LUBRICATING PERFORMANCES OF THIN LAYERS FILMS OF SILICON CARBIDE DERIVED CARBON

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Introduction

Since a decade, a new way to produce new nanoporous carbons is to use chlorination on carbide in order to etch metallic atoms and to leave the carbon matrix [1,2]. Gaseous chlorine reacts with metallic atoms at high temperature (600 – 900°C) to form most of the time gaseous chloride which is easily removed and carbon called carbide derived carbon (CDC). Many studies have been devoted to the chlorination of silicon carbide because of the multiplicity of carbon structures found after chlorination : from amorphous carbon to carbon onions and diamond [3]. However, in order to thermodynamically favor the formation of $SiCl_4$ rather than CCl_4, a chlorination temperature of about 900°C is required [4]. Another way of halogenation can be studied in order to decrease the synthesis temperature: fluorination [5]. In the same way than chlorination, fluorination of silicon carbide can form a gaseous silicon fluoride which should easily be extracted from the carbon structure. So direct fluorination using F_2 gas and fluorination by XeF_2 have been processed on silicon carbide thin films in order to partially convert the silicon carbide into carbon. The conversion mechanism has been studied by Rutterford Back Scattering (RBS) combined with Scanning Electron Microscopy and Raman spectroscopy. Finally, the tribological properties of the bimodal thin films have been evaluated.

Experimental Methods

SiC thin films were deposited by sputtering on vitreous carbon for RBS purpose. The composition of the thin films has been confirmed by RBS and its thickness determined both by sputtering rate and Scanning Electron Microscopy (SEM) is 300 nm.
Two fluorination ways were used: fluorination under 1 atm of pure fluorine gas stream and fluorination by the decomposition of XeF_2 fluorinating agent in a closed reactor.
The layer composition was investigated by RBS using 2 MeV alpha particles and 15 nA current intensity ; a charge of 10 µC was collected at 165° detection angle. SEM Micrographs were recorded using a Cambridge Scan 360 SEM operating at 1 kV.

The friction properties of the compounds were determined using a ball-on-plane tribometer under a normal load of 10N and a sliding speed of about 2 $mm.s^{-1}$. The friction coefficients were measured with a computer-based data acquisition system at the beginning of the test (three cycles) to evaluate the intrinsic lubrication properties of the fluorinated phases and after 30 cycles to underline the influence of eventual structural transformations induced by the friction process.

Results and Discussion

In order to favour both the formation of carbon and the total decomposition of silicon carbide, excess of fluorine have been set in the synthesis reactor as well as for fluorination by F_2 or XeF_2.

Table 1. Fluorination conditions.

	Fluorination temperature (°C)	Fluorination duration	Molar ratio SiC/F_2
SiC-F2-1	130	120s	1/200
SiC-F2-2	130	300s	1/80
SiC-F2-3	30	120s	1/200
SiC-XeF2-1	120	70h	1/10
SiC-XeF2-2	120	70h	1/50
SiC-XeF2-3	120	20h	1/50

Table 2. Molar composition determined by RBS spectroscopy method.

	Si	C	F	Ni	N	O
SiC-F2-1	7.0	40.4	35.3	7.0	3.0	7.0
SiC-F2-2	3.0	53.4	32.2	5.0	3.0	3.0
SiC-F2-3	3.0	25.7	50.0	9.0	3.0	9.0
SiC-XeF2-1	35.9	55.0	3.0	0	3.0	3.0
SiC-XeF2-2	0	86.0	7.0	0	2.0	5.0
SiC-XeF2-3	0	33.65	42.0	0	4.0	8.0

Whatever the fluorination conditions under F_2 fluorine gas, silicon is etched from the silicon carbide in order to form gaseous silicon tetrafluoride and carbon. The level of fluorine is high for all of the samples. Fluorine is either trapped as gaseous molecular into the amorphous porous carbon or covalently bonded with carbon dangling bonds and forms CF_2 and CF_3 groups.

For fluorination using the decomposition of XeF_2, a molar ratio SiC/F_2 1/10 is too low to totally extract all the silicon atoms from the carbide. But this result shows that, thanks to this fluorination method, partial etching is possible and a SiC/CDC composite can be made. For higher molar ratio, silicon is totally etched and higher carbon level is obtained for longer fluorination time because of outgassing of fluorine gas. Only a few carbon-fluorine bonds are formed contrary to fluorination with fluorine gas. It can be explained by the different reactive media between the two fluorination methods. Excess of pure fluorine gas is more effective than a defined amount of atomic fluorine formed during XeF_2 decomposition. Only by fluorination with XeF_2 a porous carbon surface has been successfully obtained on the non converted silicon carbide thin films (Figure 1). The porous columns are about 20 nm in diameter and have allowed the diffusion of both fluorine and silicon fluoride formed during the reaction.

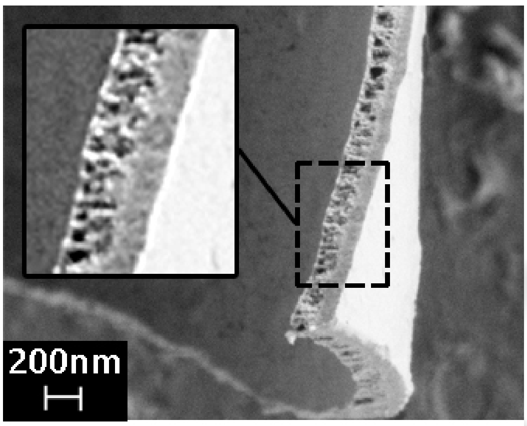

Fig. 1 SEM images of SiC carbide after fluorination with XeF_2.

Tribological measurements have been made on the SiC thin films partially or totally converted by XeF_2. The friction coefficient of raw SiC thin film is high for the first mechanical cycles, then it decreases and finally it keeps on increasing with the cycle number (Fig. 2). The carbon layer formed from the SiC thin film prevents form such evolution. A stable and low friction coefficient is obtained whatever the fluorination conditions under XeF_2. So such treatment of SiC thin films results in a thin layer of carbon which compensates the low tribological properties of SiC. Moreover such carbon is more adhesive than the classical carbon coating made on SiC pieces by CVD or PECVD; these advanced materials are used in aerospace or in mechanics.

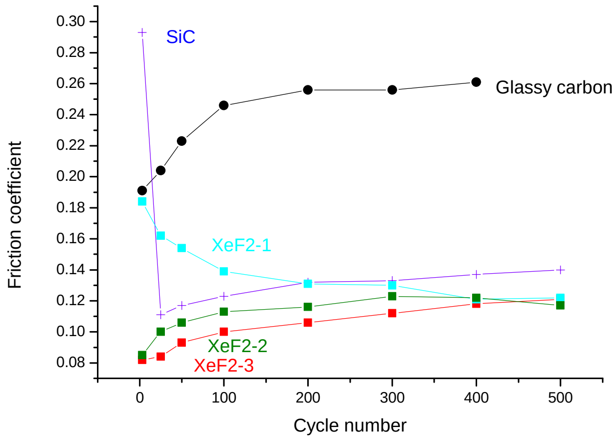

Fig. 2 Friction coefficient evolution with the number of cycles of SiC thin films before and after fluorination with XeF_2

Conclusions

Original SiC/CDC bilayer thin films, which consist in layer of ex-SiC carbon on SiC layer, have been prepared by fluorination using XeF_2. Atomic fluorine preferentially reacts with metal atoms and etches then away. Moreover, the release of SiF_4 allows a progressive cleaning of the thin films surface and this volatile fluoride is easily removed from the surface. The carbon left behind on the surface of SiC rearrange themselves to form a truly nanostructured carbon film composed of nanocrystallite of graphite. So, fluorination can be used to synthesize carbon film on carbide surface at lower temperatures than the chlorination way in order to enhance the surface properties of industrial materials for great potential technological rewards [6]. An example is given in this work : the unique microstructure of CDC thin films obtained by fluorination method is very attractive for tribological properties.

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