Compilation of erosion yields of metal-doped carbon materials by deuterium impact from ion beam and low temperature plasma

M. Balden[1], P. Starke[2], C. García-Rosales[3], C. Adelhelm[1], P.A. Sauter[1], I. López-Galilea[3], N. Ordas[3], J.M. Ramos Fernández[4], and M. Martínez Escandell[4]

[1] *Max-Planck-Institut für Plasmaphysik, EURATOM Association, 85748 Garching, Germany*

[2] *Lehrstuhl für Experimentelle Plasmaphysik, Institut für Physik, Universität Augsburg, D-86135 Augsburg, Germany*

[3] *CEIT and Tecnun (University of Navarra), E-20018 San Sebastián, Spain*

[4] *Departamento de Química Inorgánica. University of Alicante, E-03690 Alicante, Spain*

Abstract

The erosion yield by deuterium impact was determined for various doped carbon-based materials. Ion beam bombardment with 30 and 200 eV at elevated temperatures (600-850 K) and low temperature plasma exposure with 30 eV ion energy (~$7x10^{20}$ ions/m^2s) and about 170 times higher thermal atomic deuterium flux at 300 K and 630 K were performed. The total yield of fine-grain graphites doped with 4 at% Ti and Zr is reduced by a factor of 4 for 30 and 200 eV D impact at elevated temperatures at D fluences above 10^{24} m^{-2} compared to undoped graphite. Extensive carbide particle loss can be excluded up to fluences of ~10^{25} m^{-2}.

Key words: doped graphite, erosion yield, deuterium, carbon

1. Introduction

The use of carbon (i.e. Carbon Fibre-reinforced Carbon (CFC)) in the divertor will be restricted to ITER's first operation phase, because of the high reactivity of carbon with hydrogen isotopes and, therefore, high erosion rates (chemical erosion) [***1,2***]. This causes lifetime problems of the components and leads to the formation of tritium-containing co-deposited layers [*2*,***3***]. By reducing the carbon source - the erosion yield - the radiological problem with the tritium retention in deposited layers as well as the lifetime issue will be relaxed. Doping of carbon with some transition metals strongly reduces chemical erosion [***4,5,6***]. This reduction depends on the hydrogen fluence, whereas the fluence needed to achieve a specific reduction is correlated to the particle size of the dopant [*4*].

In the frame of the European integrated project ExtreMat, carbide-doped isotropic fine-grain graphites and CFCs have been developed applying various process routes. Different methods to introduce Ti and Zr were used reaching metal concentrations of 0.1 - 8 at%. After the final graphitization at temperatures above 2800 K, the final carbide particle size is between 50 nm and a few microns, depending on the process parameters [***7,8,9,10***].

The thermo-mechanical properties of these materials, e.g., thermal conductivity and flexural strength, were determined and optimized to enable the material to survive fusion relevant heat loading conditions, e.g., thermal shock and thermal fatigue [***11,12,13***]. In recent mock-up manufacturing and high heat flux (HHF) tests, the feasibility and reliability of the newly developed carbon-based materials and the corresponding joining technology to a Cu-based heat sink were shown [***14,15,16,17,18***]. Note that the properties of the tested materials cannot be found at present in any commercial graphite.

The aim of the development of the doped isotropic fine-grain graphites was to reduce the chemical erosion yield by at least a factor of 2 to 4, depending on the exposure conditions, while improving at the same time the thermal conductivity and mechanical strength of pure fine-grain graphite reaching the quality of CFCs. Therefore, the materials were investigated in respect to their erosion behaviour against deuterium impact. This study summarizes erosion data obtained by exposure to a mono-energetic ion beam and low temperature plasmas under various conditions.

2. Experimental

2.1 Materials

The investigated materials contain doped and pure isotropic fine-grain graphites, which were produced in two different institutions, whose names are abbreviated by CEIT[3] and UALI[4]. They applied various process routes. CEIT produced carbide-doped fine-grain graphites from a mixture of self-sintering synthetic naphthalene-derived mesophase pitch with TiC powder (130 nm grain size) [*8*]. UALI obtained carbide-doped fine-grain graphites from Ti-doped mesophase produced by co-pyrolysis of petroleum residue with TiC nanoparticles or titanium butoxide (TBO: $Ti(OC_4H_9)_4$) or zirconium acetyl acetonate (Zr-A: Zr $(C_5H_7O_2)_4$) [*18*,***19***].

After annealing above 2800 K for graphitizing, metal concentration of 2-4 at% are obtained, while the final carbide particle size is between 50 nm and a few microns, depending on the process parameters. Due to variation of the process parameter, the properties of the graphites were optimized, especially in respect of homogeneity of doping, thermal conductivity and flexural strength. Thermal conductivity above 150 W/mK and homogeneous dopant distribution on the 50 μm length scale were achieved by both producers [*15*,*18*]. The optimized materials

were used for mock-up manufacturing, on which HHF tests were performed [*18*]. All materials named with "MU" as last letters were used for mock-up manufacturing.

2.2 Specimens and analyses

Specimens were cut to the desired size. All specimens were polished and cleaned in ultrasonic bath before their surface was investigated using a scanning electron microscope (SEM / FEI, XL-30 ESEM) equipped with energy-dispersive X-ray spectroscopy (EDX / EDAX).

After the erosion experiment the same position on the specimens were analysed again. Due to the strong roughness after exposure, the material contrast of the backscattered electrons needed in certain cases assistance by EDX to distinguish between graphite and carbide grains.

Surface and bulk concentrations for the doped materials were obtained from backscattering of 0.8 and 4 MeV ^{4}He ion beams [***20***]. Most specimens had 4 at% Ti or Zr (in form of carbides) in the bulk, which was found to be an optimum [*5,6,7*], while the polishing leads to a slight decrease at the surface [*20*].

2.3 Ion beam exposure

The ion beam exposure was performed at the Garching high current ion source [***21***]. The specimens of maximal size of 15×12×1 mm^3 were bombarded with a mono-energetic, mass-separated ion beam. The energy of the molecular D_3^+ ions was adjusted to 90 and 600 eV, i.e., the deuterium energy was 30 and 200 eV per D atom. With a flux density of about 10^{19} D/m^{2}s averaged across the ~0.5 cm^2 large erosion spot [***22***], fluences of up to 10^{25} D/m^2 per specimen were achieved within reasonable time (~15 days).

The specimens were heated by electron bombardment from the rear and the temperature was measured with pyrometery.

The erosion yield was determined by measuring the impacting ion charge, i.e., ion fluence and the weight loss (number of eroded specimen atoms). The fluence dependence of the yield was determined by interrupting the exposure. The specimen cooled down to room temperature (RT) before each in-situ balancing.

2.4 Plasma exposure

In a small vacuum chamber (15 cm diameter, 10 cm height) specimens of maximal size of 30×30×3 mm^3 were exposed to well characterized inductively coupled RF plasmas (ICP) providing homogeneous plasma parameters and, therefore, homogeneous erosion conditions above the surface. In order to obtain ion energies of 30 eV, the cooled/heated specimen holder was biased. Exposures at RT and 630 K were performed. The incident ion flux had been determined before the measurement campaign to about $7x10^{20}$ ions/m^2s, whereas the main ion species is D^+ (~60%) [***23***]. Ion fluences of up to several 10^{25} ions/m^2 are easily achievable in a couple of hours. In addition, thermal D atoms impact simultaneously on the surface of the samples with a flux ratio of ~170 to the energetic ions (~10^{23} D^0/m^2s). Note that in ITER a high flux of neutrals to the wall is expected with energies of up to a few eV.

The overall erosion yield (eroded C atoms per incident ion) was gained from weight loss measurements scaled to the accumulated ion fluence and its fluence dependence from optical emission spectroscopy (OES) [*23*,***24***]. The time evolution of the photon flux of the C_2 swan and the CD Gerö band were measured to obtain the fluence dependent flux of eroded carbon, while the Balmer line D_γ and a He line indicated the stability of the plasma. The total C flux was scaled

to the weight loss. Details to the photon flux calibration and further experimental details can be found in [*23*,*24*].

3. Results and discussion

Fig. 1 summarizes the fluence dependencies of the erosion yield by plasma exposure (a-c) and ion beam (d) of various materials.

The measurements on *pure graphites* indicate constant, i.e., steady state erosion yield for plasma exposure (Fig. 1a). Some data are taken from previous studies and rescaled to the slight higher flux [***25,26***]. Note that the variation in the yield of pure graphite could be explained by the attack of the thermal atomic deuterium on disordered carbon structure, i.e., the yield depends on the graphitic and pore structure of the material [*25*]. Be aware that the maximum in the temperature dependent yield of pure graphite for the flux conditions of the plasma exposure is obtained above 650 K for 30 eV [***27***], while for the ion beam this maximum is at 620 K for 30 eV D and at 820 K for 200 eV D [***28***]. The yields of pure graphite for the ion beam impact are tabulated in Fig. 1d.

For *all doped materials* it is common that the erosion yield decreases with increasing fluence. It can be concluded that the steady state erosion yield has not been reached, even for the highest fluence of $4x10^{25}$ ions/m^2.

The fluence dependence of all doped materials *exposed to plasma* exhibits a steep decrease at low fluences from a large starting value. Unfortunately, the plasma needs some time to stabilize, depending on thermal stabilization and material properties, like absorption, and the status of the vessel wall [*23*,*25*,*26*]. This leads to a large uncertainty of the yields for the presented

measurement for the first fluences of $1x10^{24}$ ions/m^2 after insertion of the specimen into the vacuum chamber. Therefore, these data points will not be taken further into account. The interruption of the exposure of the material 'CEIT 21-D' at 630 K over night without venting shows that the stabilisation is faster and the reproducibility of the plasma is indicated by the same level before and after the interruption.

For fluences above $1x10^{24}$ ions/m^2, the yields decline slowly but continuously up to the highest applied fluence of $4x10^{25}$ ions/m^2 ('UALI AT-MU'). Because the absolute yield is scaled by the weight loss and the integrated carbon flux over the whole exposure containing the stabilization zone [*23*], measurements with lower total fluences exhibit a higher uncertainty in the yield scaling.

Unaffected by this, the relative yields are reliable as long as for the D_γ and He signal constancy is shown, which was always proven [*23*]. Evaluating only the data above $1x10^{24}$ ions/m^2 for each specimen separately, a reduction of the yield by a factor of ~2 at 630 K is observed for all 4 at% doped fine-grain graphites. Comparing the yield of the undoped UALI graphite with the doped ones, a reduction by a factor of about 4 for 630 K and of nearly 2 for RT could be estimated (Note the remark about absolute yields).

The materials with 2 at% Ti or Zr doping exhibit a lower reduction with fluence (data not shown). Steady state is also not reached for these materials up to the highest applied fluence of $1x10^{25}$ ions/m^2.

The *ion beam data* reveal the same tendency of continuous decreasing (Fig. 1d) at elevated temperature for 30 eV D impact, and also for 200 eV D impact: i) Steady state is not clearly reached at the highest applied fluences. ii) A reduction by a factor of 3-4 is observed for the 4 at% doped material compared to pure graphites. Similar and higher reduction factors are reported

for various doped carbon-based materials (see review [*4*] and [*5*,*6*,*9*,*20*,*23*,*25*,***29***]). Note that the total yield for the ion beam is determined in a direct way by the two independent measurements of weight loss and ion charge, while it shows a higher statistical error than the yields from the plasma exposure, which exhibits precise relative yields.

Comparing the erosion yields obtained from ion beam impact and plasma exposure for the same material, it can be concluded that both show a reduction in the same order of magnitude with a slight stronger decrease of the ion beam data [*25*]. This could be explained by the influence of the thermal atomic deuterium, which is not taken into account for the yield determination [*25*].

From the analysis of the surface morphology of the material before and after the erosion (Fig. 2) it can be concluded that extensive carbide particle loss does not appear up to fluences of ~10^{25} m^{-2}. Only sparse loss of carbide particles is observed, while the overwhelming amount of carbide grains stay in place. Figure 2 shows examples of the polished surface before the plasma exposure and after: Some burrowed carbide grains are visible as blurred areas in the BSE inlets before erosion, while they are dug out during the exposure. In principle all carbide grains detected before erosion are found after erosion. This behaviour was observed for all investigated materials.

Furthermore, the two eroded surfaces in Fig. 2 show the evolution of the morphology with fluence. The Ti-doped graphite was exposed to about four times larger fluence than the Zr-doped one. The shielding effect of the carbide grain is obvious.

Note that the mechanism observed on graphite exposed to Be-seeded plasma, i.e., sealing of C with a 100 at% coverage of Be [***30***], is not valid here. Nevertheless, in the fusion environment with re-deposition, the erosion of such mixed layers has to be accessed [***31***].

4. Conclusion and summary

Doped fine-grain graphites with 2 - 4 at% Ti or Zr concentration were exposed to D_3^+ ion beam of 30 and 200 eV per D and to a D plasma with 30 eV ion energy and 170 times higher atomic deuterium flux at surface temperatures between 300 and 830 K.

The total erosion yield was determined by measuring the mass loss and the fluence dependence by time-resolved spectroscopy in plasma (ICP, OES) and subsequent balancing (ion beam). The total yield of 4 at% metal-doped fine-grain graphites is reduced by a factor of 4 for 30 and 200 eV D impact at elevated temperatures at fluences above 10^{24} m^{-2}.

Self-passivation by shielding the graphite with carbide grains leads to a typical rough surface morphology. The erosion yield and the morphology do not even reach steady state at fluences of several 10^{25} m^{-2}. Extensive carbide particle loss can be excluded up to fluences of ~10^{25} m^{-2}; only sparse loss of carbide particles is observed, while the overwhelming amount of carbide grains stay in place. Note that fluences of ~10^{25} m^{-2} will be reached in several seconds at the strike point area in ITER [*3*].

For ion beam exposure the reduction of the yield with fluence is faster and stronger than for plasma exposure. This could be explained by the presence of the thermal atomic deuterium, which is not taken into account for the yield determination.

In conclusion, the optimized fine-grain graphite exhibits good enough thermo mechanical properties to withstand thermal loads, even those of off-normal events [14,15,16,17,18]. In addition, the achieved reduction of erosion leads to relaxation of problems of component lifetime, tritium retention in the material and co-deposited layers, and dust generation by flaking off of these layers.

Acknowledgement

Part of the work has been performed within the framework of the Integrated European Project „ExtreMat“ (contract NMP-CT-2004-500253) with financial support by the European Community. It only reflects the view of the authors and the European Community is not liable for any use of the information contained therein.

References

[1] G. Federici et al., J. Nucl. Mater. 313-316 (2003) 11-22

[2] C.H. Skinner and G. Federici, Phys. Scr. T124 (2006) 18–22

[3] G. Federici et al., Nucl. Fusion 41 (2001) 1967-2137

[4] M. Balden, Physica Scripta T81 (1999) 64-69

[5] C. García-Rosales and M. Balden, J. Nucl. Mater. 290-293 (2001) 173-179

[6] E. de Juan Pardo et al., Physica Scripta T111 (2004) 62-67

[7] N. Ordas et al., Physica Scripta T111 (2004) 190-194

[8] I. López-Galilea, Ph.D. Thesis, University of Navarra, Spain (2009)

[9] C. García-Rosales et al., J. Nucl. Mater. 386-388 (2009) 801-804

[10] A. Centeno, R. Santamaria, M. Granda, R. Menendez, C. Blanco, J. Mater. Sci. 44 (2009) 2525–2532

[11] H. Bolt et al., J. Nucl. Mater. 307-311 (2002) 43-52

[12] R. Aymar, J. Nucl. Mater. 307-311 (2002) 1-9

[13] J. Linke, Physica Scripta T123 (2006) 45-53

[14] I. López-Galilea et al., Adv. Mat. Res. 59 (2009) 288-292

[15] I. López-Galilea et al., J. Nucl. Mater.386-388 (2009) 805-808

[16] C. Gualco et al., Adv. Mat. Res. 59 (2009) 192-197

[17] A. Centeno et al., Physica Scripta T138 (2009) 014055

[18] C. García-Rosales et al,, Physica Scripta T138 (2009) 014062

[19] M. Martínez Escandell, private communication

[20] M. Balden et al., J. Nucl. Mater. 290-293 (2001) 52

[21] W. Eckstein, C. García-Rosales, J. Roth and W. Ottenberger, Sputtering Data, Tech. Rep. IPP 9/82, Max-Planck-Institut für Plasmaphysik, Garching, 1993

[22] P. Sauter and M. Balden, Physica Scripta T138 (2009) 014044

[23] P. Starke, C. Adelhelm, and M. Balden, Contrib. Plasma Phys. 47 (2007) 530

[24] U. Fantz, S. Meir, ASDEX Upgrade Team, J. Nucl. Mater. 337-339 (2005) 1087

[25] M. Balden et al., Physica Scripta T111 (2004) 123-128

[26] P. Starke et al., Journal of Nuclear Materials 337–339 (2005) 1005–1009

[27] H. Paulin, Ph.D. Thesis, University Augsburg, Germany (2000)

[28] M. Balden and J. Roth, J. Nucl. Mater. 280 (2000) 39-44

[29] W. Jacob and J. Roth, *Chemical Sputtering,* in Topics in Applied Physics Vol. 110, *Sputtering by Particle Bombardment,* R. Behrisch and W. Eckstein (Eds.), 2007, Springer

[30] K. Schmid, M. Baldwin, R. Doerner and A. Wilthner, Nuclear Fusion 44 (2004) 815-9

[31] M. Balden and C. Adelhelm, Phys. Scr. T128 (2007) 121–126

Figure Captions

Fig. 1: *Fluence dependence of the erosion yield by deuterium impact of various materials obtained by plasma (a-c) and ion beam exposure (d). Some rescaled published data and yields are included in a) and d) [25, 26]. The given yields of pure graphite for the ion beam impact in d) are taken from [28]. Note the ion fluence of the plasma exposure does not account for the neutral D and the number of D atoms in the molecular ions.*

One-column, double length, (500 words)

Fig 2: *SEM images of ZrC-doped (left) and TiC-doped (right) fine-grain graphite before (upper) and after (lower) plasma exposure at RT. Identical regions before and after erosion are marked by the ellipses. Individual carbide grains are recognised after the exposure. In the upper left corners, images from the backscattered electrons are overlaid the images from the secondary electrons.*

Two-column (500 words)

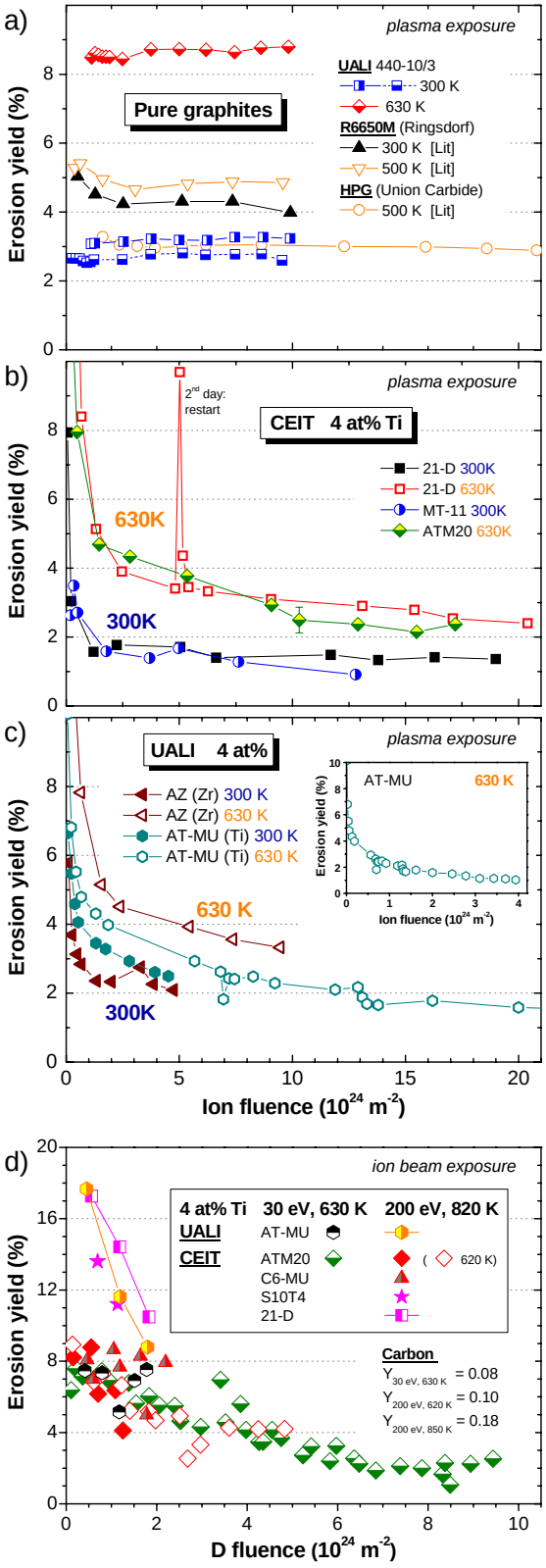

Fig. 1 (one-column, double length, 500 words)

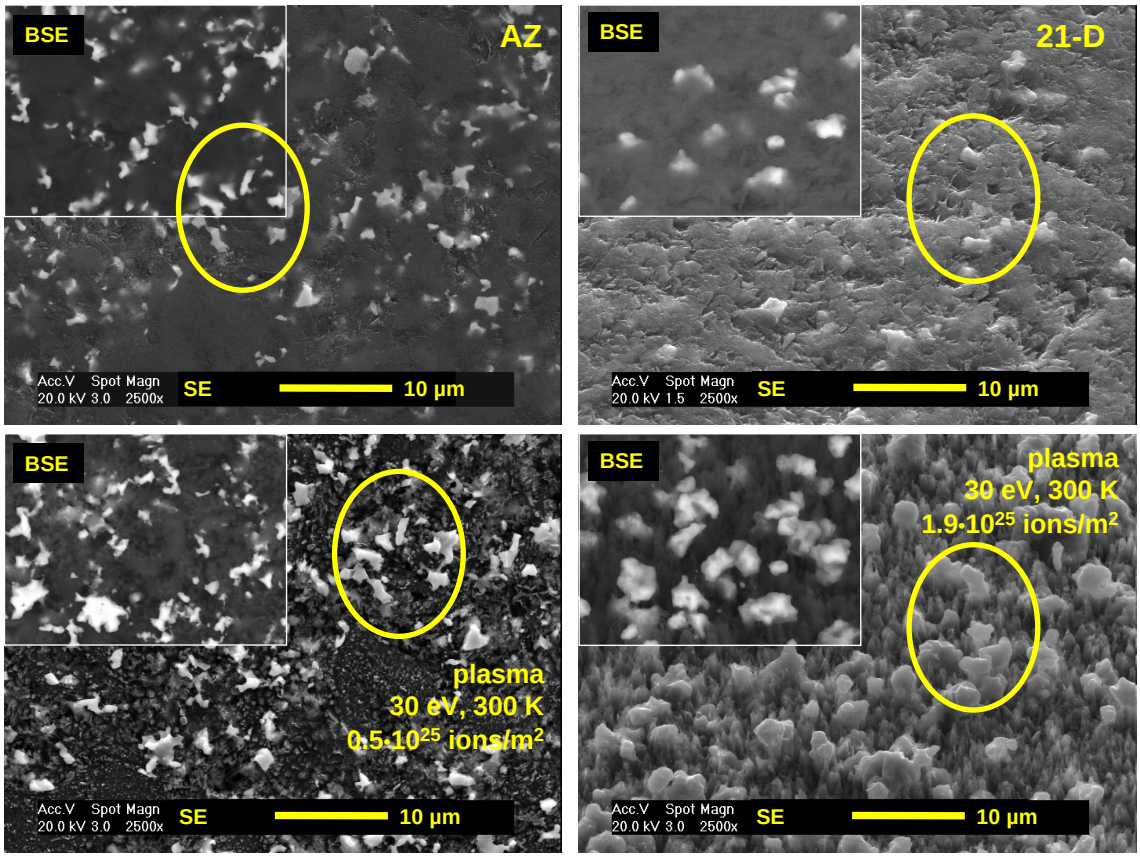

Fig. 2 (two-column, 500 words)