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Chemical erosion of carbon doped with different fine-grain carbides

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Abstract

Several carbide-doped (SiC, TiC, V_8C_7, WC, ZrC) graphites have been produced. The erosion of these materials at low-energy (eV) hydrogen ion bombardment has been investigated using the weight-loss method, mass spectroscopy, ion beam analysis, and scanning electron microscopy (SEM). The erosion yields of the WC- and V_8C_7-doped graphites are reduced by a factor of 2 for 30 eV D at 300 K compared to pure graphite. This observed reduction is partly attributed to surface enrichment of carbide due to preferential C erosion. The other part is assigned to changes in the chemical erosion process (Y_{surf}) as well as at elevated temperatures in the thermal activated process (Y_{therm}). The reduction of both erosion processes is determined for all dopants to be more than 25% of the erosion yield of the undoped graphite.

Keywords: Chemical erosion; Doped carbon; Carbide; Graphite; Ion irradiation; Ion beam analysis; Surface composition and topography

1. Introduction

In today's fusion experiments carbon materials, such as carbon fibre composites (CFC) are mostly used in the areas of high plasma loads, i.e., for limiters and divertor plates. Carbon has a low Z, it does not melt and it has good thermophysical properties. Major disadvantages of carbon materials are, however, the high chemical reactivity of carbon with energetic hydrogen ions leading to large chemical erosion [1–4] and the ability of carbon to trap hydrogen, especially in co-deposited layers [5]. The chemical reactivity has been found to be reduced for carbon materials doped with other elements, such as boron (see as reviews [3,4,6,7]).

The aim of this work is to investigate the influence of different dopings and production processes on the reduction of the chemical erosion. At the same time the thermal conductivity of the doped materials should not be degraded compared to carbon. The influence of the dopant element on the hydrogen retention in the material [8,9] and in co-deposited mixed layers [10] and the removal behaviour of these mixed layers [11] should be kept in mind.

In this paper the first results on the development of isotropic graphite doped with different carbides (α-SiC, TiC, V_8C_7, WC, ZrC) and their response concerning the processes of chemical erosion – the thermally activated process (Y_{therm}) at elevated temperatures and the surface process (Y_{surf}) at low temperatures and low impact energies [1–4] – are presented. The effects of surface composition modifications are considered [12,13].

2. Experimental

2.1. Sample manufacturing and preparation

The investigated doped graphites are produced at the Materials Department of CEIT (Spain) in the frame of a

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project consisting of the development of doped carbon-based materials with improved plasma–surface interaction properties. This project includes the investigation and optimisation of a wide range of manufacturing parameters. The manufacturing procedure and the first results of their influence on some properties (density and porosity, mechanical properties, degree of graphitisation, and thermal conductivity) will be described in detail in a forthcoming publication [14] and are presented briefly in [7]. Here, only the manufacturing parameters are shortly given for the samples used in the erosion measurements.

The manufacturing started from carbide powders (α-SiC, TiC, V_8C_7, WC, ZrC) and a self-sintering powder of microspheres of carbonaceous mesophases. To achieve homogeneous distribution and to improve the erosion behaviour [6], the carbon and carbide powders have grain sizes of 1–2 μm (Table 1), except for WC (<5 μm). Mixing and uniaxial molding were followed by sintering up to 1270 K and graphitisation up to 2370 K in an inert atmosphere. During sintering the samples lost several percent of their mass, resulting in the desired bulk concentrations of the dopants around 5 at.% (Table 1).

Before the erosion experiments, the samples were polished with diamond liquid (1 μm) and heated to 1100 K in vacuum before starting the erosion measurements. The polishing leads to a reduction of the carbide grain concentration in the near surface region. This effect was previously observed on other doped graphites [15,16].

2.2. Erosion measurements and surface characterisation

The erosion measurements were performed at the Garching high current ion source [17]. The source was adjusted to produce mass-separated ion beams of D_3^+ with energies above 3 keV. These ions were slowed down to the chosen impact energy. The flux was in the order of 10^{19} D/m^2 s. For normal incidence, the bombardment spots had a size of about 0.8 cm^2 for 30 eV D which decreased with the impact energy. The base vacuum pressure was below 10^{-6} Pa rising to about 10^{-5} Pa during bombardment consisting predominantly of the D_2 used. The target could be heated by electron bombardment from the rear to 1200 K during ion bombardment. The temperature was monitored by infrared pyrometry calibrated against optical pyrometry to ±30 K.

The erosion yield was determined by measuring the ion dose and the weight loss in situ with a sensitivity of ±1 μg. All yields were determined under the assumption that only C is eroded at 30 eV, because this energy is below the threshold for physical sputtering of the dopant elements [17]. However, for SiC a chemical erosion is reported [18].

The chemical erosion of C was observed by measuring the methane mass signal (CD_4) with a quadrupole mass spectrometer (mass range: 10–22 amu). To obtain the temperature dependence the target temperature was increased in steps (dwell time 6 min) during bombardment. For the energy dependence, mass spectra were recorded while decreasing the D impact energy in 10 min steps. The duration between the measurements was chosen to await fast transient effects and to avoid changes in the surface composition. For comparison and calibration, pyrolytic graphite (Union Carbide) was eroded and mass-spectroscopically observed always after (or before) measuring the doped graphites. To obtain the chemical erosion yields, the CD_4 signals were calibrated for all target temperatures and impact energies with the same factor: the chemical erosion yield for pyrolytic graphite is 0.1 in the maximum of the temperature dependence for 1 keV D impact [19].

To obtain the distribution of the carbide grains at the surface and the topography of the original and eroded surfaces, scanning electron microscopy (SEM) was used. Ion beam analysis was performed to determine the concentration of the dopant and its depth profile. Ion beams of 0.72, 2.0, and 4.0 MeV ^{4}He were collimated to 1×1 mm^2 onto the samples. The backscattered spectra (165°) were evaluated using the simulation program SIMNRA [20] and the cross-sections given therein.

2.3. Measurement procedure

All original samples were investigated with SEM (Fig. 1) and ion beam analysis (Fig. 2). Then a set of

Table 1
Properties of the carbide-doped graphites

Dopant	Carbide grain size (μm)	Bulk conc. (at.%)	Surface conc. original (at.%)	Depletion layer thickness (μm)	Surface concentration (at.%) pre-eroded with	
					$\sim 5 \times 10^{24}$ D/m^2	$>2 \times 10^{25}$ D/m^2
α-SiC	~1	5.0 ± 0.3	2.2 ± 0.7	0.6	11 ± 1	
TiC	~1	4.6 ± 0.2	1.5 ± 0.5	0.7	10 ± 0.1.5	
V_8C_7	1.5–2	5.4 ± 0.6	1.5 ± 0.5	1	7 ± 1	11 ± 2
WC	<5	4.9 ± 0.3	1.5 ± 0.5	2	11 ± 1	13 ± 2
ZrC	~1	4.5 ± 0.7	2.0 ± 0.7	0.6		

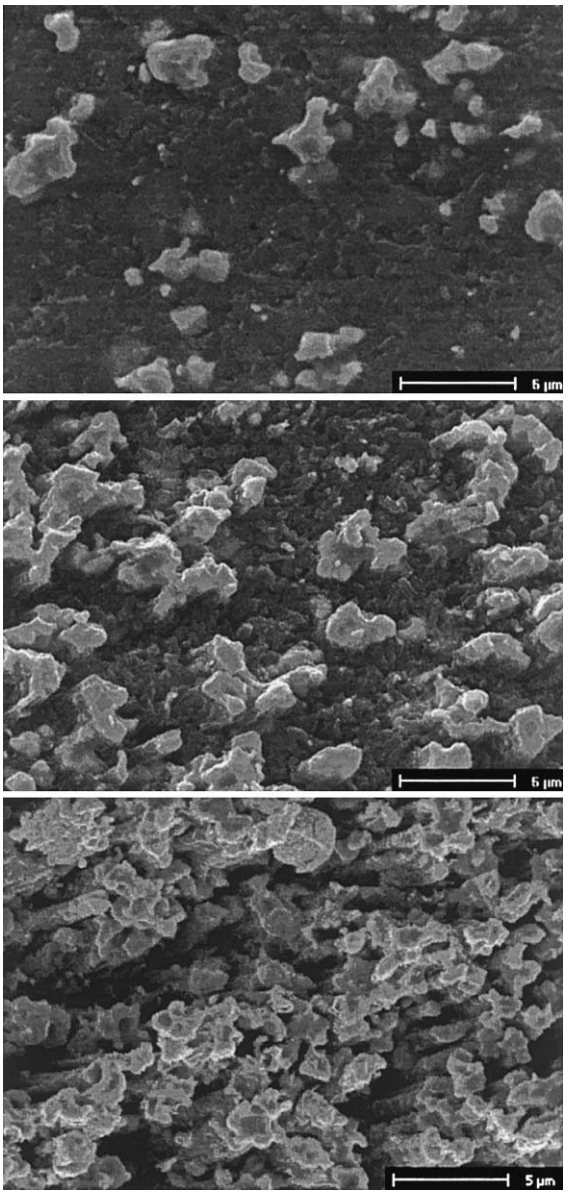

Fig. 1. SEM pictures of the V_8C_7-doped graphite of the original (top) and eroded surfaces after different D fluences (middle: 4×10^{24} D/m^2; bottom: 26×10^{24} D/m^2).

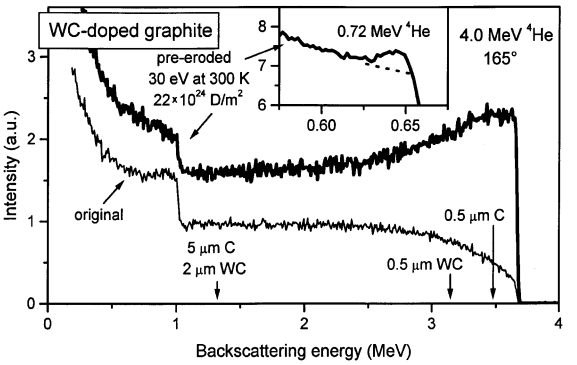

Fig. 2. Backscattering spectra of 4.0 MeV ^{4}He ions from an original (thin line) and a pre-eroded surface (thick) of the WC-doped graphite. The information depths for pure C and WC are given for selected backscattering energies. The inset shows the backscattering spectrum of 0.72 ^{4}He MeV of the pre-eroded surface. The dotted line indicates the signal level for a surface without enrichment in the outermost layer.

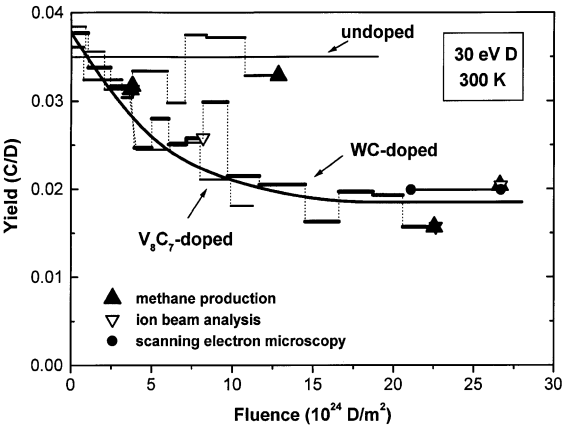

Fig. 3. Fluence dependence of the erosion yield for 30 eV D impact at room temperature of the undoped, the WC- and V_8C_7-doped graphites. The horizontal width of the data point gives the respective accumulated fluence. The solid and dotted lines are only to guide the eye and to connect the data of each sample, respectively. The symbols mark fluences, where a temperature dependence (methane production) and the surface composition (ion beam analysis, scanning electron microscopy) were measured (Table 1, Figs. 1, 2 and 4).

samples was eroded for a long period (several days) with 30 eV D at room temperature (Fig. 3). After a distinct bombarding period (marked in Fig. 3), the temperature dependence of the methane production for 30 eV and 1 keV (Fig. 4) and the surface composition (Figs. 1 and 2) were measured.

The energy dependence of the chemical erosion yield at 810 K (Fig. 5) was determined for a second set of samples with an original surface with the depletion of dopants at the surface.

3. Results and discussion

In order to separate the effects of chemistry and dopant enrichment on the erosion yield, the surface concentrations were measured prior and after the erosion measurements (Table 1). Fig. 1 shows the SEM pictures of the V_8C_7-doped sample. Such a cone-like topography of the eroded surface was previously reported [6,13,16,21–23]. The carbide grains are on top of the cones and they geometrically shield the graphite

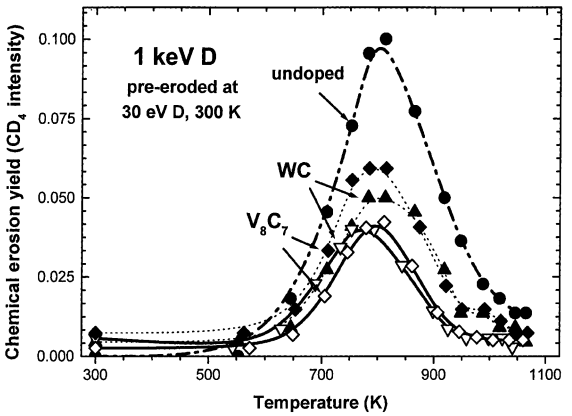

Fig. 4. Temperature dependence of the methane production due to 1 keV D impact on undoped, WC- and V_8C_7-doped graphites with pre-eroded (enriched) surfaces with 30 eV D at room temperature (filled symbols: 4×10^{24} D/m^2 (undoped: 12×10^{24} D/m^2); empty symbols: $>20 \times 10^{24}$ D/m^2 (see Fig. 3)).

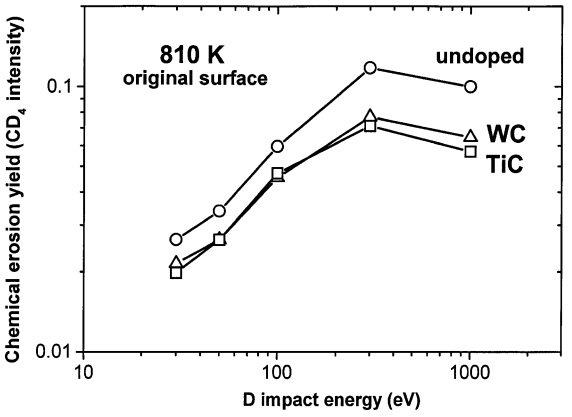

Fig. 5. Energy dependence of the methane production at 810 K of undoped, WC- and TiC-doped graphites with original surfaces.

beneath. The amount of grains is increased compared to the polished surface (Fig. 1). In Fig. 2 the backscattering spectra of an original and eroded surface of the WC-doped sample are presented. The intensity in backscattering spectra is correlated to the concentration of atomic species and the backscattering energy is correlated to a depth. The depth depends on the composition along the way of the incident and backscattered ^{4}He ions; here with the extremes of pure C and pure WC. Again, the depletion of W within a depth of 2 μm due to the polishing and enrichment due to erosion are clearly observed. The enrichment zone extends beyond the information depth (3–6 μm). The concentrations of dopants in the bulk and at the depleted and enriched surfaces are given in Table 1 for all used carbides.

Additionally, in the inset of Fig. 2 a stronger enrichment of W is observable in a very thin surface layer. Such enrichments in the very carbide surface were previously investigated with Auger electron spectroscopy [13,23]. The thickness of this layer is determined to be less than 0.01 μm.

Fig. 3 shows the erosion yield for 30 eV D impact at room temperature of the undoped, the WC- and V_8C_7-doped graphites versus the ion fluence. At the highest accumulated fluences, a reduction to about 50% of the erosion yield is found for the doped ones compared to the undoped one. However, the enrichment of carbide grains is about 13 at.% W and 11 at.% V (Table 1), corresponding to a surface area covered with carbide grains of less than 30%. Therefore, the geometrical shielding due to the enrichment of carbide grains at the surface is only responsible for about half of the observed reduction. From this observation it follows that the surface process (Y_{surf}) on WC- and V_8C_7-doped graphites is reduced. For the SiC-, TiC-, and ZrC-doped ones, fluences of about 5×10^{24} D/m^2 have only been accumulated up to now. Their fluence dependencies of the erosion yield are like the shown ones (Fig. 3) with a reduction at the highest accumulated fluences of about 30% compared with the undoped graphite. Therefore, together with the surface concentrations (Table 1), no conclusion on the surface process can be drawn for these dopants.

In order to observe effects of the dopants on the thermally activated process (Y_{therm}) the temperature dependence of the CD_4 production was measured for 30 eV and 1 keV D impact. The CD_4 production is correlated with the chemical erosion and the maximum in the temperature dependence is a signature of the thermally activated process [1–4,19]. Fig. 4 shows the temperature dependence of the CD_4 production at 1 keV D impact of pre-eroded surfaces after fluences marked in Fig. 3. A reduction of the CD_4 production is found to be below 50% to that of undoped graphite. Again, from knowledge of the enrichment of the dopant, it results that the thermal process (Y_{therm}) is reduced. A shift of the maximum in the temperature dependence is not significant or at most very small. This observation agrees with earlier measurements where only for B doping an obvious shift exists [4,6] and not for other dopants [16,21]. Furthermore, the extent of the reductions is in the same order as published ones [4,6,16,21].

The observed reduction of Y_{therm} is more significant on original surfaces due to the low concentration of dopants (Table 1). Fig. 5 shows the energy dependence of the CD_4 production of the original surfaces at 810 K. For impact energies higher than 100 eV, the maximum in the temperature dependence is at about 810 K [19]. The reduction is about 30–40% for all doped graphites over the investigated energy range, while the surface concentrations are below 2 at.%.

From the reduction of the CD_4 production, the reduction of the yield cannot be estimated directly, because shifts in the maximum of the temperature dependence as well as changes in the distribution of the different hydrocarbon species [19] are playing a major rule and could be influenced by the dopants. But the CD_4 production is a good approximation.

4. Summary

The erosion behaviour of carbide-doped graphites (SiC, TiC, V_8C_7, WC, ZrC) is investigated with the aim to separate changes in both chemical erosion processes (Y_{surf}, Y_{therm}) from the influence of the enrichment of carbide due to preferential erosion of C. All doped graphites are produced in the same manner starting from a mixture of mesophase carbon powder and carbide powders with grain sizes of around 1 μm. The final treatment is graphitisation at 2370 K. The dopant concentration in the bulk is around 5 at.% for all investigated samples. The measurements of the erosion yield, the CD_4 production, and the surface composition clearly indicate a reduction of both chemical erosion processes, Y_{surf} and Y_{therm}, due to the doping of graphite with carbides:

- From the fluence dependence of the erosion yield for 30 eV D and the surface composition and topography, it results that Y_{surf} is reduced by roughly 25% for fluences larger than 2×10^{25} D/m^2 on WC- and V_8C_7-doped graphites. The total reduction of the erosion yield is around 50%.
- The temperature and energy dependence of the mass-spectrometrically measured CD_4 production in combination with knowledge of the surface concentration indicate that Y_{therm} is reduced by about 30% for all dopants: this reduction is already observable on the original surfaces with dopant concentrations of less than 2 at.%.

Nevertheless, the observed reductions are not higher than most of the reported ones [6], and even lower than the largest reported, which come from a 10 at.% Ti-doped graphite after fluences in the order of 10^{25} D/m^2 [13]. Our experiments have to be continued, especially to complete the fluence dependence of all dopants and the influence of the bulk concentration. Up to now, none of the used dopants accentuates with respect to its effect on the erosion behaviour.

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