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Temperature Requirements and Corrosion Rates in Combustion Driven Hydrogen Fluoride Supersonic Diffusion Lasers

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A maximum F-atom yield from F_2 occurs in a combustion driven hydrogen fluoride supersonic diffusion laser (HFSDL) because the amount of fluorine reacted with hydrogen (or deuterium) continues to increase with temperature after most of the unreacted fluorine has been thermally dissociated. A small decrease from the maximum combustor F-atom yield allows a significant decrease in the required temperature and in the corrosion rates that uncooled laser nozzles would display. The temperatures that give F-atom yields equal to 95% of the maximum values were calculated for typical HFSDL combustor pressures and F-atom mole fractions and the corrosion rates of uncooled nozzles were evaluated at these temperatures. The corrosion rates of materials resistant to fluorine attack at the highest temperatures would allow HFSDL applications or test experiments up to several hours duration.

Introduction

IN recent years, the reactions of fluorine with a variety of refractory materials have been investigated.[1-16] Some of this research was directed toward the discovery of fluorine resistant construction materials for HF chemical lasers. Nickel and nickel alloys would be useful for this purpose if the required temperatures were less than 1000 K, but higher temperatures are necessary. The gas temperature in the thermal F-atom source of a hydrogen fluoride supersonic diffusion laser (HFSDL) is typically 1400-1500 K, although somewhat lower temperatures would be adequate if the source and supersonic nozzles did not require active cooling to control fluorine corrosion.

A few materials have been discovered that resist fluorine attack above 1400 K. For example, LaB_6 and yttrium metal show "near-zero" weight loss in fluorine-rich hydrogen fluorine flame tests[12] up to the melting points[17] of LaF_3 (1766 K) and YF_3 (1428 K), respectively. However, these results do not demonstrate that acceptable fluorine resistance would obtain at the throat of an HFSDL nozzle where convective mass transfer rates are large[18] and the rate of evaporation of passivating solid fluorides would exceed the values measured in the flame tests. In fact, the convective mass transfer coefficient at the throat of an HF laser nozzle is sufficient that the rate of fluoride evaporation approaches its vacuum limit.

In this paper we examine the feasibility of uncooled, combustion driven HFSDLs by considering the combustor temperatures required for efficient production of atomic fluorine from F_2 and the corrosion rates that would occur in nozzles made from the best fluorine resistant materials. The combustor pressures and F-atom mole fractions considered here are within the range of values reported[19] for HFSDL test experiments. It appears that uncooled laser nozzles may be used under most conditions of interest for HFSDL operation.

Efficient F-Atom Production

We consider a combustion driven HFSDL in which the energy necessary to produce atomic fluorine is supplied by reaction of some F_2 with H_2 (or D_2). F-atom production is considered to be efficient if the F-atom flow, $n(F)$, per unit F_2 feed, $n_0(F_2)$, is nearly maximized. The feed gases are taken to be He, F_2, and H_2 at $T = 298$ K and the combustor is assumed to operate adiabatically. The quantities of interest are the source temperature, T_0; the feed He:F_2 and F_2:H_2 ratios, $R(\mathrm{He}:F_2)$ and $R(F_2:H_2)$; and the effluent F and F_2 mole fractions, $X(F)$ and $X(F_2)$. We take $X(F)$ and P_0 as independent variables and calculate other quantities from thermodynamic data[20] under the assumption that $n(F)/n_0(F_2)$ is 95% of its maximum value. Choice of this value for $n(F)/n_0(F_2)$ is based on the observation that a large decrease in the required source temperature (and the corrosion rate) occurs if a small decrease from the maximum F-atom conversion is accepted. This is illustrated in Fig. 1, which plots $n(F)/n_0(F_2)$ vs T_0 for $X(F) = 0.10$ and $P_0 = 0.1$-5.0 atm. Figure 2 illustrates the $P_0(T_0)$ functions at 95% of the maximum F-atom yield for several values of $X(F)$. The lines drawn in the figure are accurately given by the equations

$$X(F) = 0.03, \quad \ln(P_0) = -21640/T_0 + 19.16 \tag{1}$$

$$X(F) = 0.06, \quad \ln(P_0) = -21820/T_0 + 18.07 \tag{2}$$

$$X(F) = 0.10, \quad \ln(P_0) = -21690/T_0 + 17.09 \tag{3}$$

$$X(F) = 0.20, \quad \ln(P_0) = -21460/T_0 + 15.79 \tag{4}$$

Table 1 lists other properties of the adiabatic combustor at these F-atom mole fractions and $P_0 = 0.5$ and 5.0 atm.

Zelazny et al.[19] present the combustor conditions that were employed in a variety of HFSDL test experiments. Combustor pressures and upper limits on the F-atom mole fractions for these experiments are given in Table 2, along with the appropriate operating temperature for an F-atom yield equal to 95% of its maximum value when the feed gases are He, F_2, and H_2 at 298 K.

HF Laser Nozzle Corrosion

The rates of metal fluoride evaporation at the throat of a fluoride-coated nozzle can be estimated by reference to the rates of catalytic F-atom recombination at a cooled laser nozzle wall calculated by Ferrell et al.[18] They found an F-atom wall loss rate of 1.2 lb/s ft^2 (0.0309 mole/s cm^2) at the 0.038-cm-wide throat of a fully catalytic nozzle, where the ambient gas temperature, pressure, and F-atom mole frac-

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Table 1 Properties of an adiabatic combustion driven F-atom source operated at 95% of its maximum F-atom yield. He, F_2, and H_2 feed gas temperature = 298 K

		Mole fractions			Feed ratios		F-atom
T_0, K	P_0, atm	F	F_2	HF	He/F_2	H_2/F_2	yield
1090	0.5	0.03	0.0083	0.0717	15.0	0.606	0.253
1233	5.0	0.03	0.0102	0.0834	13.1	0.625	0.224
1163	0.5	0.06	0.0107	0.0868	10.7	0.516	0.357
1326	5.0	0.06	0.0132	0.1001	8.9	0.537	0.322
1220	0.5	0.10	0.0135	0.1036	6.8	0.449	0.434
1401	5.0	0.10	0.0163	0.1189	6.1	0.473	0.398
1301	0.5	0.20	0.0194	0.1409	3.37	0.371	0.527
1513	5.0	0.20	0.0229	0.1597	3.05	0.394	0.489

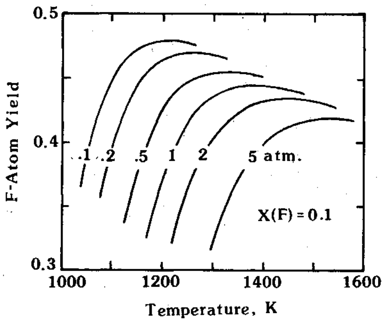

Fig. 1 F-atom yield in an adiabatic $F_2/H_2/He$ combustor with feed gas temperature = 298 K.

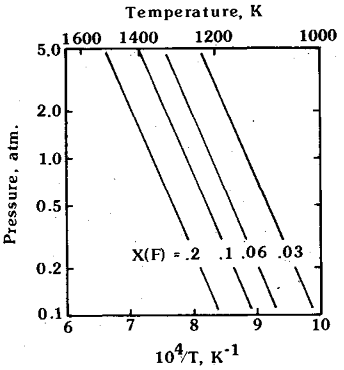

Fig. 2 Pressure vs temperature in an adiabatic $F_2/H_2/He$ combustor at 95% of the maximum F-atom yield. Feed gas temperature = 298 K.

tion, were 1500 K, 0.5 atm, and 0.272, respectively. Under these ambient conditions the F-atom flux is 0.0357 mole/s cm^2, which slightly exceeds the heterogeneous F-atom loss rate. Thus, the convective mass transfer coefficient at the throat of a laser nozzle is sufficiently large that the rate of heterogeneous reaction is determined by the intrinsic rate of the surface reaction. The corrosion rate at the throat of a metal fluoride passivated nozzle then can be calculated from the Hertz-Knudsen equation.

$$\xi(\mathrm{MeF}_x) = \alpha p(\mathrm{MeF}_x) / (2\pi mkT)^{0.5} \tag{5}$$

where ξ is the metal fluoride flux, p its equilibrium vapor pressure, and α its vacuum evaporation coefficient. From the density of LaB_6 (4.7 g/cm^3)[21] and the vapor pressure[22-26] and unit evaporation coefficient[22] of LaF_3, we calculate that the half-width w^* at the throat of an LaF_3 passivated LaB_6 nozzle would increase at the rate

$$\mathrm{d}w^*/\mathrm{d}t = \exp(-48{,}000/T + 21.8)\ \mathrm{cm/s} \tag{6}$$

where T is the nozzle wall temperature in degrees Kelvin.

Table 2 Efficient $H_2/F_2/He$ adiabatic combustor temperatures under the HFSDL test conditions reported by Zelazny et al.[19]

	Test conditions		
No.	Pressure, atm	Approximate X(F)	Temperature, K
1	6.4	0.046	1309
2	9.2	0.046	1338
3	9.3	0.032	1287
4	0.46	0.115	1230
5	0.61	0.103	1238
6	1.02	0.167	1337
7	15.0	0.091	1491
8	1.7	0.053	1229
9	6.2	0.091	1407
10	3.3	0.062	1298

A summary of vapor pressure[22-28] and melting and phase transition[17,28-31] data for the elements that form the least volatile fluorides and for nickel is given in Table 3. A few fluorides are slightly less volatile than LaF_3 but fluorine resistance much superior to that of LaB_6 cannot be expected in other substances unless the evaporation coefficients of other involatile fluorides (which have not been measured) were found to be small. It can be seen that fluoride melting point is not an important materials selection criterion for an HFSDL because the rate of fluoride evaporation would limit the use of uncooled nozzles to temperatures below the fluoride melting point.

It is clear that nickel is a poor HFSDL nozzle material above about 1000 K, where the vapor pressure of NiF_2 is 4.9×10^{-7} atm.[28] Also, MgF_2, BaF_2, and ScF_3 are relatively volatile and CeF_3 forms volatile CeF_4 in fluorine. The alkaline earth metal melting points are low, their borides are sensitive to thermal shock,[12] and CaO or BaO gave poor results in fluorine flame tests.[12] Thus, alkaline earths are unlikely major components of the best fluorine resistant refractories.

Rare earth oxides, sulfides, and carbides have not been studied in sufficient detail to obtain a general conclusion about their resistance to high-temperature fluorine attack. However, sensitivity to thermal shock, poor coating adherance, or reaction with atmospheric water vapor occurs for most of these compounds that have been studied.[12]

Promising fluorine resistant materials are the more refractory rare earth metals and the rare earth borides. Good performance of yttrium metal and LaB_6 in fluorine flames has been demonstrated[12] and reduced pressure ($p_F = 0\text{-}1.2$ Pa) kinetic studies[15] show that the F/Gd reaction is passivated by orthorhombic GdF_3 at temperatures up to 1200 K. At higher temperatures a metal rich fluoride forms on gadolinium and reaction with fluorine is rapid. This should not occur if the substrate metal activity were small, as in borides, so that metal rich phases could not form. In fact, boron rich LaB_6, whose La activity[32] is very small, is passivated by a thinner fluoride coating than is required for the stoichiometric

Table 3 Properties of metals and fluorides

Chemical formula	Melting temperature, K	Transition temperature, K	Vapor pressure at 1400 K, atm	Metal melting temperature, K	Metal vapor pressure at 1400 K, atm
NiF_2	1723		2.7(−3)[a]	1728	4.8(−9)
MgF_2	1536		6.7(−6)	923	
CaF_2	1691	1424	2.7(−7)	1112	
SrF_2	1673		5.6(−7)	1043	
BaF_2	1563		5.0(−6)	983	
ScF_3	1825		3.9(−5)	1814	7.9(−8)
YF_3	1428	1350	1.4(−6)	1795	1.5(−9)
LaF_3	1766		9.3(−7)	1191	
CeF_3	1705		2.6(−6)[b]	1071	
PrF_3	1672		1.9(−6)	1204	1.9(−8)
NdF_3	1650		1.6(−6)	1294	3.7(−7)
SmF_3	1573	763	8.7(−7)[c]	1347	
EuF_3	1535	920	1.4(−6)[c]	1095	
GdF_3	1505	1348	4.8(−7)	1586	4.3(−9)
TbF_3	1450	1225	9.4(−7)	1638	1.3(−8)
DyF_3	1430	1305	1.0(−6)	1685	1.5(−5)
HoF_3	1416	1343	9.9(−7)	1747	7.0(−9)
ErF_3	1419	1390	8.7(−7)	1802	9.3(−7)
TmF_3	1431	1326	2.2(−6)	1818	2.8(−6)
YbF_3	1435	1259	8.6(−7)	1092	
LuF_3	1457	1230	2.4(−6)	1936	7.1(−10)

[a] ( ) indicates power of ten. [b] CeF_3 forms volatile CeF_4 in fluorine. [c] Uncertain due to incongruent evaporation.

material.[16] The large decrease in Gd activity[33] that occurs over the GdB_4 homogeneity range indicates that a similar effect may be observed for the F/GdB_4 reaction.

Discussion

The HFSDL test experiments of Table 2 would require temperatures between 1229-1491 K if the combustor were efficiently operated with H_2, F_2, and He feed gases. The half-width of an LaF_3 passivated LaB_6 nozzle would increase at a rate between about 3×10^{-8} and 3×10^{-5} cm/s in this temperature range. If one assumes a 10% limit on the acceptable increase in nozzle half-width, lasers with initial nozzle half-widths equal to 0.01 cm would be operable for a period between 30 s and 9 h at the upper and lower ends of the indicated temperature range. For all but two of the test conditions, operating lifetimes in excess of 22 min are obtained. It, therefore, is apparent that corrosion rates should not prevent short to medium term HFSDL applications or laboratory test experiments with uncooled nozzles.

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