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Internal Reaction Phenomena
in Prototype Subterranean
Radiant Heater Penetrators

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Milton C. Krupka

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INTERNAL REACTION PHENOMENA IN PROTOTYPE SUBTERRENE RADIANT HEATER PENETRATORS

by

Milton C. Krupka

ABSTRACT

Internal chemical reactivity in prototype Subterrene radiant heater penetrators has been investigated by means of sectioning and examination of metallurgical samples. Formation of dimolybdenum carbide, Mo_2C , is the major reaction product formed between the base metal and the graphite receptor interface. In those regions where carbiding has occurred, temperatures have been calculated by means of measurement of the carbide layer thickness and the use of reaction rate data for the Mo-C system. These temperatures have been compared to those computed from heat transfer considerations. Agreement is reasonably good, within approximately 50K, in those regions where the carbide layer has not delaminated internally. The formation of defects in the carbide layer with resulting perturbation of normal state carbon diffusion, however, implies a limited utility to this technique for the determination of operating temperatures. A brief discussion concerning lifetime predictability is presented.

I. INTRODUCTION

Two basic design concepts, one of which has been discussed previously,¹ have been used for the fabrication of Subterrene electrically-heated penetrators. This preliminary report discusses some of the chemical problems associated with the radiant heater design concept. Thermal analysis, heat flow parameters and temperatures calculated at various locations in the penetrator have been described elsewhere.²

Interaction of the materials used in the penetrator at the suggested operating temperatures is to be expected. Fig. 1 shows a cross-sectional view of the present design and the materials used. Fig. 2 is a photograph of the actual penetrator (sectioned) without the central pyrographite stack. The gap is filled with He under approximately 3-4 atmospheres. The basic chemical reactions involve, therefore, those of the refractory metal-C system,

in this case Mo-C, with some possible contribution by impurities within the metal, C, and the He gas. Fortunately, the Mo-C system (similarly with the W-C system) has been studied extensively from both thermodynamic and reaction rate viewpoints, hence reasonably good analyses of post-test data should be made. Another reason for a study of this nature concerns the possibility of predicting penetrator lifetime, a most important economic factor. Such prediction is far from simple, however, since the internal chemical reactions will provide a partial contribution to potential failure modes. To be taken into account in addition to the above are both the external corrosion phenomena (alloy plus hot silicate glass) and the mechanical and thermal stress features at high temperature, e.g., strength and creep under load.

The lifetime of a penetrator unit must be dependent ultimately upon interaction of these major

Fig. 1. Cross-sectional view of prototype radiant heater penetrator.

factors. The present study investigates in part, the internal metal-graphite interaction for the prototype radiant heater penetrators.

II. THERMODYNAMIC AND REACTION RATE DATA

A reliable version of the equilibrium Mo-C phase diagram is shown in Fig. 3.³ The carbides to be expected upon quenching include α and β - Mo_2C and Mo_3C_2 . Cubic MoC_{1-x} is difficult to quench out nor is it stable at the operating temperature ranges. Below 1655 C, Mo_3C_2 also slowly decomposes to Mo_2C plus carbon. The Mo carbides can be formed by a variety of techniques often at relatively low temperatures. Direct elemental combination, of interest here, may occur as low as 1000 C.⁴ Mo_2C has a melting point on the order of 2450 C - 2500 C but the Mo- Mo_2C eutectic melting occurs at 2205 C. The heat of formation, $\Delta H_F^\circ(298 \text{ K}) = -11.0 \text{ kcal/mole}$.

Although there have been some previous diffusion and reaction rate studies for Mo carbides, the data used in this study has been taken from Fries et al.⁵ Conclusions derived from Fries'

Fig. 2. Cross section of Mo penetrator without central pyrographite stack.

Fig. 3. Mo-C System Phase Diagram - Ref. 3.

study include the following:

a. The carbiding mechanism for Mo in a carbonaceous and/or hydrogen atmosphere is the diffusion of carbon through the carbide layer and subsequent formation of carbide from the carbon-saturated metal at the carbide-metal interface.

b. Mo diffusion through Mo_2C is negligible relative to that of carbon.

c. In Fries' experimental setup, only Mo_2C was observed below approximately 2073 K (1800 C). The growth rate of Mo_3C_2 was too small to be observed.

d. In planar geometry, layer growth thickness is usually observed to follow Eq. (1):

$$x^2 = Kt \quad (1)$$

where x is the layer thickness, K is the parabolic rate constant and t the time. In semi-infinite cylindrical geometry, the equivalent expression

$$(B^2 \rho/2) = Kt \quad (2)$$

where $\rho = 1 - (r/B)^2 + 2(r/B)^2 \ln r/B$ and

where B is the overall sample radius and r is the radius of the uncarbided core. In Fries' work, samples were run in both geometries with good agreement. Hence calculations were made using the simpler mathematical expressions.

e. Above 1688 K (1415 C), the parabolic rate constant $K_{\text{Mo}_2\text{C}} = 4.6e - \frac{68,000 \pm 1200}{RT} \quad (3)$

Below 1688 K (1415 C), the parabolic rate constant $K_{\text{Mo}_2\text{C}} = 5.1 \times 10^6 e - \frac{114,000 \pm 2800}{RT} \quad (4)$

III. APPLICATION TO PROTOTYPE SUBTERRANE RADIANT HEATERS

The presently-used radiant heater design (Fig. 1) shows that a Mo carbide layer will form at the Mo-graphite receptor interface. The purpose of the receptor is to improve the heat transfer from a central pyrographite cylindrical stack to the Mo body. Transfer is made across a gas gap (helium gas at ~ 3-4 atmosphere pressure). An analytical model² has been assumed for this design and temperatures to be expected internally and at the penetrator surface-rock melt interface have been calculated. Temperatures can be determined experimentally with suitable thermocouples. For a number of reasons, however, there has been a limited amount of diagnostic instrumentation associated with experiments run to date. Since the carbiding process is temperature-dependent, inspection of Eqs. (1) and (3) shows that it is possible to calculate a temperature at which

the carbide layer formed. Experimentally, a measurement of the carbide layer thickness is required. Assumptions of intimate contact between reacting materials, constant reaction temperature and identification of the carbide phase or phases present are made. Carbiding in the present design is limited to the Mo-graphite receptor cylindrical and flat edge interfaces. Sectioning in longitudinal planes will provide axial temperature profiles. Radial profiles may be obtained by sectioning horizontally. Only an axial temperature profile determination is demonstrated in this preliminary report. The determination and subsequent comparison of the experimental temperature profile to the calculated one represents an interesting application of available chemical reaction rate data.

IV. EXPERIMENTAL

Two penetrators, designated PEN-1 and PEN-2 were obtained for examination. PEN-1 was a two-piece unit of similar material, Mo, with a removable tip (the tip was lost in the melted hole). The average time at temperature was 45 hours. PEN-2 had a one-piece body and was run for 31.5 h. Significant carbiding occurred during these time periods.

The penetrators were sectioned axially with a silicon carbide wheel with the cut displaced off centerline by the wheel thickness, approximately 0.16 cm. The sectioned half was metallurgically polished and etched. PEN-1, after layer measurement was further sectioned radially into smaller units and repolished for acquisition of additional data points. A series of thickness measurements were made at approximate 3 mm. intervals along the axis (Fig. 4). Measurement of the carbide layer to 0.001 mm was made with a calibrated filar microscope eyepiece at 125X magnification. Identification of the carbide phases was made independently by means of x-ray diffraction. Data are presented in Tables I, II and III. The temperature profiles, experimental and calculated, are shown in Figs. 5 and 6. Fig. 5 shows a composite curve generated from the data of Tables I and II.

V. DISCUSSION

The carbide layer as revealed by x-ray diffraction is Mo_2C with a possible large composition gradient across the thickness. A second phase at the graphite-carbide interface, possibly Mo_3C_2 , is present only in highly localized regions, is very thin

Fig. 4. Sampling scheme for axially-sectioned penetrators. Measurements taken at approximate 3 mm. intervals.

Fig. 5. Axial temperature profile-PEN-1-- data from Tables I and II.

when present and is not at all continuous. Possibly hot spots may cause this type of formation.

Observation of the carbide layers revealed a series of small, discontinuous axial cracks (Fig. 7). The great majority of these cracks terminated in depth some variable but short distance below the

Fig. 6. Axial temperature profile-PEN-2- data from Table III.

plane of observation. To normalize the thickness measurement, crack widths were subtracted out and a net thickness determined. The time of formation of these cracks, probably thermal stress-induced, was not known. Perturbation to normal carbon diffusion and heat flow was assumed to be minimal.

The formation of blisters or internal delamination within the carbide layer represents an extreme example of the axial cracking described previously. Figs. 8 and 9 show this type of delamination which developed in PEN-1. Regardless of the reasons for the localized development serious secondary effects can be anticipated with subsequent shortening of the penetrator lifetime. Higher than normal temperatures are most certainly associated with the blister formation. The high temperatures are reflected by thicker carbide layers and the blister region appears as a sharp peak in the temperature profile plot (Fig. 5). Additional evidence for the excessively high temperatures in this region is demonstrated by the increased degree of corrosion observed externally in the corresponding radial locations. Considerable scatter of the data is also evident in this region suggesting (a) serious heat flow and carbon diffusion perturbations and (b) a larger percentage error in measurement due to the large gap and the non-uniform surfaces (edges) associated with the gap. Consideration of these factors also suggests that the absolute value of the temperatures calculated are possibly on the low side.

TABLE I

Mo PENETRATOR NO. 1 (PEN-1) THICKNESS, RATE CONSTANT AND TEMPERATURE DATA FOR Mo CARBIDE LAYER

Identification	Net Thickness (cm)	Rate Constant $K \times 10^{-8} - \text{cm}^2/\text{sec}$	Temperature	
			K	C
00	0.0475	1.39	1744	1471
0	0.0627	2.43	1795	1522
1	0.0620	2.37	1793	1520
2	0.1210	9.03	1928	1655
3	0.1207	8.58	1923	1649
4	0.1097	7.43	1907	1634
5	0.1067	7.03	1901	1628
6(a)				
7	0.0960	5.69	1879	1606
8	0.0950	5.57	1877	1604
9	0.0932	5.36	1873	1600
10	0.0894	4.93	1865	1591
11	0.0785	3.80	1839	1565
12	0.0787	3.82	1839	1565
13	0.0620	2.37	1793	1520
14	0.0632	2.47	1797	1524
15	0.0523	1.69	1762	1488
16	0.0569	2.00	1777	1504
17	0.0526	1.71	1763	1489
18	0.0427	1.13	1726	1452

The lower temperatures observed as one proceeds towards the upper portion of the penetrator are in agreement with those expected. In lower absolute values suggest, however, some additional heat loss through the connecting parts not taken into account by the model. The significance of the very low temperatures in the region of the flat surfaces of the cylindrical receptor (tip and upper region) is not understood. It is difficult to conceive of such a severe temperature gradient in a short distance as shown by the carbide thickness measurement. Possibly a mechanical fit problem could help explain the minimal carbide thickness observed.

Data point scatter for the upper portion of the penetrator (PEN-1) can be correlated with the individual data in Tables I and II. A composite curve was made since the carbide layer was the same. Data from Table II yield on the average, temperatures ap-

(a) Region No. 6 carbide layer chipped

TABLE II

Mo PENETRATOR NO. 1 (PEN-1)(a) THICKNESS, RATE CONSTANT AND TEMPERATURE DATA FOR Mo CARBIDE LAYER

Identification	Net Thickness (cm)	Rate Constant $K \times 10^{-8} - \text{cm}^2/\text{sec}$	Temperature	
			K	C
00	0.0366	0.83	1699	1426
0	0.0445	1.22	1733	1460
1	0.0706	3.08	1818	1545
1a	0.0993	6.09	1886	1613
2	0.1123	7.78	1912	1639
3	0.1067	7.02	1901	1628
4	0.1049	6.79	1898	1624
3a	0.1270	9.96	1939	1666
5	0.1077	7.16	1903	1630
4a	0.1102	7.49	1908	1635
6	0.1049	6.79	1898	1624
5a	0.1037	7.02	1901	1628
7	0.1140	8.02	1915	1642
8	0.0930	5.34	1873	1600
9	0.0879	4.77	1861	1588
10	0.0897	4.97	1865	1592
11	0.0912	5.13	1869	1596
12	0.0919	5.21	1870	1597
13	0.0795	3.90	1841	1568
14	0.0711	3.12	1819	1546
15	0.0617	2.35	1792	1519
16	0.0673	2.80	1808	1535
17	0.0485	1.45	1748	1475
18	0.0488	1.47	1749	1476
19	0.0495	1.51	1752	1479
20	0.0574	2.03	1779	1506
21	0.0512	1.62	1758	1485

proximately 15 K - 25 K higher.

Data generated from PEN-2, operated for a shorter time period, is shown in Fig. 6. Observation of the carbide layer showed the small axial cracks but no major region of delamination. Again a very sharp drop in carbide thickness and reflected as a low temperature was evident at the edges of the cylindrical receptor. The temperatures agree reasonably well (within approximately 50 K) with those calculated from the analytical model although somewhat lower. Of more importance, perhaps, is the remarkable agreement of the net temperature distri-

(a) Data taken after radial sectioning of penetrator into smaller samples

TABLE III
Mo PENETRATOR NO. 2 (PEN-2) THICKNESS, RATE CONSTANT
AND TEMPERATURE DATA FOR Mo CARBIDE LAYER

Iden- tifi- cation	Net Thickness (cm)	Rate Constant $K \times 10^{-8} - \text{cm}^2/\text{sec}$	Temperature	
			K	C
CO	0.0282	0.70	1685	1412
0	0.0514	2.33	1791	1518
1	0.0610	3.29	1824	1551
2	0.0616	3.35	1826	1553
3	0.0690	4.19	1848	1575
4	0.0703	4.36	1852	1579
5	0.0698	4.29	1851	1577
6	0.0737	4.79	1862	1588
7	0.0748	4.93	1865	1591
8	0.0724	4.62	1858	1585
9	0.0685	4.14	1847	1574
10	0.0685	4.14	1847	1574
11	0.0672	3.98	1843	1570
12	0.0630	3.50	1830	1557
13	0.0628	3.48	1830	1557
14	0.0606	3.24	1823	1550
15	0.0569	2.85	1811	1537
16	0.0559	2.76	1807	1534
17	0.0523	2.41	1794	1521
18	0.0473	1.97	1776	1503
19	0.0299	0.79	1695	1422

bution as evidenced by the approximate parallelness of the two curves.

Further observations made on PEN-2 noted that a gap had been created between the Mo carbide layer and the POCO graphite receptor. This gap was equivalent to a 0.015-0.018 cm reduction in thickness of the receptor. The receptor was not loosely fitting but was stuck to the carbide layer and held in place by randomly located and randomly growing crystals of Mo carbide projecting out from the carbide surface. It would appear, therefore, that the supply of carbon to the carbide layer necessary for normal diffusion and layer growth would be diminished except in highly localized regions. Vaporization of graphite (in vacuo) across this gap at a temperature, for example, of 1950 K is minor, $\sim 10^{-12}$ moles/cm² - sec. The high pressure He atmosphere would reduce this rate even further.

VI. CONCLUSIONS

This preliminary study has examined internal chemical changes which have occurred in the proto-

Fig. 7. Small axial cracks observed in Mo carbide layer - 50X.

type radiant heater penetrators. Conclusions drawn include the following:

a. A dimolybdenum carbide layer, Mo₂C, forms between the body and graphite receptor interface as expected. The analytical model does not take into account effects of this layer. It should be noted, however, that most refractory carbides are good thermal and electrical conductors at high temperatures. Carbiding should also be expected at the bottom surface of the central pyrographite stack.

Fig. 8. Metallurgical sample showing blister (delamination) region - 7X.

b. Within the limitations noted in d. below, it is possible to calculate temperatures in those regions where carbiding occurs using available reaction rate data for the refractory metal-carbon system. Sectioning of the penetrator in a wide variety of planes will permit the determination of both axial and radial temperature distributions (profiles) in the carbided regions.

c. These experimentally-derived temperature values provide an independent check upon the heat transfer calculations. The thermal analysis results

Fig. 9. Enlarged region showing blister (delamination) within carbide layer - 50X.

were approximately 50 K higher than those determined experimentally. Comparison is probably most useful during the early operating hours of the penetrator.

d. Limitations to this method for providing temperatures are basically those of the creation of barriers or impediments to normal state carbon diffusion and heat flow such as gaps, cracks, blisters and delaminations. Development of these barriers are probably gradual but the times are not known.

e. The experimental method is a destructive

one although at this stage of penetrator development, this is of no concern, and indeed should be of some interest in order to acquire as much information as possible.

f. The experimental technique described in this report should be applicable to penetrators fabricated from other refractory metal-carbon systems for which appropriate reaction rate data are available. In particular, the next "generation" of penetrators fabricated from tungsten should undergo equivalent chemical reactions.

g. Potential complications due to refractory metal (Mo) grain growth over long operating times and formation of at least two carbide phases due to higher operating temperatures have not been explored.

h. The present radiant heater design is considered superior to that using the molybdenum-boron nitride-carbon set of materials⁽¹⁾ in view of a marked reduction in the complexity and number of potential chemical reactions. Higher operating temperatures are also possible.

i. This study sheds a little light on the difficult problem of lifetime predictability for the penetrator as presently designed. Consideration of an ideal case whereby the entire receptor, 0.1 cm thick, disappears through the mechanism of carbiding does not imply that the penetrator should fail mechanically or electrically. Because of different physical characteristics, a dimensional change in the gas gap between the pyrographite stack and the carbide wall should occur as well as a surface emissivity change in the carbide relative to graphite. Changes in power requirements (probably greater) would be required to maintain a constant temperature at the rock melt-penetrator interface. In the real situation, it appears that a gap is created, carbiding slows and the receptor has a much longer lifetime. The gap itself may induce some changes in power requirements. Problems associated with carbiding are more serious when major delaminations occur which may cause hot spots, unknown thermal and mechanical stresses and other unknown secondary effects, thereby reducing penetrator lifetime.

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