_{Al} is negligible loss of aluminium is about 2 times more than that of oxygen in atom%). It is thus necessary that the aluminium content in the metal thermit should be much higher compared to that of oxygen.

Vanadium metal has the least tendency for aluminium deoxidation among the group V metals as evident from equation (40). The deoxidation process in this case becomes still more complex as the vanadium metal itself has high vapour pressure ($> 10^{-3}$ torr) at 2000 K. The removal of oxygen by sacrificial deoxidation is also not very much feasible from the vanadium metal due to the same reason. It is thus necessary in this system to have higher aluminium contents compared to that in the niobium or tantalum metal thermit for complete removal of the residual oxygen. Thus, complete deoxidation could be achieved from the niobium metal thermit containing only 2.2 wt% aluminium and 0.78 wt% oxygen (Table IV), whereas in the vanadium metal thermit amount of aluminium incorporated was upto 11.1 wt% for complete removal of only 0.29 wt% oxygen as reported by Carlson et al.¹⁹.

By comparing equations (39-41) with (22) it can be seen that the aluminium deoxidation of group V metals is much more feasible than in the case of group IV metals. However, the extent of deoxidation in this case would be poorer compared to that with carbon deoxidation of

the same metals. The one advantage in this case is that after achieving complete deoxidation, the residual aluminium can be easily knocked off by pyrovacuum treatment of the alloy at higher temperature.

In the carbon deoxidation the main vapouring species was only CO, whereas in the aluminium deoxidation 3 or 4 vapour species (Al_2O , Al, MO and M) are present. Further, the activity data for aluminium and oxygen in the alloy are also not known. For these reasons, the present thermodynamic analysis for the aluminium deoxidation has been only qualitative. Nevertheless, the foregoing treatment has described the importance and relative feasibility of the aluminium deoxidation in the various metals of groups IV and V. A similar thermodynamic treatment can also be made for silicon deoxidation of these metals.

4. CONCLUSIONS

(1) Carbon deoxidation tendencies of the refractory metals are in the following order :



(2) Expressions have been theoretically derived relating concentration product of carbon and oxygen in the metal as function of temperature and pressure for various M-C-O systems.

(3) A substantial amount of aluminium and oxygen can be removed from M-Al-O alloys of group V metals by evaporation of $\text{Al}_2\text{O}(\text{g})$. The process is not equally feasible for group IV metals.

(4) Fair agreements have been observed in most of the cases between estimated and reported values based on the experimental

observations.

Most of the foregoing treatment was based upon the estimated activity values of carbon, oxygen and aluminium in the metal. Much more reliable experimental thermodynamic data are required for an actual quantitative evaluation of these potentially useful deoxidation processes.

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Table I

ESTIMATED VALUES OF CARBON DEOXIDATION TENDENCIES
OF THE METALS AT 2273 K & 10^{-4} torr

Metal	$W_C \cdot W_O$ (wt. % C x wt. % O)
V	4.6×10^{-3}
Nb	4.6×10^{-4}
Ta	1.3×10^{-3}
Cr	6.2×10^{-6}
Mo	9.6×10^{-9}
W	5.0×10^{-10}

Table II

COMPARATIVE DATA FOR CONCENTRATION PRODUCT
 $W_C \cdot W_O$ IN METAL-CARBON-OXYGEN SYSTEMS

System	Temperature °C	Pressure (torr)	$W_C \cdot W_O$ (wt. % C x wt. % O)		Reference
			Estimated values	Reported values	
V-C-O	1650	1×10^{-4}	2.4×10^{-1}	1.2×10^{-2}	7
	1700	5×10^{-5}	8.7×10^{-2}	7.2×10^{-3}	8
	2050	5×10^{-5}	1.4×10^{-3}	5.6×10^{-3}	9
Nb-C-O	1800	5×10^{-3}	2.2×10^{-1}	2.0×10^{-2}	10
	2000	5×10^{-4}	2.2×10^{-3}	2.2×10^{-3}	11
	2100	1×10^{-4}	1.7×10^{-4}	5.0×10^{-3}	8
	2150	5×10^{-4}	5.4×10^{-4}	9.0×10^{-3}	12
Ta-C-O	2750	5×10^{-4}	1.2×10^{-5}	7.0×10^{-6}	13
Cr-C-O	1400	1×10^{-2}	3.2×10^{-1}	2.4×10^{-2}	14

Table III

$\left[N_{Al} \right]^{2/3} \left[N_{NbO} \right]$ VALUES BASED ON THE REPORTED
 VALUES OF RESIDUAL ALUMINIUM AND OXYGEN CONTENTS
 OF AS-REDUCED METAL THERMIT

Aluminium and Oxygen contents of as-reduced metal thermit in wt. %		$\left[N_{Al} \right]^{2/3} \left[N_{NbO} \right]$	Reference
Al	O		
0.25	3.60	8.49×10^{-3}	Kamat & Gupta ²²
1.09	3.00	1.61×10^{-2}	
2.00	1.50	1.32×10^{-2}	
4.00	0.30	3.96×10^{-3}	
2.22	0.78	7.55×10^{-3}	Wilhelm et al. ²¹
11.10	0.29	6.18×10^{-3}	

Table IV

**MATERIAL BALANCE* FOR NIOBIUM METAL
THERMIT DURING PYROVACUUM TREATMENT**

Element	(Wilhelm et al.)		(Kamat et al.)	
	As-reduced metal thermit	Pyro-vacuum threated at 2273 K and 5×10^{-5} torr	As-reduced metal thermit	Pyrovacuum treated at 2000 K and 10^{-3} torr
	(in wt. %)		(in wt. %)	
Al	2.200	0.120	2.000	0.200
O	0.780	NIL	1.500	0.550
Si	0.135	0.035	0.130	0.020
C	0.025	0.008	0.068	0.008
Other impurities	0.141	0.014	0.254	0.081
Total impurities	3.281	0.177	3.952	0.859
Total loss of metal (as reported)		5.30		4.80

Material Balance

Total loss of impurities	3.10	3.09
Loss of Nb	2.20	1.71
Loss of \bar{O} as NbO	0.38	0.29
Loss of \bar{O} as CO	0.02	0.08
Loss of \bar{O} as SiO	0.06	0.06
Loss of \bar{O} (as reported)	0.78	0.95
Loss of \bar{O} as Al_2O_3	0.32	0.52
Loss of Al as Al_2O_3	1.08	1.75
Total loss of Al (as reported)	2.08	1.80

(*) While the analytical data (for Al, O, Si and C) and the total loss of metal are those reported by Wilhelm et al. and Kamat, the material balances for oxygen loss and aluminium loss in both the cases have been freshly worked out based on the present discussion.

