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The impact of larger clusters formation C_5, C_6, C_7, C_8, C_9, and C_{10} on the rates of carbon sublimation at elevated temperatures

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Abstract

To estimate the exact amount of the loss of material during the plasma disruption or during slow transients is critically important to design and component lifetime analysis. Over the years, a number of simulation experiments, using as heat sources electron beams, and laser beams on investigation of the influence of heat loads on the amount of sublimated carbon materials were carried out. In addition, computer programs and analytical techniques have been developed to estimate the loss of material from sublimation. For purpose of component life time assessment and comparison between theoretical calculation and experimental results, a detailed knowledge on sublimation behaviours of carbon materials at high temperature has therefore become indispensable. The sublimation behaviour of carbon at high temperature is a complex, because of the formation of stable carbon clusters. At present, in most of the literature, only the species C_1, C_2, C_3 and C_4 were taken into account to assess the sublimation rates. In this work, based on theoretical investigation, an analysis of the formation of larger clusters C_5, C_6, C_7, C_8, C_9 and C_{10}, as a function of temperature were performed and the total rate of sublimation of carbon materials was deduced. The consequence of this results on rates of carbon sublimation at elevated temperature is discussed.

1. Introduction

In selecting materials for plasma facing components, the lifetime of the components is one of the most critical issues. Plasma disruption, ELMs, sputtering erosion behaviour and neutron effects on the properties of materials will significantly affect the lifetime of components [1,2]. Particular, Disruption and slow transients, which can occur as off-normal events as the result of a transition from detached divertor operation to attached operation damage to plasma facing materials in a magnetic fusion reactor is a major concern for safe, successful, and reliable reactor operation. During plasma disruption or slow transients, a high heat flux is deposited onto the PFC materials for a short time, which cause extremely in increasing the target temperature, and leads to high sublimation, evaporation and melting, depending on the intensity. In the International Thermonuclear Experimental Reactor (ITER), for example, the heat loading during thermal quench of disruption is evaluated to be in the range of 10–200 MJ/m2 for a very short duration of 0.1–3 ms and a heat loading of 20 MW/m2 with a duration of 10 s is expected for a slow transients event. Among the low-Z materials, Carbon materials (graphites and CFCs) have been being seriously considered as plasma facing material for ITER, because of widely experiences as first wall and divertor plate protection in present TOKAMAKs, and their excellent thermal shock resistance and high melting point.

To estimate the exact amount of eroded material during the plasma disruption is critically important to reactor design and component lifetime analysis. Over the years, a number of simulation experiments, using as heat sources electron beams, neutral/hydrogen beams, and laser beams on investigation of the influence of heat loads on the amount of evaporated materials were carried out [3,4]. In addition, computer programs and analytical techniques have been developed to estimate the

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Table 1
The atomization energies (kcal/mol) for C_n used in this calculation

Atomization energy of carbon clusters (kcal/mol)								
C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
145.1	314.4	426.1	594.0	708.0	870.9	992.9	1149.6	1343.1

loss of material from evaporation. A detailed knowledge on sublimation behaviours of carbon materials at extremely high temperature has therefore become indispensable for accurate assessment.

The sublimation behaviour of carbon at high temperature is a complex, because of the formation of stable carbon clusters. The sublimation rates of the C species C_1, C_2, C_3 and C_4 as a function of temperature were discussed in detailed elsewhere [5]. In addition to the previous work, an analysis of rates of sublimation of larger clusters C_5, C_6, C_7, C_8, C_9 and C_{10} as a function of temperature were performed.

2. Structure and vibrational frequency of carbon clusters C_5, C_6, C_7, C_8, C_9 and C_{10}

It has been generally agreed on from theoretical and experimental work that the carbon clusters with an odd number of atoms such as C_3, C_5, C_7 and C_9 are linear with a ${}^1\Sigma_g^+$ ground state, whilst the structures of C_6, C_8, C_{10} are linear cumulene type with ${}^3\Sigma_g^-$ ground state. The frequency of the clusters has been predicted by ab initio calculation at MP2/6-31 G* level and published elsewhere [6,7].

3. Atomisation energies and free energy functions of clusters: C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9 and C_{10}

Very recently, a series of papers have been reported by Gingerich et al. [8,9] on the results of Knudsen effusion experiments of atomisation energies of C_2–C_7 and Martin and Taylor presents the results of ab initio theoretical calculation on atomisation energies of the C_n clusters ($n = 2$–10). The results of calculation by Martin and Taylor agree well with the reported experimental results of Gingerich et al. on C_3, C_4, C_5, C_6, and C_7. The atomisation energies for C_n ($n = 2$–10) are shown in Table 1. The free energy function of C, C_2, C_3, and C_4 are given in JANAF tables, and that for C_5, C_6, C_7, C_8, C_9 and C_{10} have been calculated. For the calculation, the structures of C_5, C_7, C_9, linear cumulenic isomer with ${}^1\Sigma_g^+$ were assumed, whilst the structures of C_6, C_8, C_{10} a linear cumulene type ${}^3\Sigma_g^-$ structure were used for calculation. The free energy function of C_1, C_2, C_3, C_4 is given in Table 2 and the calculated free energy function of C_5, C_6, C_7, C_8, C_9 and C_{10} as a function of temperature is given in Table 3.

4. Partial pressures of C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9 and C_{10} as a function of temperature

The partial pressures of C_1, C_2, C_3 and C_4 as a function of temperature have been discussed previously. A systematic compilation up to 6000 K is given in JANAF tables. The partial pressures of C_5, C_6, C_7, C_8, C_9 and C_{10} were calculated by the following equations:

$$P_{C_5} = (P_c)^5 \exp\left\{\frac{D_0^o(C_5)}{RT} + \frac{\Delta\left[\left(G_T^o - H_0^o\right)/T\right]}{R}\right\},$$

$$P_{C_6} = (P_c)^6 \exp\left\{\frac{D_0^o(C_6)}{RT} + \frac{\Delta\left[\left(G_T^o - H_0^o\right)/T\right]}{R}\right\},$$

Table 2
The free energy function of C_1, C_2, C_3, C_4

Temperature (K)	Free energy function – $\left(G_T^o - H_0^o\right)/T$ (cal mol^{-1} deg^{-1})			
	C_1	C_2	C_3	C_4
298	37.76	47.73	56.68	54.54
500	38.32	48.74	57.69	56.03
800	39.55	51.01	59.96	59.61
1000	40.29	52.33	61.38	61.94
1200	40.95	53.50	62.68	64.11
1400	41.54	54.54	63.88	66.12
1600	42.07	55.49	64.98	67.97
1800	42.55	56.34	66.00	69.68
2000	42.99	57.13	66.96	71.28
2200	43.40	57.86	67.85	72.76
2400	43.78	58.54	68.68	74.15
2600	44.13	59.17	69.47	75.46
2800	44.46	59.77	70.21	76.70
3000	44.77	60.33	70.92	77.86
3200	45.06	60.87	71.59	78.97
3400	45.35	61.38	72.23	80.02
3600	45.61	61.86	72.84	81.02
3800	45.86	62.32	73.43	81.98
4000	46.10	62.76	73.99	82.90
4200	46.33	63.19	74.53	83.77
4400	46.55	63.60	75.05	84.62
4600	46.76	63.99	75.55	85.43
4800	46.96	64.37	76.03	86.21
5000	47.16	64.74	76.50	86.96
5200	47.35	65.10	76.95	87.69
5400	47.54	65.44	77.39	88.39
5600	47.72	65.77	77.82	89.07
5800	47.89	66.10	78.23	89.73
6000	48.06	66.42	78.63	90.36

Table 3
The free energy function of C_5, C_6, C_7, C_8, C_9 and C_{10}

Temperature (K)	Free energy function – $(G^o_T - H^o_0)/T$ (cal mol^{-1} deg^{-1})					
	C_5	C_6	C_7	C_8	C_9	C_{10}
298	52.67	53.55	58.58	60.73	65.34	62.27
500	59.91	60.39	67.87	69.82	76.96	73.08
800	67.54	69.29	78.15	80.76	90.03	86.08
1000	71.56	72.88	83.67	87.25	97.11	93.35
1200	75.01	77.26	88.48	93.19	103.30	99.81
1400	78.07	81.47	92.75	98.56	108.81	105.63
1600	80.81	85.40	96.60	103.42	113.78	110.89
1800	83.29	89.02	100.09	107.82	118.31	115.74
2000	85.57	92.32	103.30	111.83	122.46	120.19
2200	87.67	95.33	106.26	115.53	126.31	124.33
2400	89.60	98.10	109.01	118.94	129.88	128.18
2600	91.42	100.66	111.59	122.11	133.22	131.78
2800	93.09	103.03	114.00	125.06	136.35	135.17
3000	94.70	105.25	116.27	127.84	139.31	138.35
3200	96.21	107.32	118.42	130.45	142.10	141.39
3400	97.64	109.27	120.45	132.92	144.75	144.26
3600	98.99	111.11	122.38	135.26	147.26	146.98
3800	100.28	112.86	124.22	137.48	149.66	149.58
4000	101.53	114.51	126.00	139.59	151.95	152.08
4200	102.71	116.08	127.66	141.62	154.13	154.45
4400	103.86	117.59	129.27	143.55	156.24	156.73
4600	104.95	119.02	130.82	145.40	158.24	158.94
4800	106.03	120.39	132.31	147.18	160.19	161.05
5000	107.04	121.72	133.74	148.89	162.06	163.09
5200	108.05	122.99	135.12	150.54	163.87	165.05
5400	109.01	124.21	136.46	152.12	165.60	166.95
5600	109.96	125.39	137.74	153.65	167.29	168.78
5800	110.87	126.53	138.99	155.14	168.91	170.56
6000	111.77	127.63	140.20	156.58	170.48	172.27

$$P_{C_7} = (P_c)^7 \exp\left\{\frac{D^o_0(C_7)}{RT} + \frac{\Delta\left[\left(G^o_T - H^o_0\right)/T\right]}{R}\right\},$$

$$P_{C_8} = (P_c)^8 \exp\left\{\frac{D^o_0(C_8)}{RT} + \frac{\Delta\left[\left(G^o_T - H^o_0\right)/T\right]}{R}\right\},$$

$$P_{C_9} = (P_c)^9 \exp\left\{\frac{D^o_0(C_9)}{RT} + \frac{\Delta\left[\left(G^o_T - H^o_0\right)/T\right]}{R}\right\},$$

$$P_{C_{10}} = (P_c)^{10} \exp\left\{\frac{D^o_0(C_{10})}{RT} + \frac{\Delta\left[\left(G^o_T - H^o_0\right)/T\right]}{R}\right\},$$

where P_c is the equilibrium partial pressure of atomic carbon in atmospheres, and $D^o_0(C_5)$, $D^o_0(C_6)$, $D^o_0(C_7)$, $D^o_0(C_8)$, $D^o_0(C_9)$, and $D^o_0(C_{10})$ are atomisation energies of the clusters C_5, C_6, C_7, C_8, C_9 and C_{10}, respectively. $\Delta\left[\left(G^o_T - H^o_0\right)/T\right]$ is the change in the free energy function for the reactions: $C_5 = 5$ C; $C_6 = 6$ C; $C_7 = 7$ C; $C_8 = 8$ C; $C_9 = 9$ C and $C_{10} = 10$ C.

The partial pressure and free energy function of atomic carbon are taken from JANAF tables, whilst the atomisation energies D^o_0 and free energy functions of clusters C_5, C_6, C_7, C_8, C_9 and C_{10} were taken from calculated values (Table 1).

The calculated partial pressures p (atmospheres) of the carbon clusters, C_5, C_6, C_7, C_8, C_9 and C_{10} as a function of temperature T (K) are given in Table 4, which can be expressed by following equations:

$$\log p_5 = -\frac{54911.4}{T} + 12.148,$$

$$\log p_6 = -\frac{67933.9}{T} + 13.323,$$

$$\log p_7 = -\frac{66603.1}{T} + 13.168,$$

$$\log p_8 = -\frac{78726.2}{T} + 14.599,$$

$$\log p_9 = -\frac{79562.1}{T} + 14.871,$$

$$\log p_{10} = -\frac{72908.6}{T} + 12.587.$$

Table 4
The partial pressures of carbon clusters

Temperature (K)	Partial pressure of carbon cluster (atm)						
	C_1	C_5	C_6	C_7	C_8	C_9	C_{10}
2000	3.34×10^{-11}	1.799×10^{-16}	2.072×10^{-22}	4.426×10^{-22}	9.347×10^{-27}	3.518×10^{-27}	2.109×10^{-26}
2600	6.71×10^{-7}	6.644×10^{-10}	4.043×10^{-14}	7.432×10^{-14}	4.052×10^{-17}	2.456×10^{-17}	3.336×10^{-17}
3000	5.43×10^{-5}	5.277×10^{-7}	1.92×10^{-10}	3.234×10^{-10}	7.525×10^{-13}	5.618×10^{-13}	3.863×10^{-13}
3600	6.25×10^{-3}	6.835×10^{-4}	1.706×10^{-6}	2.586×10^{-6}	2.895×10^{-8}	2.663×10^{-8}	8.692×10^{-9}
4000	6.67×10^{-2}	2.451×10^{-2}	1.598×10^{-4}	2.314×10^{-4}	5.611×10^{-6}	5.769×10^{-6}	1.291×10^{-6}
4400	4.60×10^{-1}	4.459×10^{-1}	6.331×10^{-3}	8.605×10^{-3}	4.024×10^{-4}	4.474×10^{-4}	7.215×10^{-5}
4600	1.066	1.585	3.159×10^{-2}	4.230×10^{-2}	2.614×10^{-3}	2.998×10^{-3}	4.280×10^{-4}
4800	2.296	5.101	1.362×10^{-1}	1.796×10^{-1}	1.434×10^{-2}	1.708×10^{-2}	2.131×10^{-3}
5000	4.656	14.56	1.593×10^{-1}	6.666×10^{-1}	6.739×10^{-2}	8.268×10^{-2}	9.151×10^{-3}
5200	8.933	39.13	1.784	2.246	2.828×10^{-1}	3.575×10^{-1}	3.518×10^{-2}
5400	16.29	94.31	5.398	6.673	1.105	1.307	1.160×10^{-1}
5600	28.51	219.9	15.46	18.68	3.43	4.545	3.634×10^{-1}
5800	47.86	479.5	40.95	48.66	10.68	14.28	1.047
6000	77.63	990.5	100.2	116.9	30.06	40.74	2.727

5. Rate of sublimation of carbon clusters C_5, C_6, C_7, C_8, C_9 and C_{10}

From the partial pressures of the clusters C_5, C_6, C_7, C_8, C_9 and C_{10}, the rates of sublimation were calculated, the rates of sublimation Z_j (atoms, cm^{-2} s^{-1}) as a function of temperature T (K) are given in Table 5. It is seen, that the rate of sublimation of the cluster C_5 exceeds the value of C_1 at temperature higher than 4800 K. The dominant species at high temperature are C_5, C_3, C_2, C_1, C_7 and C_6. The rates of sublimation of all carbon clusters up to carbon C_{10} can be expressed by following equations:

$$Z_j = \frac{2.674 \times 10^{25}}{2\sqrt{3jT}} \exp\left[\frac{D^o_{0,j} - j\sigma(T) + \alpha_j T^{\beta_j}}{RT}\right]$$

and the total sublimation rate of carbon clusters up to C_j ($C_1 + C_2 + \cdots C_j$) is

$$S_{k,l}(T) = \frac{2.674 \times 10^{25}}{2\sqrt{3T}} \sum_{j=k}^{l} \frac{1}{\sqrt{j}} \exp\left[\frac{D^o_{0,j} - j\sigma(T) + \alpha_j T^{\beta_j}}{RT}\right],$$

where

$$\sigma(T) = 84262.3R - 18.3959RT + 20.7628T^{1.09617}.$$

j	α_j	β_j
1	20.7628	1.09617
2	21.2397	1.13067
3	24.2047	1.13476
4	14.8329	1.20738
5	12.8950	1.24864
6	8.93438	1.30689
7	11.5356	1.28791
8	9.57839	1.32246
9	11.2419	1.31353
10	9.00562	1.34030

Table 5
The rates of sublimation of carbon clusters

Temperature (K)	Rate of sublimation of carbon cluster (atoms, cm^{-2} s^{-1})						
	C_1	C_5	C_6	C_7	C_8	C_9	C_{10}
2000	5.765×10^{12}	1.389×10^{7}	1.460×10^{1}	2.888×10^{1}	5.703×10^{-4}	2.024×10^{-4}	1.151×10^{-3}
2600	1.016×10^{17}	4.498×10^{13}	2.499×10^{9}	4.252×10^{9}	2.168×10^{6}	1.239×10^{6}	1.597×10^{6}
3000	7.653×10^{18}	3.326×10^{16}	1.105×10^{13}	1.723×10^{13}	3.750×10^{10}	2.639×10^{10}	1.721×10^{10}
3600	8.041×10^{20}	3.932×10^{19}	8.963×10^{16}	1.257×10^{17}	1.317×10^{15}	1.142×10^{15}	3.536×10^{14}
4000	8.141×10^{21}	1.338×10^{21}	7.963×10^{18}	1.067×10^{19}	2.421×10^{17}	2.347×10^{17}	4.982×10^{16}
4400	5.353×10^{22}	2.321×10^{22}	3.008×10^{20}	3.785×10^{20}	1.656×10^{19}	1.735×10^{19}	2.655×10^{18}
4600	1.213×10^{23}	8.068×10^{22}	1.468×10^{21}	1.820×10^{21}	1.052×10^{20}	1.137×10^{20}	1.541×10^{19}
4800	2.558×10^{23}	2.542×10^{23}	6.197×10^{21}	7.563×10^{21}	5.651×10^{20}	6.345×10^{20}	7.509×10^{19}
5000	5.083×10^{23}	7.108×10^{23}	2.314×10^{22}	2.751×10^{22}	2.601×10^{21}	3.009×10^{21}	3.159×10^{20}
5200	9.562×10^{23}	1.873×10^{24}	7.796×10^{22}	9.088×10^{22}	1.070×10^{22}	1.276×10^{22}	1.191×10^{21}
5400	1.711×10^{24}	4.431×10^{24}	2.315×10^{23}	2.650×10^{23}	3.768×10^{22}	4.577×10^{22}	3.855×10^{21}
5600	2.941×10^{24}	1.014×10^{25}	6.508×10^{23}	7.282×10^{23}	1.251×10^{23}	1.563×10^{23}	1.185×10^{22}
5800	4.851×10^{24}	2.173×10^{25}	1.695×10^{24}	1.864×10^{24}	3.815×10^{23}	4.825×10^{23}	3.357×10^{22}
6000	7.736×10^{24}	4.414×10^{25}	4.076×10^{24}	4.404×10^{24}	1.059×10^{24}	1.353×10^{24}	8.593×10^{22}

6. Results and discussion

Gingerich et al. [8,9] have employed high temperature mass spectrometer to measure the partial pressures of C_5, C_6, and C_7 clusters up to a temperature of 2800 K. The calculated partial pressures of C_5, C_6 and C_7 agree well with the measured values. It is interesting to note, that the cluster C_5 has highest partial pressure at temperature higher than 4800 K. The species C_5, C_3, C_2, C_1, C_7 and C_6 contribute the major fraction of the total sublimation of carbon at high temperature regime.

By comparison of the rate of sublimation of the summation of C_1, C_2, C_3, C_4 and the summation of C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9 and C_{10}. There is almost no deviation up to 3400 K. However, the total rate of sublimation of C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9 and C_{10} exceeds the total rate of sublimation of C_1, C_2, C_3, C_4 at 3600 K, the total sublimation rate of C_1–C_{10} is about 50% higher than that of the sublimation rate of C_1–C_4 at 6000 K. It implies, that rate of sublimation of carbon will be underestimated, if only C_1, C_2, C_3, and C_4 were taken into account at temperature >3600 K. The deviation of the ratio of total sublimation rate of C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9 and C_{10}. $\sum_1^{10} Z_j(T)$, to the total sublimation rate of C_1, C_2, C_3, C_4, $\sum_1^4 Z_j(T)$, as a function of temperature is:

T (K)	$\sum_1^{10} Z_j(T) / \sum_1^4 Z_j(T)$
3000	1.001
3200	1.003
3400	1.005
3600	1.010
3800	1.016
4000	1.027
4200	1.043
4400	1.062
4600	1.089
4800	1.123
5000	1.164
5200	1.216
5400	1.270
5600	1.338
5800	1.414
6000	1.498

7. Conclusions

In the present study, a theoretical investigation of the formation of larger carbon clusters is performed. The partial pressures and the rates of sublimation of the species C_5, C_6, C_7, C_8, C_9 and C_{10} have been calculated as a function of target temperature up to 6000 K, and the following conclusions can be made:

1. The calculated partial pressures of C_5, C_6, C_7 as a function of target temperature agree well with the experimental values ($\leqslant$ 2800 K) of Gingerich [9].
2. The carbon clusters C_5, C_6, C_7, C_8, C_9 and C_{10} have negligible contribution to the total rate of sublimation at temperature <3400 K. However, at temperature >3600 K, they become more dominant.
3. At temperature below 3600 K, the major carbon species are C_3, C_2, C_1 whilst in the temperature range of 5000–6000 K, the dominant species are the larger clusters C_4, C_5, C_6, C_7, C_8 and C_9.
4. At temperature $\geqslant$ 6000 K, the rate of sublimation of carbon by taking account of the species C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10} is about 50% higher than the sublimation rate calculated based on only C_1, C_2, C_3, and C_4.
5. More detailed experimental investigations are required to verify these predictions.

References

[1] C.H. Wu, U. Mszanowski, J. Nucl. Mater. 218 (1995) 293.
[2] H.D. Pacher et al., J. Nucl. Mater. 241–243 (1997) 255.
[3] A. Hassanein et al., L. Nucl. Mater. 241–243 (1997) 288.
[4] A.E. Koniges et al., J. Nucl. Mater. 241–243 (1997) 244.
[5] C.H. Wu, NET Report, NET/IN/84-075.
[6] J.L. Martin, P.R. Taylor, J. Chem. Phys. 102 (1995) 8270.
[7] J.L. Martin, P.R. Taylor, Structure and vibrations of small carbon clusters from coupled-cluster calculation, to be published.
[8] K.A. Gingerich, Chem. Phys. Lett. 196 (1992) 245.
[9] K.A. Gingerich, H.C. Finkbeiner, R.W. Schmude, J. Am. Chem. Soc. 116 (1994) 3884.