Reduction of the chemical erosion of doped graphite due to surface modification during low energy D^+ bombardment

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Abstract

The chemical erosion yield of pure graphite during hydrogen bombardment is strongly reduced by dopants like Ti, Si, or B. Preferential sputtering and changes of the surface composition as well as influences of the dopant–carbon bonding on methane formation consequently change the erosion yield. Surface changes may be accentuated at low energy hydrogen ion bombardment and elevated temperatures. The changes of the surface compositions of titanium doped graphites and of pure TiC during bombardment with D^+ ions below an ion energy of 1 keV and temperatures up to 1000 K was investigated. Ti concentrations up to 75 at% at room temperature and stoichiometric TiC concentrations at enhanced temperatures were found. Qualitative investigations of the Auger carbon signal fine structure confirms the phase changes. Due to these changes in material composition the chemical erosion yield is suppressed and the erosion dominated by physical sputtering.

Keywords: Physical sputtering; Chemical erosion; Low Z wall material; Wall structure

1. Introduction

The erosion yield of graphite during bombardment with hydrogen ions is strongly temperature dependent due to chemical erosion, i.e. formation of volatile hydrocarbon molecules. In fusion devices the temperature range of first wall plates may cover the high chemical erosion regime of graphite. Since chemical erosion is only weakly dependent on ion energy, the completely detached high confinement regime found in front of tokamak divertor plates [1] which is characterized by a drop of the plasma temperature from 40 eV below 5 eV does not crucially change the erosion yield. However, doping of graphite with atoms like Ti, Si, or B reduces the chemical erosion up to a factor of 8 [2]. Additionally, low ion energy bombardment of multicomponent materials may strongly change the surface state: The ion range and energy deposition as well as formation of volatile hydrocarbon molecules occurring at the end of the ion range is surface-near, and threshold effects play a more important role in surface changes than during bombardment with high energy ions. A thin overlayer consisting of dopant atoms and carbidic bondings may develop altering the sputtering behavior. To gain more insight in surface changes and their potential influence on sputtering yield at elevated temperatures, we have investigated the surface composition of Ti doped graphite as well as of pure TiC during bombardment with low energy D^+ ions and measured their sputtering yield.

2. Experimentals

The targets used in our experiment were LT10, manufactured from a powder mixture consisting of graphite grains with diameters between 0.5 and 4.1 μm, TiC grains with diameters between 1.4 and 5.2 μm [3], and plasma sprayed TiC on Inconell, manufactured by Krupp, Germany.

The targets were bombarded with a 3 keV monoenergetic D^+ ion beam perpendicular to the surface at the garching high current ion source. Applying a bias voltage at the target the ions could be decelerated down to 10 eV without excessive decrease of the ion current density of $5 * 10^{15}$ D/cm^{2}s. The surface concentration was measured in situ using a four grid retarding field Auger spectrometer

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mounted in front of the sample with a grounded entrance tube for the ions in the middle of the spherical grids. The analyzing primary electron beam impinged at an angle of 17° to the target surface plain. The target could be heated ohmically from room temperature up to 1000 K; a more detailed description of the experimental setup can be found in [4]. Quantitative calculation of the surface concentration was done by normalizing the Auger signal heights to signals of pure elemental samples. The Auger fine structures of the carbon signal were qualitatively compared with the signals of pure carbon and TiC. Total erosion yields were determined from the weight changes measured in-situ using a microbalance with sensitivity of ± 1 μg.

3. Results and discussion

The samples were bombarded at room temperature and the surface composition recorded in off beam time intervals. After equilibrium concentration was reached, the target temperature was switched and the samples further bombarded. The steady state Ti surface concentration developed during bombardment of LT10 and TiC with ion energies between 20 and 500 eV are plotted versus temperature in Fig. 1 [5] and Fig. 2. The surface changes of both samples are similar. At room temperature and low ion energies high Ti concentrations developed decreasing to

Fig. 2. The surface concentration of TiC versus temperature is similar to concentrations of LT10. At elevated temperatures the concentration equals the bulk concentration.
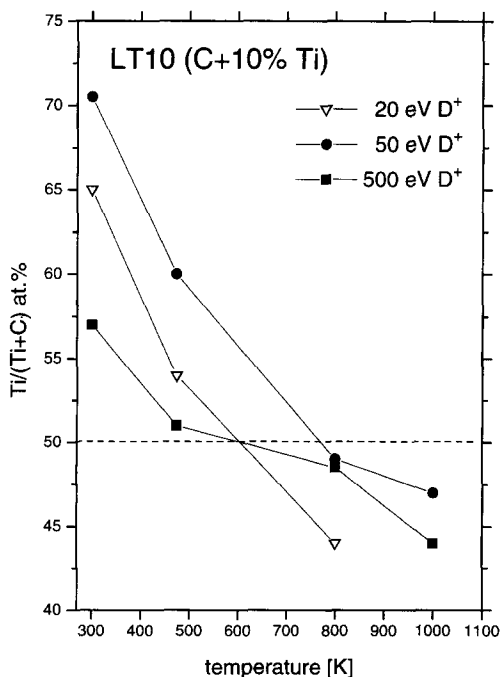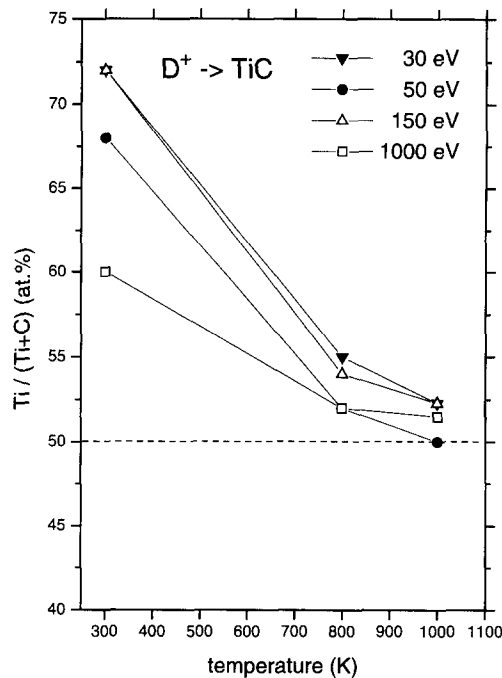

Fig. 1. Surface concentration of LT10 versus temperature during different ion energies. The Ti concentration is up to 7 times of the bulk. At high temperature the concentration approaches values of stoichiometric TiC [5].

about 50 at% at elevated temperatures. Furthermore, the Ti concentration at room temperature increased with decreasing ion energy due to preferential chemical sputtering of C, while physical sputtering of the heavier Ti atoms decreased to a threshold energy of 50 eV [6]. The temperature dependent surface changes involved solid state chemistry as well as diffusion processes. Diffusion of C from the bulk to the surface must be responsible for the reduction of the high Ti concentration at room temperature to around 50 at% above 800 K. In spite of the high C surface concentrations at elevated temperatures, weight loss measurements did not show an enhanced erosion due to chemical sputtering (Figs. 4 and 5) indicating that annealing and bond formation takes place. Recently, XPS-experiments with Ti films evaporated onto a graphite substrate showed formation of carbidic TiC_2 and TiC after annealing the sample above 450 K [7]; the carbon had diffused from the bulk into the film. These observations are in accordance with our results on LT10 and TiC.

Information about the chemical state of carbon can be obtained from the fine structure of the carbon Auger signal. In Fig. 3(b) the line shape of carbon in graphite as well as carbidic carbon, bound with Ti-atoms, is shown. No chemical shift between the TiC- and graphite-carbon signal is found, but differences in the line shape are easily seen between 230 and 270 eV. The maximum around 265 eV is due to bonds between C and Ti and not present in pure graphite having a maximum around 230 eV. Fig. 3(b)
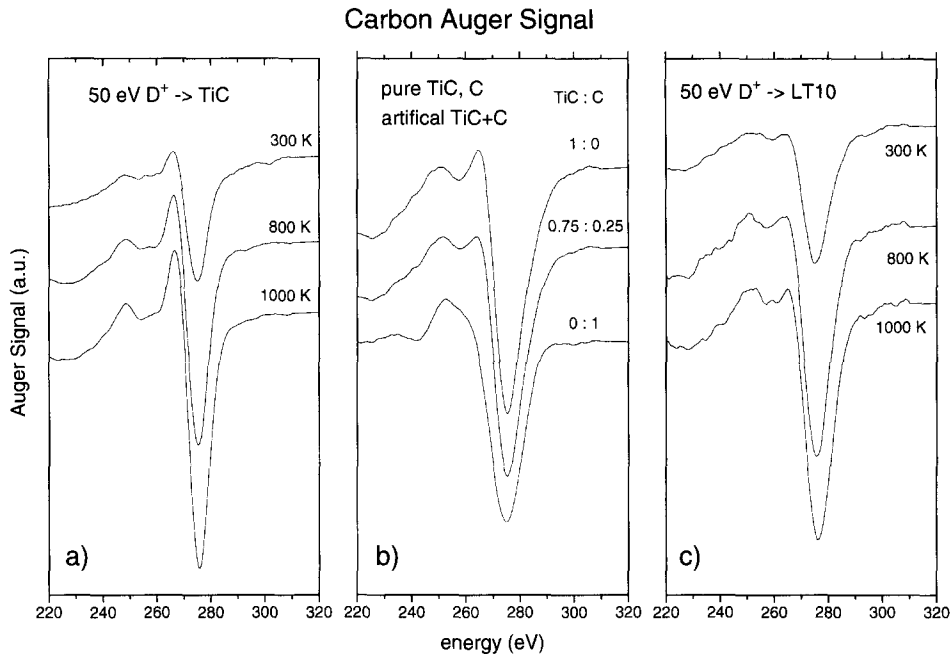
Carbon Auger Signal

Fig. 3. The carbon Auger signal of TiC (left), pure TiC together with graphite and a superposition of TiC and graphite (middle), and LT10 (right).

includes also an artificial carbon signal produced by super-position of 0.75 times the carbon signal of TiC and of 0.25 times the signal of graphite [5]. In Fig. 3(a) and (c) a qualitative comparison between the carbon signal of TiC and LT10, respectively, during 50 eV D^+ bombardment at different temperatures are presented.

For LT10, Fig. 3(c), at temperatures above 500 K the line shapes exhibit mixed carbidic and graphitic structures. They can best be fitted by the artificial Auger signal of Fig. 3(b). However, at room temperature the carbon signal for LT 10 shows a broad graphitic part between 240 and 260 eV and a small carbidic part around 265 eV. The construction of the measured signal out of pure graphite and TiC in the same way as for signals above 500 K is not possible. Presumably a phase mixture of graphite, carbide and broken bonds between C atoms itself as well as between Ti and C is building up the surface, while at elevated temperatures annealing takes place resulting in phase formation exhibiting TiC-like as well as graphitic compositions. Contrary to LT10 are the results for pure TiC, plotted in Fig. 3(a). At room temperature only the peak-to-peak signal height of carbidic carbon is reduced while the typical TiC fine structure between 230 and 270 eV is only weakly affected indicating that C atoms on the surface are almost entirely bound with Ti. Because there are more Ti- than C-atoms at the surface, at least two phases have to be formed, a TiC and a Ti phase. Enhancing the temperature, the phases change to a TiC composition, as seen by the growing carbon signal intensities at 800 and 1000 K, approaching carbidic values.

The phase formations may affect the erosion yield: For pure TiC no enhanced erosion due to chemical sputtering occurs, only physical erosion takes place. The results of our sputtering yield measurements are plotted in Figs. 4 and 5. In both figures the solid lines represent values for graphite and are calculated from a theoretical model fitted to experimental data [8], while for TiC and LT10 respectively, the experimental values are plotted. In Fig. 4 the
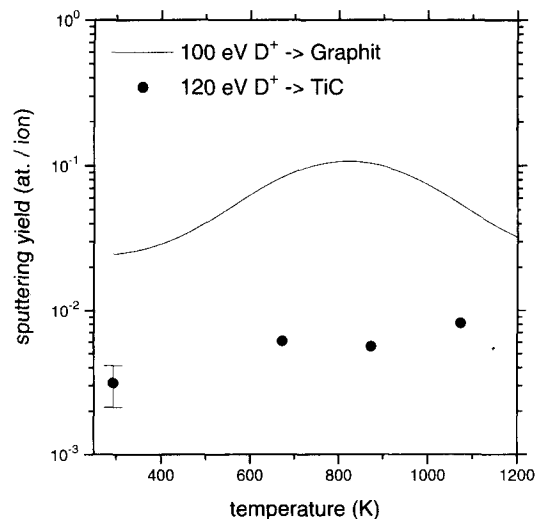

Fig. 4. Sputtering yield of TiC versus temperature compared with pure graphite.
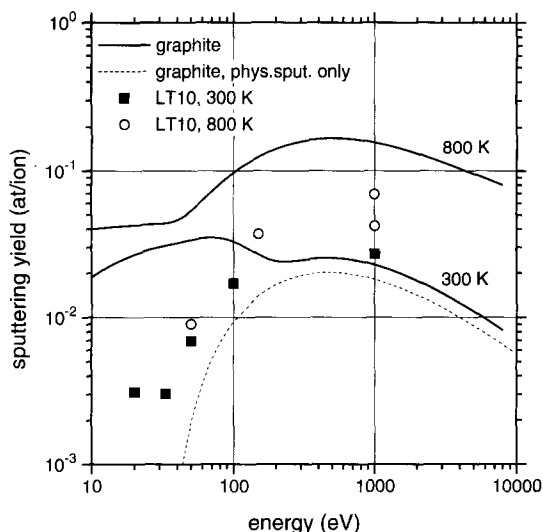
Fig. 5. Sputtering yield of LT10 versus energy compared with pure graphite at room temperature and 800 K.

erosion dependence of TiC versus temperature during 120 eV D^+ bombardment is shown. It is one magnitude order smaller than for pure graphite and only weak dependent on temperature. Especially around 800 K where maximum chemical erosion of graphite takes place, the sputtering yield of TiC is more than a factor 10 reduced. The slight increase of the sputtering yield of TiC with increasing temperature may be due to chemically enhanced physical sputtering, i.e. kinetic ejection of only weakly bound surface hydrocarbon complexes by momentum transfer. In Fig. 5 the sputtering yield of LT10 versus ion energy is compared with pure graphite at room temperature and 800 K. Graphite has no threshold energy due to chemically enhanced sputtering even at room temperature, while LT10 approaches the physical sputtering of graphite indicated by the dashed line [6]. At 800 K the erosion of LT10 did not change significantly compared with the erosion at room temperature. The small differences may be due to chemically enhanced physical sputtering as observed too for TiC.

The sputtering behavior can be explained in view of surface changes, i.e. postulating a relation between surface composition and erosion yield: At low ion energy and room temperature a Ti rich surface prevents chemical

erosion of carbon. Enhancing the temperature, C segregates to the surface forming carbidic bonds inhibiting the formation of precursors of hydrocarbon molecules — the erosion becomes almost independent from temperature.

4. Conclusion

The erosion of LT10 and TiC at low ion energy was found to be independent from temperature. Both materials show a threshold energy for sputtering and the sputtering yield is one magnitude order smaller than for pure graphite. In contrast to the erosion yield, the surface compositions of LTI0 and TiC are strongly dependent on target temperature during low energy D^+ bombardment. Both samples develop high Ti concentrations at room temperature and concentrations similar to stoichiometric TiC at elevated temperatures. At room temperature, C is preferentially eroded leaving a Ti rich surface protecting the underlying bulk from further chemical erosion. By increasing the temperature, C segregates from the bulk to the surface and forms TiC like bonds which shelters the C from further chemical erosion.

Exploring the complicated solid state reactions and understanding the influence of the bulk composition and structure on the erosion mechanisms at the surface may lead to designing of new materials having good thermomechanical properties of the bulk and a favorable surface composition in view of erosion behavior.

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