THE DIFFRACTION OF CARBIDES AND THEIR COMPOUNDS AT HIGH TEMPERATURES IN THE FLOW OF CHEMICALLY ACTIVE GASES

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We examine the interaction of refractory carbides and their compounds with flows of chemically active gases at high temperatures. We evaluate their relative chemical stability in comparison with graphite.

Refractory carbides (SiC, ZrC, HfC, TaC, etc.) and their compounds with graphite are of considerable interest for use in high-temperature chemically active gas flows.

Experience shows that when acted on by such oxidizers as oxygen, water vapor, and carbon dioxide, carbide metals change into oxides (solid or liquid, depending on temperature), while the carbon of the carbide is gasified to carbon dioxide or monoxide.

For certain carbides (ZrC, HfC) we have noted that for a working-surface temperature that is lower than the melting point of the metal oxide, the surface is covered with a solid oxide film which prevents the further oxidation of the material layers underneath. At a surface temperature greater than the melting point for the oxide we observe the formation of an oxide film which melts and is entrained by the flow. In this case, the chemical processes lead to the destruction and removal of the material at a rate that is determined by the rate of the chemical oxidation reaction.

The rate of the chemical reaction depends on the area in which it takes place, i.e., the kinetic region or the diffusion region. We know, for example, that under conditions simulating entry into the dense layers of the atmosphere, the rate of the graphite oxidation reaction below 1300°K is limited by the kinetics; this is then followed by a small transition region, and then from 1500 through 3000-3500°K (depending on the stagnation pressure) the process of graphite destruction is determined by the velocity of the oncoming oxidizer diffusion [1]. This is the region of active interaction between the gas flow and the material.

The regions in which the chemical reactions occur for carbides and their compounds with graphite have not been extensively studied at this time. The noticeable destruction of silicon carbides with formation of silicon dioxide begins, according to our observations, approximately at 2500°K and continues in the diffusion region up to 3000-3200°K. The intensity of liquid-film formation increases with rise in temperature.

It might be assumed that the process of zirconium and hafnium carbide destruction after the melting of the oxide film also takes place in the diffusion region.

It has been established that the rate of graphite mass removal in the diffusion region [2] is governed by the equation

$$\dot{m}_D = \frac{\mu_C}{\mu_0} \frac{\alpha}{c_{p_w}} \sum_i X_i. \tag{1}$$

The mechanism by which carbides and their compounds are destroyed is considerably more complex than the destruction of graphite, and has presently not been studied in sufficient detail. The mathematical description of the progress of destruction in most cases is held to be impossible. However, bearing in mind

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TABLE 1. Experimental Data from [3] on the Entrainment of Hypereutectic Carbide Compounds and Graphite in a Plasma Jet

Material	q	τ	$v_{MeC-C}\cdot 10^3$	Average	(v_{MeC-C}/v_{ATI}) [av]
HfC–C alloy, produced in an arc furnace	6500 6500	30 30	0,153 0,162	0,1575	1,45
ZrC–C alloy, produced in an arc furnace	6500	30	0,292	0,292	2,7
TaC–C alloy, produced by hot extrusion	6500	30	0,254	0,254	2,35
ATI graphite (cylindrical specimens with a flat end)	6500	30	0,108	0,108	
HfC–C alloy, produced in an arc furnace	6600 6120 7000	15 15 15	0,118 0,206 0,101	0,162	1,83
ATI graphite (cylindrical specimens with a rounded leading edge)	6100	15	0,076	0,0885	

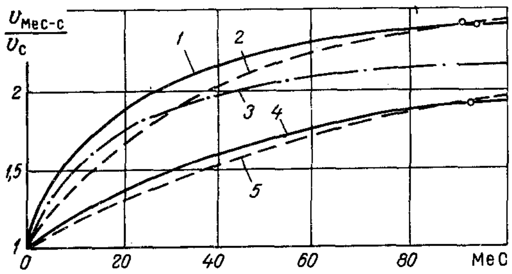

Fig. 1. Relative linear entrainment velocity as a function of carbide-phase content in the compound (v_{MeC-C}/v_C is dimensionless, while MeC is expressed in terms of wt. %): 1) HfC–C; 2) ZrC–C; 3) TaC–C; 4) TiC–C; 5) SiC–C; ○) are the eutectic points.

that the behavioral nature of the carbides and their compounds in oxidizing media at high temperatures is close to that of graphite, to evaluate the rate of their destruction in the diffusion region, we can apparently utilize formula (1).

Let us evaluate the resistance of these materials in comparison with graphite under the following assumptions:

1. The temperature of the material surface is higher than the melting point of the carbide metal oxide.

2. The decisive mechanism for the destruction of the materials is the chemical interaction with the oncoming stream.

3. Carbides react with the same gases as graphite.

4. All products of reaction that are formed (in any phase) are removed by the flow.

5. Oxidation reactions are limited by diffusion.

6. No consideration is given to the effect of the viscosity of the oxide film on the rate of removal, nor to the possible occurrence of reverse reactions leading to the formation of carbon or carbide at the reacting surface.

According to (1), the relative rate of mass removal and the relative linear velocity can be expressed by the following equations:

$$\frac{\dot m_{MeC-C}}{\dot m_C} = \frac{\left(\frac{\alpha}{c_{p_w}}\right)_{MeC-C} \mu_{MeC}}{\left(\frac{\alpha}{c_{p_w}}\right)_C \mu_C}, \tag{2}$$

$$\frac{v_{MeC-C}}{v_C} = \frac{\left(\frac{\alpha}{c_{p_w}}\right)_{MeC-C} \mu_{MeC-C}\,\gamma_C}{\left(\frac{\alpha}{c_{p_w}}\right)_C \mu_C\,\gamma_{MeC-C}}. \tag{3}$$

The relative linear removal velocity as a function of carbide-phase content in the compound for HfC–C, ZrC–C, TaC–C, TiC–C, SiC–C, calculated from (3) for $(\alpha/c_{p_w})_{MeC-C} = (\alpha/c_p)_C$, is shown in Fig. 1.

We have calculated the molecular weight of the compound from the equation

$$\mu_{MeC-C} = \mu_{MeC}\, n + \mu_C\, n_1,$$

and its density on the basis of an analogous equation. We assumed the graphite density at $1.9\cdot 10^3$ kg/m^3.

TABLE 2. Comparative Data on Entrainment of Graphite and Silicon Carbide in a Plasma Jet

Material	$d\cdot 10^3$	$\gamma\cdot 10^{-3}$	T_0	p_0'	T_w	$v\cdot 10^3$	$v_{cp}\cdot 10^3$	$\left(\frac{v_{SiC}}{v_C}\right)_{av.\ exp}$	$\frac{\alpha}{c_{p_w}}$	$\left(\frac{\alpha}{c_{p_w}}\right)_{av}$	$\left(\frac{v_{SiC}}{v_C}\right)_{av.theor}$
V-1 graphite	9,7	1,92	4650	5,1	3000	0,27	0,204	1,94	2,207	2,045	2,46
	13,9	1,92	5550	5,6	3000	0,19			1,964		
	13,5	1,92	5300	5,5	3000	0,22			1,927		
	13,8	1,92	4700	6,7	3000	0,17			2,119		
	13,8	1,92	4250	6,2	3000	0,17			1,994		
Silicon carbide	8,8	3,2	4700	6,5	2750	0,44	0,395		3,143	2,52	
	9,93	3,2	4700	5,0	2750	0,39			2,672		
	12,6	3,2	5550	5,6	2750	0,39			2,167		
	13,2	3,2	4500	6,5	2750	0,36			2,205		

We see from Fig. 1 that the greater the carbide-phase content in the compound, the higher its relative linear removal velocity. For all carbides it is greater by a factor of 1.95-2.4 than in the case of graphite.

The carbide-phase content which corresponds to the eutectics for three compounds is shown in the figure. Thus, for ZrC–C the eutectic corresponds to 90 wt. % of ZrC. Compounds with smaller carbide-phase contents are classified among the hypereutectics.

It is pointed out in [3] that the hypereutectic carbide compounds HfC–C, ZrC–C, TiC–C exhibit high resistance to heat. Their linear removal [entrainment] velocities are given, and these have been derived in tests performed in air-arc generators, as compared to grade ATI graphite and tungsten.*

We noted on HfC–C specimens that up to a specific heat-flow value (5560 kcal/m^2·sec) the solid oxide film protected the material, while at a higher value (T_W above 3070°K) it melted, as a result of which there was a sharp rise in material erosion.

The values for the linear entrainment velocities from this study for the hypereutectic carbide compound in comparison with graphite are given in Table 1. We calculated the average entrainment velocities and the ratios $(v_{MeC-C}/v_{ATI})_{av}$.

As we can see from the cited data, in all cases the linear entrainment velocity for the carbide compounds is greater than for the ATI graphite: for HfC–C alloys, it is greater by a factor of 1.45 and 1.83; for the ZrC–C alloy it is greater by a factor of 2.7; and for the TaC–C alloy it is greater by a factor of 2.35. The paper does not give the compositions of these alloys, and the experimental entrainment velocities cannot be compared with the theoretical values. However, we can point out that they are close in order of magnitude.

As regards the chemical stability of the graphite and the silicon carbide, we were able to make a judgment based on results from tests conducted on specimens of these materials in the supersonic air jet of an electric-arc installation.

The specimens were cylindrical in shape, with a flat end, 9-14 mm in diameter and 50 mm in height. The specimens were prepared from grade V-1 graphite, as well as this same graphite coated with silicon carbide, the coating produced by deposition from the gaseous phase (the SiC content equal to 96-98 wt. %). The coating is approximately 1 mm thick. The specimens were held in Textolite holders along the jet axis at a distance of 10 mm from the nozzle outlet. The test lasted 20 sec. A steady-state thermal regime set in within 1-1.5 sec. The brightness temperature of the surface was determined by a photopyrometric method. The specimens were photographed to determine the changes in linear dimensions and in temperature at a frequency of one frame per second. The error in the determination of the linear entrainment velocity did not exceed ±5%. The results of these tests are shown in Table 2. As we can see from the table, the average linear entrainment velocity for the silicon carbide is higher than the average linear entrainment velocity for the graphite by a factor of 1.94.

Table 2 also gives the values of the true surface temperature, of the heat-transfer coefficient, and of the relative average linear entrainment velocity for the silicon carbide, calculated from (3) on the basis of the average value for the mass-transfer coefficient. The mass-transfer coefficient was determined from

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*Grade ATI graphite is an industrial fine-grained material with a density of 1.73 · 10^3 kg/m^3.

the relationship with respect to the heat flow to the specimen, expressed in terms of the enthalpy difference. The calculated entrainment velocity is greater than the experimental velocity by a factor of 1.27.

The existing experimental data thus provide a basis for the assumption that under these the rate of destruction for refractory carbides and their compounds with graphite is higher than the rate of destruction for solid graphite. The rate of destruction for these materials in the diffusion region, in first approximation, can apparently be estimated from (1). For definitive conclusions, additional experimental data are needed.

NOTATION

$\dot{m}$	is the mass entrainment velocity, $kg/m^2 \cdot sec$;
α/c_{p_w}	is the mass-transfer coefficient, $kg/m^2 \cdot sec$;
α	is the heat-transfer coefficient;
c_{p_w}	is the heat capacity of the gases near the wall;
X_i	is the molar fraction of the gas component in the mixture, chemically active with respect to the carbon;
μ	is the molecular weight;
v	is the linear entrainment velocity, m/sec;
γ	is the density, kg/m^3;
d	is the specimen diameter, m;
T_0	is the temperature, °K;
T_w	is the surface temperature, °K;
p'_0	is the stagnation temperature, bar;
q	is the heat flow, $kcal/m^2 \cdot sec$;
τ	is the test time, sec;
n, n_1	are the relative fractions of the carbide and carbon phases in the compound.

Subscripts

D	denotes the diffusion region;
C	denotes the carbon (graphite);
MeC	denotes the carbide;
MeC–C	denotes the carbide–graphite compound;
av	stands for an average value;
0	denotes the gas mixture;
exp	denotes experimental;
theor	denotes theoretical.

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