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in the Mo-BN-C System.
Application to
Prototype Subterrene Penetrators

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M. C. Krupka

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THERMODYNAMIC STABILITY CONSIDERATIONS IN THE Mo-BN-C SYSTEM

APPLICATION TO PROTOTYPE SUBTERRANEAN PENETRATORS

by

M. C. Krupka

ABSTRACT

Materials capable of operation for extended lifetimes at high temperatures are required for use as rock-melting penetrators. Prototypes presently designed use molybdenum, boron nitride and high density graphite as high temperature materials. The integral design features of the penetrator system suggest that consideration be given, from a thermodynamic viewpoint to the potential for chemical reactivity among the components. Standard Gibbs free energy calculations at selected temperatures have been made for the composite system and the relative potential for chemical reactivity assessed. Postmortem examination has been made of some penetrators and the observations are discussed within the framework of the calculations. Suggestions for minimizing chemical reaction are given under the assumption that these materials may be retained for future designs of penetrators.

I. INTRODUCTION

The high temperatures reached in the Subterranean penetrator system require a set of materials maintaining not only structural and physical integrity but a high degree of chemical inertness over extended periods of time. Realization of this ideal situation becomes difficult at the suggested operating temperatures of the system, viz., 1400°-2000°C and possibly higher in the case of certain radiant heater designs. The range is wide because of a high power density that must be transmitted to a central core so that ample heat flux can be conducted to the surface in contact with rock. Since most materials will react with one another to some degree in this temperature range an intrinsic thermodynamic lifetime limitation will be provided. The lifetime, however, may be extended by virtue of the kinetic behavior of the system.

II. STANDARD FREE ENERGY CALCULATIONS FOR THE SYSTEM Mo-BN-C

Equilibrium thermodynamic calculations demonstrate whether or not a particular choice of materials will exhibit a degree of stability at specific temperatures. Calculation of the Gibbs free energy, ΔG° , at temperature for sets of potential reactions will at least suggest the probability of occurrence for any one reaction.

Engineering choice at this time, in view of favorable electrical, heat transfer and mechanical properties, is to use Mo as the major structural member, BN as the electrical insulator and high density graphite (POCO) as the electrically-heated axial core of the penetrator system. W was considered also as a structural equivalent but is not in use at this time. Thermodynamically, there is sufficient similarity between Mo and W so that the conclusions herein presented should be applicable at least in part to a W system. Calculations have been made using an average temperature of 2000°K (1727°C). In those regions where higher

temperatures are anticipated, additional data are presented. Thermodynamic data have been taken or estimated from sources listed in the references.¹⁻⁶ In view of the potential complexity of interactions in the composite system, analysis has been conducted in the form of binary or ternary subsystems. The thermodynamic equations used, reference data and calculated results for many of the specific reactions mentioned below are given in Appendices A-C.

A. The Partial System Mo-B

The Mo-B system is complex containing at least five borides and high and low temperature crystallographic configurations for some.⁷ Mo_2B and MoB are the most stable borides on a per atom B basis ($\Delta H_f^\circ(298^\circ\text{K})$).⁵ For this reason calculations were not made for some of the higher borides.

B. The Partial System Mo-N

There are two compounds in this system, possibly three, of which Mo_2N and MoN are more established.⁷ These nitrides, as well as the other Group VI-B nitrides (Cr, W) are characterized by their thermodynamic instability and their formation would not be expected at high temperatures, particularly in the presence of borides. They become more stable as the temperature is reduced, i.e., $<1000^\circ\text{C}$.

C. The Partial System Mo-C

This system contains three compounds, α - and β - Mo_2C , Mo_3C_2 (γ - MoC_{1-x}) and cubic MoC_{1-x} .^{8,17} Only Mo_2C is stable at room temperature although Mo_3C_2 (hexagonal) can be quenched from $>1655^\circ\text{C}$. The metal carbides readily, even at low temperatures, depending on the preparatory technique used. Calculations are concerned with Mo_2C only. In addition to thermodynamic data, there is available reasonably good reaction rate data for both Mo and W carbides.⁹

D. The Partial System B-N

The degradation of BN due to high temperature (disregarding surface interaction with surrounding components for the moment) may be represented by the following equilibria:

Reaction (1) is most probable and has been experimentally verified.¹⁰ If one arbitrarily considers $P > 10^{-5}$ atm. (0.01 torr) to be significant, then temperatures $> 2500^\circ\text{K}$ must be achieved in the system for the other equilibria. Free boron is not expected to exist at these temperatures in contact with surrounding components but should react on the surface and internally (see Section J.).

E. The Partial System B-C

B_4C is the only well-established compound although controversy exists for some other formulations.⁷ Decomposition of B_4C proceeds as shown.

At sufficiently high temperatures, e.g., 2500°K , the gas BC_2 is significant.¹¹

F. The Partial System C-N

The formation of both CN(g) and $\text{C}_2\text{N}_2(\text{g})$ may be expected from the reaction of hot graphite in a nitrogen atmosphere.

N_2 gas arises from two sources, a) decomposition of BN and b) artificial inclusion of N_2 within the atmosphere surrounding the composite system. As mentioned previously, if one arbitrarily assumes $P(\text{CN or C}_2\text{N}_2) > 10^{-5}$ atm. (0.01 torr) to be significant then temperatures $> 2500^\circ\text{K}$ must be achieved in the system. The equilibria further show that high pressures of N_2 gas will result in additional graphite erosion.

G. The Partial System Mo-B-N

Equilibria under consideration concern the formation of Mo borides. Those equilibria concerning Mo_2N are probably not realistic in view of the instability of Mo_2N at these temperatures but are included for the sake of completeness.

borides

Reactions (9), (10) and (11) proceed readily generating relatively high N_2 partial pressures and have been experimentally tested at $1800^\circ K$ under both ~ 0.5 atm Ar and N_2 .¹² In the analogous W-B-N system, it has been demonstrated for reaction (15) that $\Delta G^\circ < 0$ at $1820^\circ K$ but that $\Delta G^\circ > 0$ at $1373^\circ K$.

Work in this system is summarized in Fig. 1.¹³ Since these reactions proceed with an increase in volume, sufficient N_2 gas overpressure should cause equilibria reversal. Conversely, in a system whereby the N_2 gas is removed by inert gas flushing, additional metal boride formation would be expected.

H. The Partial System B-N-C

Equilibria under consideration include:

At $2000^\circ K$, only reaction (16) is significant since the N_2 gas partial pressure is several orders of

magnitude higher than all of the other potential gases. At $2500^\circ K$ and higher, partial pressures of the other gases assume greater significance. Under these circumstances, additional gas-gas equilibria are probable, the complexities of which are not discussed here.

I. The Quaternary System Mo-B-N-C

The formation of Mo_2B , MoB , B_4C and Mo_2C has been suggested by thermodynamic calculation. The eventual total degradation of BN will permit localized contact between some of the reaction products permitting additional solid state reactions. Examples are listed below where $\Delta G_f^\circ(2000^\circ K) < 0$.

These reactions show that $B(s)$ and $B_4C(s)$ would not be expected to exist in contact with a Mo or Mo borided surface. A ternary compound could also form.¹⁴

J. Effect of Oxygen-Containing Impurities on the Mo-BN-C System

The direct oxidation of materials such as Mo, BN and C has been extensively studied over wide ranges of oxygen potential and temperature and need not be discussed here except to say that these materials oxidize readily in the unprotected state. The reputed oxidation resistance of BN is contrary to the calculated thermodynamics and may in part be due to surface energy effects concerning the recombination of atoms to form the stable N_2 molecule. What is of interest however, is the effect of certain oxygen-bearing impurities upon the system.

1. Boron Oxide, $B_2O_3(l,g)$

Sources of B_2O_3 include (a) BN impurity, (b) secondary reactions (see 3. below), and (c) formation from residual free oxygen of a surrounding inert atmosphere. B_2O_3 is usually present as a sinter aid in BN to the extent of 1-3 weight percent. High temperature vacuum outgassing can remove the B_2O_3 , at least in principle. At $2000^\circ K$, the vapor pressure is high, 3.9×10^{-2} atm (29.6 Torr). Diffusion rate out of the BN could be a limitation. Equilibria under consideration include:

Fig. 1. Ternary phase diagram W-B-N system (Ref. 13).

Minimal reaction is expected between Mo, MoB and $B_2O_3(l,g)$. In sharp contrast, high partial pressures of $CO(g)$ can be generated when $B_2O_3(l,g)$ attacks graphite. Thus erosion of graphite can be expected by this mechanism. The volatility of B_2O_3 will permit permeation of areas beyond those in direct contact.

2. Boron Oxide Dimer, $B_2O_2(g)$

The gas molecule B_2O_2 has been studied mass spectrometrically,¹⁵ and arises from reaction (31).

$B(s)$ is theoretically available from BN degradation. Reaction with graphite is expected.

3. Water Vapor, $H_2O(g)$

Sources of $H_2O(g)$ include (a) residual impurity in a surrounding inert atmosphere and (b) water-cooling system mechanical design defects. The following types of equilibria are of interest:

The dissociation of $H_2O(g)$ at 2000°K is minor, ~0.55%, increasing to ~3.0% at 2500°K. Numerically large equilibrium constants are obtained for reactions (34), (35) and (36) suggesting a high probability of reaction. Reactivity with Mo and MoB is to be expected also but not to the same degree. A very interesting set of equilibria is demonstrated by reactions (39) and (40). Work with this species $HBO_2(g)$,¹⁶ has been done up to 1500°K.

The calculation extends this to 2000°K. The main interest is in the fact that this is a third mechanism whereby boron may be transported in the vapor phase to parts of the system beyond the expected surface contact areas.

4. Molybdenum Trioxide, $MoO_3(g)$

Although MoO_3 is highly volatile and not considered an impurity in the sense of B_2O_3 , the equilibria below suggest that $MoO_3(g)$ derived from primary or secondary sources reacts extensively with both graphite and BN.

K. Formation of Liquid Phases Below 2000°C (2273°K)

A survey of the literature has been made to determine whether or not liquid phases may exist at temperatures below 2000°C (2273°K). Several binary and ternary combinations have been checked and are listed below.

In the Mo-B system,¹⁷ a low melting eutectic exists at 1920°C between Mo_2B_5 and B. Boron itself melts at 2070°C. The Mo- Mo_2B eutectic is at 2175°C.

In the Mo-C system,^{17,2} the Mo- Mo_2C eutectic is at 2200°C.

Data is not generally available for the ternary Mo-B-C system. A liquid phase between MoB- Mo_2C (60/40 mole %) was shown to exist at 2175°C¹² but this contained Mo_2BC as a reaction product. In the system W-B-C¹⁷ a low melting binary eutectic, WB_4 -B occurs at 1970°C and a ternary eutectic at 1950°C for WB_4 -B- B_4C . An analogous region should exist in the Mo-B-C system except that the temperatures should be even lower.

Effect of nitrogen in the system could not be ascertained. BN itself is reputed to have a melting point in excess of 3000°C under several atmospheres of N_2 but degradation is initiated prior to reaching this temperature.

A possible B- B_4C "eutectic"¹⁷ is reputed to exist at 2075°C but this is suspiciously similar to the melting point of boron. The B_4C -C eutectic is at 2375°C.

III. APPLICATION TO PROTOTYPE ELECTRIC SUBTERRANEAN PENETRATOR HEAD DESIGNS

In the previous sections, several types of reactions and their probability of occurrence have been examined from a thermodynamic viewpoint. Post-mortem analyses can now be conducted on actual penetrator units that have been in service so that causes of realistic corrosion may be determined and some corrective measures suggested.

It might be appropriate at this point to emphasize that the free energy calculations refer to the products and reactants in their standard state only, i.e., a reaction may or may not proceed (depending on the sign of ΔG^0) categorically providing each material is in the standard state. Further, the calculated partial pressures represent equilibrium pressures and maximum vaporization rates. Under other conditions, for example in a catalytic system, reactions may occur even though the prediction would be otherwise. In addition, mass transport phenomena based on diffusion and kinetic factors, will often have an overriding effect upon the net reaction.

Specifically, the detailed observations which follow refer to several one-inch and two-inch axial graphite heater designs generally water-cooled, see Figs. 2 and 3 (typical designs).

Fig. 2. Schematic of a penetrator head design-hollow electrode.

Fig. 3. Schematic of a penetrator head design-solid electrode

A gas-cooled version has also been examined. An unfortunate complication of the analysis is that precise temperatures have never been established for various components except in restricted locations with the remaining temperature profile inferred from heat transfer calculations.

At the present time, the "average" lifetime of the penetrator (failure due to open circuitry) is on the order of six hours.* Erratic electrical behavior is observed prior to failure. Axial sectioning shows variable corrosion along the entire length. The type of corrosion is common to both one-inch and two-inch sizes.

In the discussion that follows, the system has been sub-divided for purposes of clarity in analysis.

A. The Partial System Mo-C

In all regions where the Mo body contacts the graphite directly, for example, the tip, electrical lead-in pins or in radiant heater designs, extensive carbiding occurred. It is important to realize that despite the very high melting temperatures of

* A penetrator has been tested to approximately 45 hours since but the design is that of a radiant heater whereby BN has been eliminated.

the Mo carbides, actual carbiding occurs at much lower temperatures. For components remaining in intimate contact, the diffusion of carbon through the carbide layer will be the rate-determining factor for the buildup of the initial Mo_2C layer.⁹ Unless the Mo-carbide-C surfaces remain under continued contact, it is possible to create a void at the interface between the Mo carbide and C. It is suggested that this may have occurred in at least one case causing partial discontinuity of electrical circuit. Erosion via the H_2O or B_2O_3 vapor phase mechanism could cause additional void enlargement. The carbides are good conductors at high temperatures so that observable effects are not immediately evident. However, thin wall graphite sleeves in contact with a Mo wall may in time become totally carbided thereby destroying their initial function.

B. The Partial System Mo-B-N

Extensive boriding at the Mo-BN interface was observed. X-ray diffraction of the boride layer showed the components to be a minor phase of Mo_2B (thin layer next to the Mo wall), a major phase of MoB and a very thin outer layer whose unequivocal identification was not possible by this technique. The most probable choices could be a higher boride or either Mo_2BC or Mo_2C (carbon becomes available after total dissolution of BN). Boride wall thicknesses of up to 16 mils were observed in some locations. Stress cracking was observed in the layer up to the Mo surface. These cracks may negate any diffusion limitation imposed by the growth rate of the layer itself. Calculations (Sec. I) suggest a variety of mechanisms whereby Mo borides can form emphasizing the heavy buildup of MoB. Reaction rate data on these borides are lacking. A single experiment run at 1600°C under an inert atmosphere in a Mo crucible with pure boron showed a buildup of a boride layer 24-27 mils thick in 24 h.¹²

C. The Partial System B-N-C

B_4C was observed at the C-C interfacial region as expected but in small quantity. No rate data is available but again a single experiment using pure boron in a graphite crucible under an inert atmosphere run at 1800°C produced a thickness of B_4C of 13-15 mils in 24 h.¹² Thus the reaction rate to produce B_4C is much slower than that producing Mo_2B -MoB. Of greater significance was the observation that B_4C was detected at depth within the cavities

and "porous areas" of the graphite central electrode in greater quantity (estimated from x-ray diffraction relative line intensity comparisons). This suggests an additional mechanism, probably vapor phase, transporting boron into regions otherwise inaccessible (a liquid phase could of course do the same). Possibilities include: (a) higher than predicted temperatures thereby involving B(g) ; (b) transport via the gaseous boron oxides; (c) transport via HBO_2 gas derived from a water leak; and (d) simultaneous reactions involving graphite corrosion and subsequent deposition of B_4C within the area. B_2O_3 is known to be an impurity; in these cases 1.05 weight percent (analyzed) was present. Water leaks were also known to be present.

D. Suggestions For Corrective Action

The calculations and subsequent analyses of actual penetrator internal systems suggest a number of approaches to alleviate at least in part some of the problems encountered. Admittedly, not all is known about the Mo-BN-C system at this time but these suggestions may prolong the lifetime of the penetrator unit, presently designed with these materials.

1. A dry, oxygen-free atmosphere should surround the components in the unit. A heavy inert gas such as argon is preferred kinetically whereas helium is probably preferable from a heat transfer point of view.

2. A nitrogen gas overpressure ($P_{\text{N}_2} >$ decomposition pressure for the specific reactions concerned) should be helpful minimizing N_2 gas product reactions. A mixture of gases, viz., $\text{He} + \text{N}_2$, is acceptable particularly if the relative proportions of the gases are optimized to provide the corrective effects described above. The effect of N_2 upon graphite becomes of concern as higher temperatures are reached. Protection of the graphite by deposition of a coat impervious to N_2 and stable in its presence would alleviate this problem. For example, tantalum carbide, TaC, is known to be stable in a N_2 atmosphere. The formation of refractory metal nitrides is possible upon cool-down of the system but is not expected to be a problem at operating temperature.

3. Elimination of oxygen-bearing impurities is necessary. High temperature vacuum outgassing of BN is recommended. An unfortunate side effect

occurs in that the BN also degrades mechanically as the B_2O_3 is eliminated. Water leak problems can be eliminated by going to gas-cooling or designing more reliable gasketing or cooling systems. It should be emphasized, however, that the observed corrosion effects will not go away upon elimination of H_2O . Observation of the gas-cooled penetrator unit showed remarkably similar corrosion effects, some porous graphite regions, MoB, B_4C , etc., although not to the same degree as shown in Figs. 4 and 5. As a

Fig. 4

Fig. 5

possible assist with respect to BN, vapor-deposited pyrolytic BN should be more attractive. As fabricated it is theoretically dense and impervious and reaction rates should be reduced. Oxygen content is not known but should be considerably less than that present in the usual sintered stock.

4. Solid state reaction of BN with Mo and C may be prevented by insertion of thin wall diffusion barriers. The relative rate of reactivity of BN with the barrier should be known since it is doubtful that a totally inert barrier can be found for these operating temperatures. Degradation of the BN may still occur for other reasons.

5. Carbiding at electrical contact regions can be minimized by insertion of thin wall diffusion barriers against carbon migration such as TaC (a good electrical conductor at high temperature). Power lead-in refractory metal pins can be spring-loaded to take up void formation or be moved to lower temperature areas to minimize carbiding.

6. Improved heat transfer will permit operation (internally) at lower temperatures, still permit the necessary surface temperatures for melting to be attained, thus allowing kinetics to play an important role by slowing down reaction rates.

7. Finally, consideration should be given to BN removal for some designs. This leads to two alternatives, (a) radiant heater systems with gas insulation and (b) use of a substitute material in the same system. At the present time, minimal work has been done to implement option b.

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APPENDIX A

STANDARD THERMODYNAMIC CALCULATIONS-BASIC EQUATIONS

$$1. \Delta G_{(f,T)}^{\circ} = \sum (\Delta G_{(f,T)}^{\circ})_P - \sum (\Delta G_{(f,T)}^{\circ})_R$$

where $\Delta G_{(f,T)}^{\circ}$ = standard free energy of formation change at temperature for the reactants and products.

$$2. \Delta G_{(f,T)}^{\circ} = -RT \ln K \text{ at equilibrium}$$

where the activities of solid and liquid phases are taken as $a = 1$. For gas-solid or gas-gas reactions, the equilibrium constant K will be related to the partial pressures of the gaseous reactants and products.

$$3. \frac{\Delta G_{(f,T)}^{\circ}}{T} = -R \ln K = \frac{\Delta H_{(f,T_{\text{ref}})}^{\circ}}{T} + \Delta f_{\text{ef}}(T)$$

where: $\Delta H_{(f,T_{\text{ref}})}^{\circ}$ = standard heat of formation at reference temperature

$\Delta f_{\text{ef}}(T)$ = change in free energy function at temperature

APPENDIX B

STANDARD FREE ENERGY OF FORMATION DATA AT 2000° and 2500°K

Material	Value-Kcal/mole	
	$\Delta G_{f(2000^{\circ}\text{K})}^{\circ}$	$\Delta G_{f(2500^{\circ}\text{K})}^{\circ}$
Mo ₂ S(s)	- 13.046	—
MoB(s)	- 10.288	—
MoB ₂ (s)	- 17.82	—
Mo ₂ B ₅ (s)	- 39.92	—
Mo ₂ N(s)	10.33	—
Mo ₂ C(s)	- 13.0	—
Mo ₂ SiC(s)	—	—
MoO ₃ (g)	- 52.620	—
B(g)	61.935	44.857
BN(s)	- 17.310	- 6.524
BN(g)	101.477	89.805
B ₄ C(s)	- 7.171	- 5.679
BC(g)	105.812	84.516
BC ₂ (g)	—	—
CN(g)	60.960	49.367
C ₂ N ₂ (g)	53.006	47.672
B ₂ O ₃ (l)	-192.120	—
B ₂ O ₃ (g)	-179.178	-174.105
B ₂ O ₂ (g)	-119.932	-121.528
CO(g)	- 68.353	- 78.247
CH ₄ (g)	31.187	44.483
H ₂ O(g)	- 32.401	- 25.439
HBO ₂ (g)	-111.051	-104.176

APPENDIX C
THERMODYNAMIC EQUILIBRIA AT 2000°K

Reaction No.	System	Equilibrium Constant K in terms of Partial Pressures	Gas	Partial Pressure	
				Atm	Torr
1	$\text{BN(s)} \rightarrow \text{B(s)} + 0.5\text{N}_2(\text{g})$	$P_{\text{N}_2}^{0.5} = 10^{-1.80}$	N_2	1.6×10^{-4}	1.2×10^{-1}
2	$\text{BN(s)} \rightarrow \text{B(g)} + 0.5\text{N}_2(\text{g})$	$P_{\text{N}_2}^{0.5} P_{\text{B}} = 10^{-8.87}$	N_2 B	1.1×10^{-8} 2.1×10^{-8}	8.4×10^{-4} 1.7×10^{-3}
3	$\text{BN(s)} \rightarrow \text{BN(g)}$	$P_{\text{BN}} = 10^{-11.09}$	BN	8.2×10^{-12}	6.2×10^{-9}
4	$\text{B(s)} \rightarrow \text{B(g)}$	$P_{\text{B}} = 10^{-8.77}$	B	1.7×10^{-7}	1.3×10^{-4}
5	$0.25\text{B}_4\text{C(s)} \rightarrow \text{B(g)} + 0.25\text{C(s)}$	$P_{\text{B}} = 10^{-6.98}$	B	1.1×10^{-7}	8.4×10^{-5}
6	$0.25\text{B}_4\text{C(s)} + 1.75\text{C(s)} \rightarrow \text{BC}_2(\text{g})^*$	$P_{\text{BC}_2} = 10^{-5.54}$	BC_2	2.9×10^{-6}	2.2×10^{-3}
7	$\text{C(s)} + 0.5\text{N}_2(\text{g}) \rightarrow \text{CN(g)}$	$\frac{P_{\text{CN}}}{P_{\text{N}_2}^{0.5}} = 10^{-6.88}$	CN N_2	2.2×10^{-7} 1.0	1.7×10^{-4} 7.6×10^2
8	$2\text{C(s)} + \text{N}_2(\text{g}) \rightarrow \text{C}_2\text{N}_2(\text{g})$	$\frac{P_{\text{C}_2\text{N}_2}}{P_{\text{N}_2}} = 10^{-5.79}$	C_2N_2 N_2	1.6×10^{-6} 1.0	1.2×10^{-4} 7.6×10^2
9	$2\text{Mo(s)} + \text{BN(s)} \rightarrow \text{Mo}_2\text{B(s)} + 0.5\text{N}_2(\text{g})$	$P_{\text{N}_2}^{0.5} = 10^{-0.47}$	N_2	1.1×10^{-1}	8.4×10^1
10	$\text{Mo(s)} + \text{BN(s)} \rightarrow \text{MoB(s)} + 0.5\text{N}_2(\text{g})$	$P_{\text{N}_2}^{0.5} = 10^{-0.77}$	N_2	2.8×10^{-2}	2.1×10^1
11	$\text{Mo}_2\text{B(s)} + \text{BN(s)} \rightarrow 2\text{MoB(s)} + 0.5\text{N}_2(\text{g})$	$P_{\text{N}_2}^{0.5} = 10^{-1.08}$	N_2	7.1×10^{-3}	5.4
16	$\text{BN(s)} + 0.25\text{C(s)} \rightarrow 0.25\text{B}_4\text{C(s)} + 0.5\text{N}_2(\text{g})$	$P_{\text{N}_2}^{0.5} = 10^{-1.70}$	N_2	3.9×10^{-4}	3.0×10^{-1}
17	$\text{BN(s)} + 1.25\text{C(s)} \rightarrow 0.25\text{B}_4\text{C(s)} + \text{CN(g)}$	$P_{\text{CN}} = 10^{-8.38}$	CN	4.3×10^{-9}	3.3×10^{-6}
18	$2\text{BN(s)} + 2.5\text{C(s)} \rightarrow 0.5\text{B}_4\text{C(s)} + \text{C}_2\text{N}_2(\text{g})$	$P_{\text{C}_2\text{N}_2} = 10^{-9.20}$	C_2N_2	6.4×10^{-10}	4.9×10^{-7}
19	$\text{BN(s)} + \text{C(s)} \rightarrow \text{B(s)} + \text{CN(g)}$	$P_{\text{CN}} = 10^{-8.58}$	CN	2.8×10^{-9}	2.1×10^{-6}
19 (a)	$\text{BN(s)} + \text{C(s)} \rightarrow \text{B(g)} + \text{CN(g)}$	$P_{\text{B}} P_{\text{CN}} = 10^{-15.33}$	B CN	2.2×10^{-8} 2.2×10^{-8}	1.7×10^{-5} 1.7×10^{-5}
20	$\text{BN(s)} + \text{C(s)} \rightarrow \text{B(s)} + 0.5\text{C}_2\text{N}_2(\text{g})$	$P_{\text{C}_2\text{N}_2}^{0.5} = 10^{-4.79}$	C_2N_2	2.6×10^{-10}	2.0×10^{-7}
20 (a)	$\text{BN(s)} + \text{C(s)} \rightarrow \text{B(g)} + 0.5\text{C}_2\text{N}_2(\text{g})$	$P_{\text{B}} P_{\text{C}_2\text{N}_2}^{0.5} = 10^{-11.58}$	B C_2N_2	2.4×10^{-8} 1.2×10^{-8}	1.8×10^{-5} 9.1×10^{-8}
21	$\text{BN(s)} + \text{C(s)} \rightarrow \text{BC(g)} + 0.5\text{N}_2(\text{g})$	$P_{\text{BC}} P_{\text{N}_2}^{0.5} = 10^{-13.48}$	BC N_2	1.3×10^{-9} 6.7×10^{-10}	9.9×10^{-7} 5.1×10^{-7}
27	$\frac{1}{3}\text{B}_2\text{O}_3(\text{l}) + \frac{7}{6}\text{C(s)} \rightarrow \frac{1}{6}\text{B}_4\text{C(s)} + \text{CO(g)}$	$P_{\text{CO}} = 10^{+0.80}$	CO	4.0	3.0×10^3
27 (a)	$\frac{1}{3}\text{B}_2\text{O}_3(\text{g}) + \frac{7}{6}\text{C(s)} \rightarrow \frac{1}{6}\text{B}_4\text{C(s)} + \frac{P_{\text{CO}}}{P_{\text{B}_2\text{O}_3}} \frac{1}{3} = 10^{+1.07}$		CO^{**} B_2O_3	4.0 3.9×10^{-2}	3.0×10^3 3.0×10^1

* 2500°K only.

** Vapor Pressure of $\text{B}_2\text{O}_3(\text{g})$ at 2000°K from $\text{B}_2\text{O}_3(\text{l}) \rightarrow \text{B}_2\text{O}_3(\text{g})$

APPENDIX C
THERMODYNAMIC EQUILIBRIA AT 2000°K

Reaction No.	System	Equilibrium Constant K in terms of Partial Pressures	Gas	Partial Pressure Atm	Torr
28	$B_2O_3(l) + 3 Mo(s) \rightarrow 2MoB(s) + MoO_3(g)$	$P_{MoO_3} = 10^{-12.99}$	MoO_3	1.0×10^{-13}	7.8×10^{-11}
28 (a)	$B_2O_3(g) + 3Mo(s) \rightarrow 2MoB(s) + MoO_3(g)$	$\frac{P_{MoO_3}}{P_{B_2O_3}} = 10^{-11.58}$	$MoO_3(**)$ B_2O_3	1.0×10^{-13} 3.9×10^{-2}	7.8×10^{-11} 3.0×10^1
29	$B_2O_3(l) + 2MoB(s) \rightarrow 2MoB_2(s) + 3/2 O_2(g)$	$P_{O_2}^{3/2} = 10^{-19.35}$	O_2	1.3×10^{-13}	9.9×10^{-11}
30	$B_2O_3(l) + 2Mo(s) \rightarrow 2MoB(s) + 3/2 O_2(g)$	$P_{O_2}^{3/2} = 10^{-18.74}$	O_2	3.2×10^{-13}	2.4×10^{-10}
32	$0.5B_2O_2(g) + 1.25C(s) \rightarrow 0.25B_4C(s) + CO(g)$	$\frac{P_{CO}}{P_{B_2O_2}^{0.5}} = 10^{+1.11}$	Variable - dependent upon available $P_{B_2O_2}$		
34	$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$	$\frac{P_{CO} P_{H_2}}{P_{H_2O}} = 10^{+3.93}$	Variable - dependent upon available P_{H_2O}		
35	$H_2O(g) + 1.5C(s) \rightarrow 0.5CH_4(g) + CO(g)$	$\frac{P_{CH_4}^{0.5} P_{CO}}{P_{H_2O}} = 10^{+2.22}$	Variable - dependent upon available P_{H_2O}		
36	$3H_2O(g) + 2BN(s) \rightarrow B_2O_3(l) + N_2(g) + 3H_2(g)$	$\frac{P_{H_2}^3 P_{N_2}}{P_{H_2O}^3} = 10^{+6.58}$	Variable - dependent upon available P_{H_2O}		
37	$H_2O(g) + 2/9 MoB(s) \rightarrow 1/9 B_2O_3(l) + H_2(g) + 2/9 MoO_3(g)$	$\frac{P_{H_2} P_{MoO_3}^{2/9}}{P_{H_2O}} = 10^{-0.18}$	Variable - dependent upon available P_{H_2O}		
38	$H_2O(g) + 1/3 Mo(s) \rightarrow 1/3 MoO_3(g) + H_2(g)$	$\frac{P_{H_2} P_{MoO_3}^{1/3}}{P_{H_2O}} = 10^{-1.62}$	Variable - dependent upon available P_{H_2O}		
40	$HBO_2(g) + 2.25C(s) \rightarrow 0.25B_4C(s) + 2CO(g) + 0.5H_2(g)$	$\frac{P_{CO}^2 P_{H_2}^{0.5}}{P_{HBO_2}} = 10^{+3.00}$	Variable - dependent upon available P_{HBO_2}		
41	$MoO_3(g) + 3BN(s) \rightarrow MoB(s) + 3/2 N_2(g) + B_2O_3(l)$	$\frac{P_{N_2}^{3/2}}{P_{MoO_3}} = 10^{+10.67}$	Variable - dependent upon available P_{MoO_3}		
42	$1/3 MoO_3(g) + 7/6 C(s) \rightarrow 1/6 Mo_2C + CO(g)$	$\frac{P_{CO}}{P_{MoO_3}^{1/3}} = 10^{+5.79}$	Variable - dependent upon available P_{MoO_3}		

** Vapor Pressure of $B_2O_3(g)$ at 2000°K from $B_2O_3(l) \rightarrow B_2O_3(g)$