

Ceramic coatings by ion irradiation of polycarbosilanes and polysiloxanes

Part II *Hardness and thermochemical stability*

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The hardnesses of polycarbosilane and polysiloxane coatings subjected to irradiation with increasing doses of He, C and Au ions were measured by means of nanoindentation tests. Diamond-like carbon clusters which are formed during irradiation enhance the hardnesses of the ceramic films which reach in some cases three times that of conventionally annealed specimens. When submitting irradiated films to an additional anneal, the clusters resulting from the segregation of atoms from methyl groups remain more diamond like than those formed directly by radiolysis of phenyl rings, especially when the radiolytic transformation is incomplete (the film having received a low irradiation dose). Moreover, owing to the selective release of hydrogen and the recombination of free radicals at room temperature, no evolution of CH_x and CO_x nor oxidation of unpaired Si atoms occurs during this post-irradiation anneal, contrary to the observations during direct thermal conversion.

1. Introduction

In Part I of this study [1] it was shown that ion irradiation of polycarbosilane and polysiloxane films converts them into amorphous ceramic SiC or SiOC coatings containing clusters of free carbon with a more or less diamond-like hybridization state. The kinetics of radiolytical evolution of hydrogen and the combination probability of residual radicals depend on the energy per nucleon of ions, so that films bombarded with light ions are less stable with respect to atmospheric oxygen at room temperature. Therefore, it was interesting to investigate the resistance of irradiated films to oxidation at high temperatures and to the evolution of silanes and methane, in comparison with pristine films directly converted with a thermal treatment. Moreover, if the idea of annealing films after irradiation seems to contradict the preliminary goal of using it as a process alternative to heat treatment, it could be of practical interest in some applications where insulating films with a high hardness and an ability to withstand high working temperatures are needed.

Hardness, a property highly sensitive to structural transformations especially in ion-irradiated polymers [2, 3], was measured by means of one of the nanoindentation tests developed in the past few years [4].

These tests allowed us to correlate hardness values to changes in structure, and more especially to the hybridization state of carbon in clusters produced by irradiation.

2. Experimental procedure

Films were prepared from polycarbosilanes and polysiloxanes pre-ceramic polymers and irradiated as described in Part I of this study [1]. SiOC coatings were obtained from SR350, SR355 silicone resins and PTES alkoxide solution, while SiC coatings were produced by polycarbosilanes PCS and AHPCS precursors. Some pristine and some irradiated samples were annealed for 1 h at 1000 °C under a vacuum of 10⁻⁶ Torr. Changes in composition and structure due to the annealing were analysed with the same analytical techniques already described [1]. The following abbreviations will be used hereafter for the treatments: I, irradiation; A, annealing; IA irradiation and then annealing.

Depth-sensing indentation tests with a resolution of 50 nm were performed using a soft machine in conditions similar to those described in [3]. The indenter shape is noteworthy with respect to that of most published experiments of this type. As shown by

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slip-line field calculations [5] and confirmed by tests on standard films [6], using a trigonal diamond with an apex angle of 35° enables us to perform measurements with a much better depth resolution than with the Berkovitch indenter preferred by other workers simply because its angle (65°) and ratio, k , of contact area to square of depth are nearly the same as for the Vickers indenter used in tests on a micrometre scale (allowing easier comparisons). After establishing the contact under zero load, the load, L , is increased continuously at a rate depending on the range of L useful for penetrating through the studied film (for collecting a comparable number of data points, of the order of 500) and then decreased at the same rate. The penetration depth, D_t , of the diamond tip is measured simultaneously and the ratio, L/kD_t^2 (where k is the geometrical constant mentioned above), would give directly the mean hardness, H_a , on the tested range of depths if the material was fully plastic, and if the diamond tip exhibited a perfect shape (constant k). D_t must first be corrected for the elastic contribution, D_e , which is recovered during unloading. Since this contribution is measured only for a given size of plasticized volume (that corresponding to the maximum, L_{\max} , of each test), one must increment this maximum value in a series of 10–15 tests on different areas, in order to interpolate a continuous $D_e(L)$ curve to subtract from averaged $D_t(L)$ curves to obtain the useful $D_p(L)$ curve of plastic deformation. Note that unloading curves are generally linear over a noticeable range of depth (more than two thirds) and then exhibit a curvature due to the recovery in the angle of indents. One draws the initial tangent to the curve to measure the intercept, D_e , with the load axis (as proposed in the Loubet *et al.* [7] model) and calculating a recovery parameter, $R = D_e(L_{\max})/D_p(L_{\max}) = (D_t - D_p)/D_p = H_a(1 - \eta^2)(k\pi)^{1/2}/2E$, where η is Poisson's ratio and E is the biaxial elastic modulus. Theoretically, the slope of the unloading curve gives the elastic compliance, $1/E$, and the ratio, $R = H_a(1 - \eta)^2/E$, of the material. However, both the slope and R are affected by the compliance of the experimental set-up and frictional forces (reversible and varying with the same power law of D_t as the elastic resistance); the latter forces induce an artefactual increase in H_a measured conventionally by Vickers tests [8], but not in nanoin-

dentation tests since they appear as an additional elastic resistance. Paradoxical procedures, implying that the modulus is known at least over some range of depths, have been proposed to correct the data for the frame compliance [9, 10] but not for the friction, which is particularly noticeable in the case of C-containing ceramics. Therefore the fact that R for the films currently studied increased progressively from 5% to $40 \pm 5\%$ after conversion will just be mentioned here. On the other hand, changes in the geometrical factor k with depth induced by tip imperfections are unavoidable at the scale of measurements. All authors agree that a correction factor $k(D_p)$ calibrated on some standard specimen such as a Si wafer should be applied [9, 10]. Our guiding principle is to take a new diamond tip each time that this $k(D_p)$ becomes higher than twice the theoretical value k_{th} at depths smaller than 100 nm and differs by more than 5% at larger depths, because the tip was damaged in the course of an experiment (one principal cause being the cracking of the indented film). Finally, two hardness $H_a(D_p)$ curves are extracted from $D_p(L)$ variations: an integrated hardness, $H_{ai} = L/k(D_p)D_p^2$, neglecting gradients, and a derivative hardness $H_{ad} = \delta L/k(D_p) \delta D_p^2$ which *a priori* is more meaningful but tends to show more statistical fluctuations. Generally they are the same within 5% until penetration of 90% of the film thickness, t , with the indenter used (while the substrate contributes to the measured hardness when the indented depth exceeds 20% of t , as proposed by Bückle [11], with Berkovitch indenters). The measurement is considered to be reliable if H_{ai} and H_{ad} are not very different, especially in the outer 100 nm where they may be affected by an uncertainty in the depth.

3. Results

3.1. Compositional and structural changes during annealing

$Si_1C_xO_yH_z$ stoichiometry changes are summarized in Tables I and II. As already stated in Part I of this study, while no loss of C is observed during I treatments of all the studied polymers, a noticeable loss occurs during A treatments of pristine films, increasing from about 40% of C atoms in PTES, SR355 and SR350 to 60% in PCS, evolved as methylsilanes, CH_4 ,

TABLE I Changes, Δx , ($= \Delta x_{IA} - x_i$), Δy and Δz , in concentration after annealing: polysiloxanes (Note that, while negative values of Δx and Δz always account for the evolution of film atoms, negative Δy often mean that the excess O introduced by oxidation of free radicals post-irradiation was released and the original stoichiometry restored)

Ion	Dose $\times 10^{15}$	SR350				SR355				PTES			
		Δx	Δy	Δz	z	Δx	Δy	Δz	z	Δx	Δy	Δz	z
	0	-0.40	-0.22	-2.40	0.52	-1.70	-0.13	-3.85	0.40	-2.50	+0.20	-4.50	1.50
He	0.1	-0.23	-0.30			-1.05	+0.33			-2.00	+0.16		
He	1	-0.13	-0.15	-1.09	0.08	-0.50	-0.26			-1.25	-0.37		
He	5	-0.03	-0.08			-0.25	-0.01	-1.90	0.34	-0.70	-0.36		
He	10	0.00	-0.05	-0.35	0.01	-0.20	0.00	-1.45	0.54	-0.55	-0.07		
He	50	0.00	-0.05	-0.28	0.01	0.00	+0.02	-0.90	0.30	-0.40	0.00	-0.63	0.73
C	10	0.00	0.00	-0.34	0.02	0.00	-0.03	-0.90	0.05	-0.11	0.00	-0.83	0.36
Au	0.1	-0.04	+0.10	-0.92	0.02	-0.40	+0.40	-1.65	0.35	-0.56	+0.20	-2.55	0.75
Au	1	-0.02	-0.05	-0.53	0.02	-0.05	-0.06	-1.00	0.15	-0.13	-0.05	-1.42	0.085

TABLE II Changes, Δx , ($= \Delta x_{IA} - x_1$), Δy and Δz , in concentration after annealing: polycarbosilanes (Note that, while negative values of Δx and Δz always account for the evolution of film atoms, negative Δy often mean that the excess O introduced by oxidation of free radicals post-irradiation was released and the original stoichiometry restored)

Ion	Dose $\times 10^{15}$	PCS				HPCS			
		Δx	Δy	Δz	z	Δx	Δy	Δz	z
	0	-1.20	+0.20	-4.25	0.25				
He	1	-0.50	+0.35						
He	50	0.00	-0.09	-0.80	0.20				
C	0.1	-0.45	+0.32						
C	0.5	-0.09	+0.12						
C	1	-0.05	0.00	-0.90	0.21				
C	5	-0.02	-0.02	-0.54	0.06	-0.05	+0.10	-0.60	0.04
Au	0.01	-0.54	+0.10	-2.50	0.50	-0.03	+0.21		
Au	1	-0.10	-0.01	-0.58	0.04	0.00	+0.08	-0.44	0.02

C_2H_6 and CO_x . Si atoms with dangling bonds oxidize but some oxygen is also released as CO in polysiloxanes, and local spallings occur so that the areal amount of O atoms decreases during A treatments (apart for polycarbosilanes). It is often difficult to determine accurately the composition and thickness of A films, the analysis by means of several techniques of exactly the same area of a given specimen, free of cracks and defects, being nearly impossible. However, polymeric coatings submitted to "slight" irradiation converting them only very partially into ceramics do not flake off during subsequent annealing and the areal amount of oxygen (in these IA films) generally increases with respect to that after the I treatment. Note, however, that it may decrease if they reacted with atmospheric oxygen and water just after the irradiation (especially those irradiated with He ions), and thus the oxygen stoichiometry changes in Tables I and II are sometimes negative. The annealing of films already converted as much as possible by C or Au ion irradiation yields a nearly total release of the remaining H (residual H content $z \approx 0.01-0.03$), without any loss of C or oxidation, even of PCS (according to the O areal density of about $\sim 2 \times 10^{16} \text{ cm}^{-2}$, which is a more critical parameter than the stoichiometry reported in Tables I and II.

On the basis only of the O, C and H contents after annealing, films heavily irradiated with He ions seem less converted than those having received the same amount of energy by C or Au ions. For instance, PCS films retain more oxygen and PTES coatings still evolve some carbon. The comparison of ion mass effects is, however, a little more complicated because the resistance to oxidation or C evolution also depends on the initial structure. SR350 specimens are already fully stabilized after irradiation with 5×10^{15} He ions, 10^{15} C ions or 10^{14} Au ions, PCS specimens with 5×10^{15} He ions, $5 \times 10^{14}-1 \times 10^{15}$ C ions or $(1-2) \times 10^{15}$ Au ions, while the critical doses are 2.5×10^{16} He ions, 10^{16} C ions or 10^{15} Au ions for SR355 and still a little higher for PTES samples. Hardness changes give further evidence of the less complete conversion induced by He ion irradiation, despite a degree of compaction and H release at high fluences similar to that produced by the other ions.

The density of PCS irradiated with high C ion doses and annealed was overestimated in a previous paper [12]. In fact, annealing of irradiated PCS films leads to a density increase from 65 to $75 \pm 5\%$ of that of bulk SiC, remaining a little smaller than that afforded by A treatments ($79 \pm 5\%$). One must keep in mind that this density value reflects only the retention of C atoms (decreasing the mean mass with respect to stoichiometric SiC) and not a lower degree of compaction. Ion irradiation treatments provide SR350 films with relative densities of $83 \pm 2\%$ with respect to the reference value of 2.35, increasing to 100% after subsequent annealing at 1000°C as against 76% for A films. The densities of SR355 and PTES films which are the most converted by irradiation do not increase after subsequent annealing (74%).

The proportion of sp^2 hybridization of C atoms in IA films (including AHPCS) increases with respect to that in the same specimen before annealing but remains lower than in A films of the same polymer according to the degree of splitting in the two components D and G of the Raman carbon peak (Fig. 1). This proportion is a little larger in SiOC films formed from phenyl-containing polymers.

Investigations of the structure by means of glancing-angle X-ray diffraction showed that all irradiated films are amorphous, and that annealing treatments resulted in a partial crystallization of β -SiC only in A-PCS (average size of crystallites, 2.0 nm), IA-PCS (2.5 nm), and A-PTES (4.5 nm). However, more significant differences in the crystallization behaviour linked to the retention of C and to the formation of clusters need to be investigated in the future.

3.2. Hardness

Some indentation curves recorded from a few specimens of the SR355 polysiloxane irradiated with He or C ions are displayed in Fig. 2. The part of the curves relative to the loading stage of tests (starting at the origin) is the average of 10-15 measurements. Only one or two individual unloading curves from each specimen are plotted for clarity, and no curves relative to an unirradiated film are reported because the necessary load for penetrating $1 \mu\text{m}$ was about 0.5 mN. The decreasing slope of the loading curves

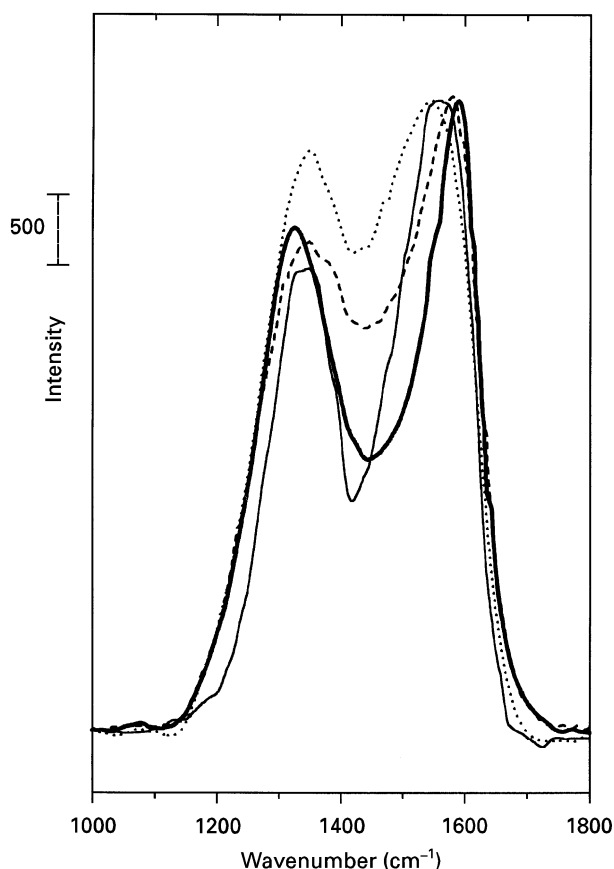


Figure 1 Raman spectra of SR350 films (—, A; (·····), IA) and PTES films (—, A; (-----), IA) irradiated with 1×10^6 C ions.

in Fig. 2a accounts for the progressive hardening with the He ion irradiation dose. In many tests on A specimens or IA specimens partially converted by a slight irradiation before annealing, an abrupt increase was observed during the loading stage when the indenter tip reached the film substrate interface, as shown by one of the loading curves relative to the A film in Fig. 2b. This discontinuity is characteristic of an adhesion failure when occurring at a reproducible depth (otherwise it could be ascribed to a vibration) [2]. The other curves displayed in Fig. 2b give evidence of the fact that irradiated films harden or on the contrary soften, according to their degree of irradiation-induced conversion, after annealing.

There are many common trends between the variation in the hardness, H_a , as a function of $S_e\Phi$ and those of Δt or ΔH reported in Part I, but the hardening is not proportional to the logarithm of $S_e\Phi$. It increases generally more steeply and along curves depending on the ion mass and on the C content of the polymer (Fig. 3). The saturation of the hardening above a critical amount of energy is especially clear in the case of Au ion irradiations because this critical value decreases with increasing mass of ions. For any $S_e\Phi$ values, the hardness of He irradiated polysiloxanes decreases with increasing C content and, on the contrary, that of Au irradiated films increases a little. The hardnesses of C irradiated films are more comparable.

The differences between the hardening kinetics of PTES and SR355 films submitted to similar irradiations are well correlated to those of compaction.

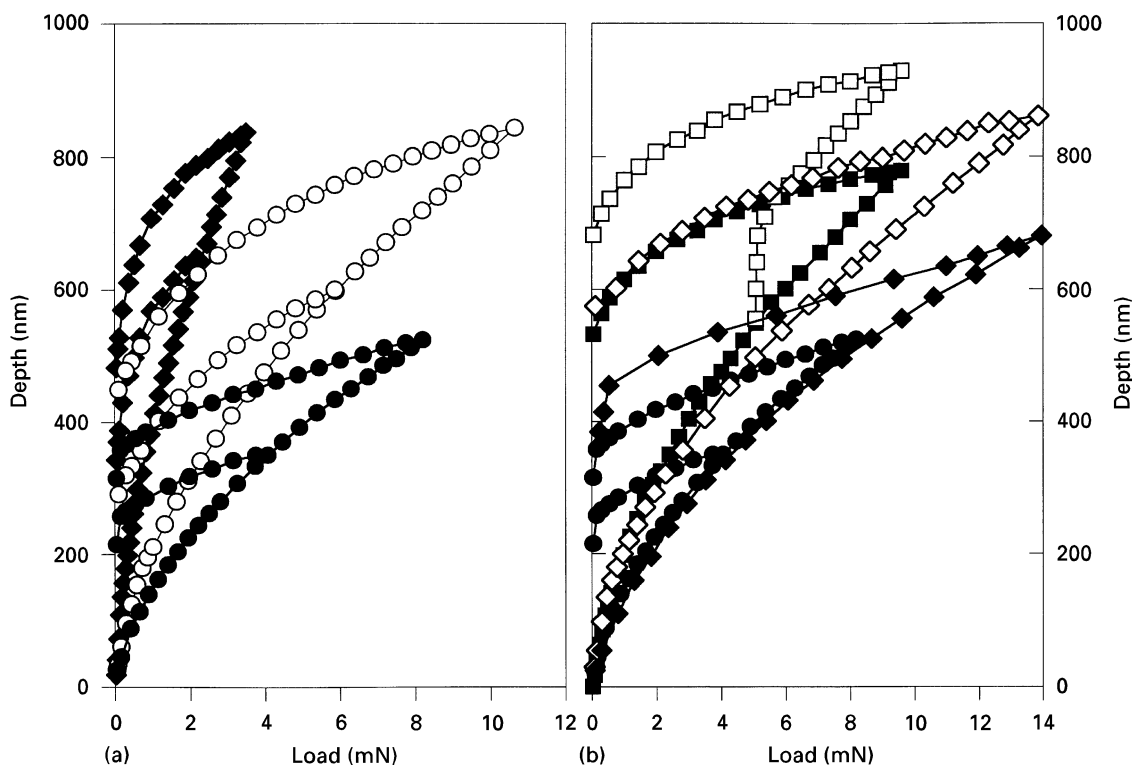
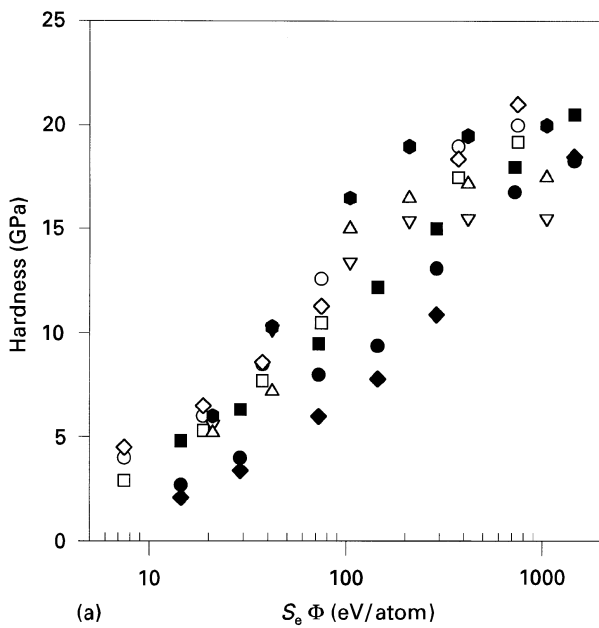
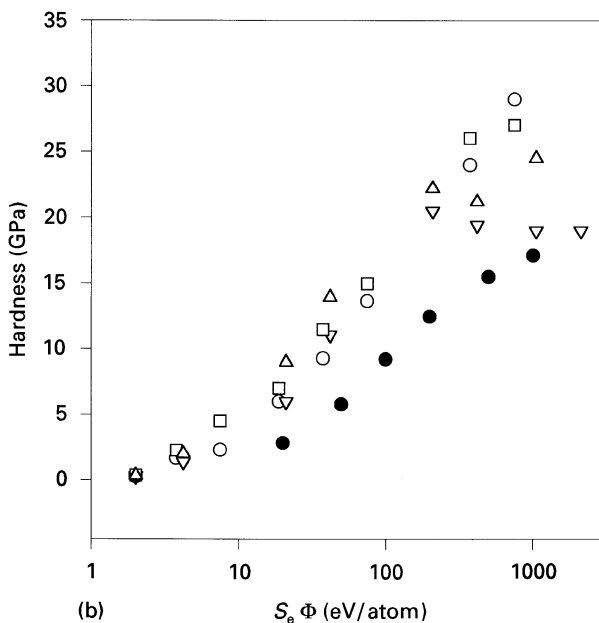


Figure 2 (a) Indentation tests in I films of SR355 irradiated with He ions at the following doses. (\blacklozenge), 5×10^{14} ; (\circ), 5×10^{15} ; (\bullet), 5×10^{16} . (b) Indentation tests in SR355 films irradiated with C or He ions, in the I and IA states. (\blacklozenge), 1×10^{16} C, I and IA (\diamond), 5×10^{16} He, IA; (\bullet), 5×10^{16} He, I; (\blacksquare), (\square), A. For the latter, two different curves are displayed for depths over 600 nm, of which one (\square) shows film cracking.



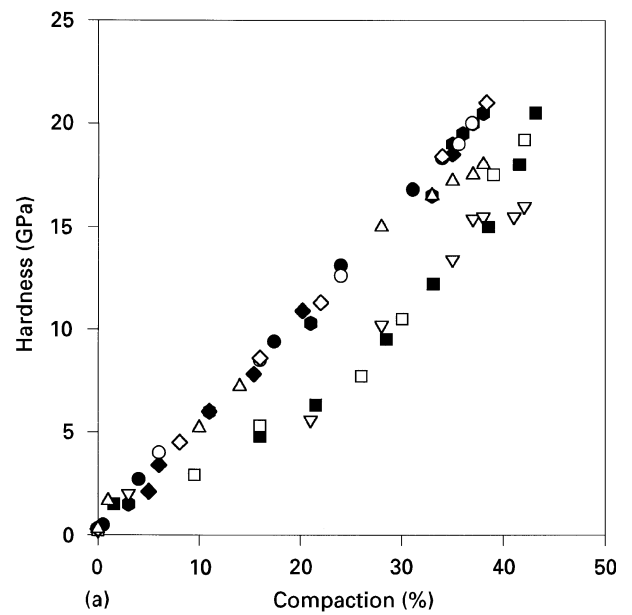
(a) $S_e \Phi$ (eV/atom)



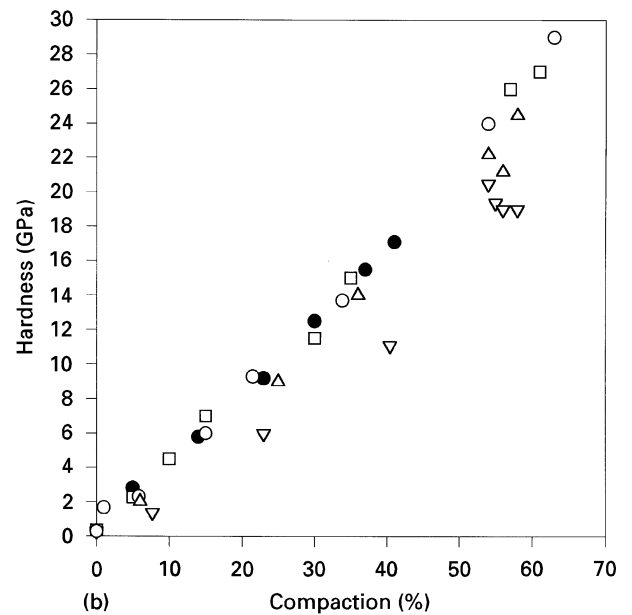
(b) $S_e \Phi$ (eV/atom)

Figure 3 (a) Hardness variation for polysiloxanes as a function of $S_e \Phi$ for irradiation with various ions (●), SR355, He; (■), SR350, He; (◆), PTES, He; (○), SR355, C; (□), SR350, C; (◇), PTES, C; (△), SR355, Au; (▽), SR350, Au; (●), PTES, Au. (b) Hardness variation for polycarbosilanes as a function of $S_e \Phi$ for irradiation with various ions (○), PCS, C; (□), AHPCS, C; (▽), PCS, Au; (△), AHPCS, Au; (●), PCS, He.

Indeed, when plotting their hardness as a function of the compaction (Fig. 4a) the same linear dependence is found whatever the ion species. The hardening behaviour of SR350 films is completely different. While both yields of compaction and hardening versus $S_e \Phi$ increase distinctly faster than those of the other polysiloxanes containing phenyl groups, at least when bombarded with He ions, its hardness increases more slowly as a function of the compaction. In fact, the slope of the $H_a(\Delta t)$ curves increases progressively so that H_a values reached at saturation of the compaction by He or C irradiation are comparable with those of other polysiloxanes. The hardening kinetics of PCS versus the deposited energy are very



(a) Compaction (%)



(b) Compaction (%)

Figure 4 (a) Hardness variation for polysiloxanes as a function of the compaction. The same symbols as in Fig. 3a are used. (b) Hardness variation for polycarbosilanes as a function of the compaction. The same symbols as in Fig. 3b are used.

comparable when irradiated with C or Au ions and slower with He ions. As for polysiloxanes, a relative softening is observed at high Au fluences with respect to C irradiation, i.e., the hardness levels off while that of films irradiated with lighter species still increases (and He irradiated specimens become nearly as hard). The variations in H_a with Δt reported in Fig. 4b also show that, contrary to polysiloxanes, atomic displacements induced by Au ions have a strong effect on the hardness even at low fluences. Astonishingly, the hardness of AHPCS films is less affected by these displacements, and it would be interesting to investigate whether the hardening kinetics of this polymer by He irradiation is also similar.

If the hardness of the polysiloxanes increases with increasing C content when irradiated with heavy ions,

TABLE III Comparison of hardnesses as a function of film nature, and of their change after annealing according to their degree of irradiation-induced conversion

Ion	Dose $\times 10^{15}$	Hardness									
		SR350		SR355		PTES		PCS		HFCS	
		I	IA	I	IA	I	IA	I	IA	I	IA
	0	0.23	7.0	0.32	6.8	0.35	8.4 ^a	0.28	19.0	0.35	n.m.
He	1	6.3	18.5	4.0	7.0	3.4	8.0	2.8	14.5	n.m.	n.m.
He	5	12.2	19.0	9.4	8.1	6.8	7.7	9.2		n.m.	n.m.
He	10	17.0	19.0	13.1	9.1	10.9	7.4	12.5	22.0	n.m.	n.m.
He	50	21.0	21.0	18.3	20.3	18.5	12.0	17.1	25.5	n.m.	n.m.
C	1	10.5	19.0	12.6	13.0	11.3	7.5	13.7	33.0	14.5	n.m.
C	10	18.5	21.0	20.5	19.0	21.0	19.5	29.0	36.0	27.0	34.0
Au	0.1	10.3	16.7	7.20	8.5	10.3	7.0	11.1	n.m.	16.0	n.m.
Au	1	15.5	18.5	17.2	19.0	20.5	17.5	19.4	34.6	23.0	33.0

^aActually measured for a He ion dose of 10^{14} because pristine films always spalled during heat treatments
n.m. = not measured.

the reverse is observed after annealing these films (Table III). In fact, the hardness of SR350 specimens irradiated with doses as low as 10^{14} Au ions, 10^{15} C ions or even 10^{15} He ions increases after annealing up to the maximum value measured for I films, and the relative softening due to Au irradiation at high doses vanishes. On the contrary, the hardnesses of SR355 and PTES films decrease all the more as they contain more C and are irradiated with lighter ions. The hardening effect of irradiation is completely suppressed after annealing, with respect to that of annealing a pristine film of these phenyl-containing polymers, when the irradiation dose is less than 10^{14} Au, 10^{15} C or 10^{16} He ions.

4. Discussion

4.1. Thermal stability

In addition to their conversion into amorphous composite ceramics harder than those formed by thermal conversion, the irradiation treatment has two effects: an increase in the adhesion and an increase in the chemical stability during further heat treatments. The former is probably due in a large part to the mixing of atomic layers at the interface. In this respect, Au irradiation is some thousand times more efficient than He irradiation, according to the ratio of nuclear stopping powers. A noticeable improvement is already observed after irradiation with astonishingly low He doses (about 10^{14} – 10^{15}) and films exhibit fewer radial cracks. This radial cracking is caused by firstly the lateral shrinkage under the effect of the thermal conversion and secondly the mismatch of dilatation coefficients while cooling, on which a very partial conversion by irradiation has little effect. Therefore one must rather invoke an effect of keying pre-existent flaws: bubbles, end of chains, etc.

The increase in chemical stability is of a triple nature. First of all, C atoms having already lost some of their H neighbours can no longer evolve as silanes, CO_x or methane (in some respects this retention of C is not necessarily beneficial). The effect is already significant for doses as low as 10^{13} Au,

5×10^{13} C or 10^{15} He. Indeed, polycarbosilanes and the SR350 polysiloxane irradiated at these doses lose half the C that pristine films do, while the degree of conversion before annealing, according to Δt and ΔH values, is about 10%. C atoms are fully stabilized by irradiation with ion doses depending on the nature of the side groups in the polymers. The doses are ten times higher for ceramic films derived from PTES and SR355 precursors containing phenyl groups than from SR350 resin. The PCS films converted into silicon carbide (few experiments being made with AHPCS polymer) exhibit a particular behaviour, since it is stabilized by He or C doses similar to those for SR350-derived oxycarbide coatings, but by a ten times higher Au dose. This finding is probably correlated to the more important effect of the chemical disordering induced by atomic displacements in the case of the carbide material, as also the strong difference in hardness with respect to He or C irradiation. In the case of polysiloxanes, an additional factor of C retention is certainly its precipitation because the probability of reacting with O neighbours of the matrix to evolve as CO_x decreases.

The beneficial character of the two other types of chemical stabilization is more obvious. The second, the improvement in oxidation resistance especially for polycarbosilanes, is linked to the carbon retention. Si atoms become indeed reactive as their bonds with C are broken. The third effect is that C clusters formed during irradiation have less tendency to rearrange into turbostratic C than during direct thermal conversion. Only part of the C:H atoms form buckles of sp^2 defects, as generally observed in most amorphous C coatings when H is released. H is in fact voluntarily added in the atmosphere used for coating processes to increase the diamond-like character of the C films [13]. The transitory transformations in C:H clusters during irradiation of polymers favours a similar behaviour in the course of subsequent annealing. On the contrary, a pile-up of C atoms with a trigonal coordination, closer to the equilibrium state of pure C, is more probable in A films. This graphite-like arrangement is of course also easier in the byproduct of phenyl rings.

4.2. Hardening factors and comparison of hardness values with those of related materials

The hardness exhibits the same dependence on the amount of energy transferred to electrons as the radiolysis and compaction, and at least the hardening kinetics does not appear to be affected by the precipitation of carbon clusters. As long as atomic displacements have less effect than ionizations (He and C irradiation at any dose and Au irradiation until a critical dose) the hardening is in perfect proportion to the compaction. However, when the chemical ordering is affected by these displacements, the bond strength decreases. This explains why high Au irradiation doses cause less hardening of the films than C or He irradiation, and sometimes they even have a softening effect, as observed in some of our samples.

The comparison of the hardness values with those of related materials (obtained with the same indentation test for all values reported hereafter) emphasizes the efficiency of ion irradiation in converting soft polymers into hard ceramics. The hardnesses of as-deposited films are of the same order of magnitude as those of organic polymers. At saturation of the irradiation effect, I or IA treatments afford to polysiloxanes a hardness twice that of pure silica (10 ± 0.5 GPa), regardless of their C content. It is also significantly higher than the hardness of SiOC amorphous films deposited by co-sputtering of silica and carbon, with C-to-SiO₂ ratios in the range 0.1–1, of 16 ± 1 GPa (as well as films as-deposited and after an anneal inducing the precipitation of C [14]). A specimens of SR350 and SR355 (PTES specimens exhibited too many cracks to test) are on the contrary softer than silica and become as hard only when annealed at about 1100 °C, probably because they have lost some C. This low hardness is understandable when the fact that the hardness of turbostratic C (Carbon Lorraine grade) is only 0.9 GPa is taken into account; A films actually contain inclusions of this material. If clusters in I or IA films of the three polysiloxanes exhibited an atomic arrangement close to that in the best films of amorphous diamond (with hardnesses of about 100 GPa [15]), PTES films would be the hardest. However, at their maximum degree of conversion by irradiation with light ions, and also with Au ions after annealing, SR350 films appear as hard as PTES films. They are even harder than IA films of PTES submitted to a similar irradiation when the conversion was not completed by the I treatment. As discussed in Part I of this study, the results of Raman analyses indicate that clusters formed by segregation of C atoms from methyl groups undergo more diamond-like hybridization than those resulting from the amorphization of phenyl rings on the spot. Note that the hardest films of PTES and SR355 are also 1.5 times more elastic than SR350 films (with the same hardness), according to the recovery parameters, $R \propto H/E$, which were measured. This result is understandable since the “composite” material formed during the conversion of phenyl-containing polymers contains more compressible nanoparticles.

When compared with β -SiC (hardness, 40 ± 1 GPa), polycarbosilane films are about 30% softer, but they are only 5–10% softer than amorphous SiC obtained by irradiating a crystal with relatively low ion doses (this amorphization is induced by atomic displacements and not at all by ionizations, but the required amount of energy transferred to atoms is only about 2 eV atom^{-1} , i.e., $10^{15} \text{ cm}^{-2} (\text{C ions})^{-1}$ or $10^{14} \text{ cm}^{-2} (\text{Au ions})^{-1}$ [16]), for which a hardness of 32 ± 2 GPa was measured. This well-known softening of ceramics when amorphized is due for a large part to the distortion of bonds which affects their strength. When additional atomic disorder is produced by high ion doses, the mechanical strength still decreases. This effect helps us to understand the noticeably smaller hardness of PCS films irradiated with Au ions comparatively with films irradiated with light ions. The observed difference is somewhat larger than in polysiloxanes (Fig. 4) because the chemical order is of more importance. In the case of diamond-like carbon films obtained by irradiating organic polymers ($H_a \approx 18$ GPa) it has no importance and similar degrees of compaction and hardening are produced by Au or C irradiations [3, 17].

5. Conclusions

It was shown that even a partial conversion by irradiation protects the precursor against the thermal evolution of C atoms under the form of methane or silanes and against the oxidation of Si atoms with dangling bonds resulting from this evolution. The very good oxidation resistance of irradiated PCS with respect to Nicalon fibres containing up to 15 at% O in pristine and A states (demixing when the annealing temperature is above 1200 °C in SiC crystals surrounded by a C + SiOC layer) is noteworthy. Partial conversion by slight irradiation treatments also greatly increases the resistance to cracking, probably by an effect of keying structural defects such as chain ends and bubbles.

When considering that the main practical interest of polycarbosilane films is their yield of conversion into very hard crystalline SiC, ion irradiation performs less well than heat treatments under ultrahigh vacuum since an excess of C is retained in PCS. However, this retention is detrimental only if the films are annealed at a temperature at which graphite crystallizes. The improvements in cracking and oxidation resistance, and also in the ability to perform the conversion without considering the melting point of the substrate or its reactivity (for instance, the formation of silicides or carbides is highly probable with most metallic substrates) are appreciable compensations. Moreover, the protection against wear afforded to a substrate by a hard film depends as much on its thickness and continuity as on its hardness, and thicker films can be treated by irradiation. Note also that little difference is observed between the hardnesses of PCS and AHPCS, the precursor of stoichiometric SiC films, and both contain clusters of free carbon in the I, IA and A states (for anneals at 1000 °C). Astonishingly, AHPCS seems less affected by atomic displacements than PCS is.

The mechanical properties of SiOC films obtained by irradiation of polysiloxanes are very promising for applications as insulating and hard films since they are twice as hard as silica, and in their case the C retention is beneficial since it controls the hardness. An investigation of their electrical properties is needed but we can already suppose that the segregation of C atoms in diamond-like clusters helps to provide a more insulating character by avoiding the hopping of electrons between C atomic shells or between graphitic clusters in A films. This segregation is also interesting for optical applications because firstly it hampers the closing of the optical gap, and secondly it is a necessary condition of radiative de-excitations which causes photoluminescence in SiOC films.

Acknowledgements

Thanks are due to J. Salomon of the Laboratoire des Musées de France, at Louvres in Paris, and to G. Sagon of LASIR CNRS Center at Thiais near Paris, for their help in NRA and Raman analyses. The authors are also grateful to W. Sherwood of Starfire Systems Inc. (Watervliet, NY) for kindly donating the AHPCS preceramic polymer used in the experiments.

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*Received 25 March
and accepted 29 May 1997*