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Contribution of core-loss fine structures to the characterization of ion irradiation damages in the nanolaminated ceramic Ti_3AlC_2

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Abstract

The effect of low energy ion irradiation in the nanolaminated Ti_3AlC_2 is investigated by means of X-ray diffraction, transmission electron microscopy, electron energy loss and X-ray absorption spectroscopy. The chemical sensitivity and local order probing from core-loss edges provide new insight in the understanding of structural modifications induced under irradiation. From the analysis of the C K energy loss near edge structure (ELNES) and Al K X-ray absorption near edge structure (XANES) by *ab initio* calculations, the influence of the layered structure of this compound on the irradiation damage is demonstrated, with preferentially localized damage in aluminum planes of the structure. On the basis of comparisons between calculations and the experimental spectra, a structural model is proposed for the irradiated state. This study emphasizes the utility of core-loss fine structure analysis to further understanding of ion irradiation induced damage in complex crystalline materials.

Keywords:

1. Introduction

Discovered in Vienna half a century ago by Nowotny *et al.* [1], MAX phases are the subject of increased interest since the work of Barsoum and El-Raghy in 1996 [2]. These

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Figure 1: Ti_3AlC_2 unit cell.

compounds are ternary carbides and nitrides, with chemical formula $\text{M}_{n+1}\text{AX}_n$, where M is an early transition metal, A is a III-A or IV-A group element, X is carbon or nitrogen, and $n = 1$ to 3 [3]. The crystal structure can be described as a stacking sequence of M_6X octahedra layers interleaved with pure A element layers (cf. Fig. 1), which leads to a complex electronic structure involving charge transfers between the three elements [4]. As a consequence, these materials combine the properties of metals and ceramics such as the refractoriness, damage tolerance, thermal shock, oxidation and corrosion resistance, and mechanical properties conserved at high temperatures indicating that they could be of interest when facing extreme environments (high temperature, high pressure, and radiation). Typically, MAX phases properties fulfill the requirements that materials in the core of future fast neutron reactors and gas-cooled reactors (gas fast reactors (GFR)) must reach for fuel cladding [5, 6].

Ion irradiation has turned out to be a very effective tool to simulate the neutron induced damage and to study the stability and the structural evolution of these compounds without specific radioprotection equipment. There are only few studies about the behavior of MAX phases under ion irradiation, almost exclusively focused on Ti_3AC_2 ($\text{A} = \text{Si}, \text{Si}_{1-x}\text{Al}_x, \text{Al}$) [7, 8, 9, 10, 11, 12, 13, 14, 15], in addition to $(\text{Ti}_{0.95}\text{Zr}_{0.05})_3\text{SiC}_2$ [16] and $(\text{Ti},\text{Al})\text{N}/\text{Ti}_2\text{AlN}_x$

multilayers [17]. They highlight a strong tolerance to damage induced by ion irradiation and a retained crystalline structure, to the exception of Cr_2AlC and Cr_2GeC , which amorphize at moderate fluence (10^{13} - 10^{14} Xe.cm^{-2}) [18]. In most of these studies, X-ray diffraction (XRD), transmission electron microscopy (TEM) and atomic force microscopy are combined to provide information on a global scale, unfortunately without chemical sensitivity in the crystal structure. Albeit these studies clearly show evidence of structural damage, they do not provide clear insight into its localisation into the structure. Identifying the nature of ion irradiation induced structural damage at the atomic scale is a key to understanding the behavior of MAX phases under irradiation. Channelling Rutherford backscattering spectroscopy would be a technique of choice for this purpose, but typically requires single crystals. This is a limitation for MAX phases, which are essentially made as polycrystalline pellets or as thin films, and rarely exist as single crystals [19, 20, 21].

In this context, core-loss spectroscopies are of potential interest to bringing significant quantitative structural information about the induced damages. The relevance of Extended X-Ray Absorption Fine Structures (EXAFS) in the monitoring of structural modifications induced by ion beams has already been demonstrated [22, 23, 24, 25, 26, 27]. Near edge fine structures were also used in order, for instance, to analyze charge transfers and coordination changings of boron and silicon atoms in borosilicate glasses under electron irradiation [28], to investigate hybridization and charge transfer modifications between Ni and Al in irradiated Ni-Al nanocrystalline films [29], boron stability and coordination in borophosphate glasses [30], or to determine titanium coordination environment in amorphized zirconolite ceramics [31]. The hability of near edge structures (X-ray Absorption Near Edge Structures - XANES - or Energy Loss Near Edge Structures -ELNES) to provide information about chemical bonding with chemical selectivity and at a local scale is a direct consequence of the fact that such experiments involve the probe of the Dynamic Form Factor (DFF) of the material under investigation:

$$S(\omega) \propto \sum_f \left| \langle \Psi_i | \hat{D} | \Psi_f \rangle \right|^2 \delta(\omega - E_f + E_i) \quad (1)$$

where $\hat{D}$ is expressed in terms of the momentum transfer between the swift electron and the material in EELS or the electric field polarization vector in XAS. Ψ_i and Ψ_f are respectively the initial and final state of the system. In the single particle approximation the DFF can be simply understood in terms of the local unoccupied projected density of states of the excited atom perturbed by the core-hole [32]. Interestingly, these experimental spectral features can be quantitatively understood from *ab initio* calculations.

Although widely used in materials science the combination of EELS/XAS to *ab initio* calculations is more delicate concerning the characterization of structural disorder as observed in ion-irradiated samples. To tackle this particular point, several approaches can be used. For calculations based on periodic boundary conditions, special quasi random structures, cluster expansion or virtual crystal approximations approaches can be used [33, 34, 35]: these approaches however involve time-consuming calculations due to both the number of configurations to be generated and the use of supercells to describe the system. Another possibility is to use real space approaches based on the multiple scattering theory where the description of disordered systems is much more straightforward [36]: the XANES or ELNES spectrum can then be computed from the average of a sufficient number of reference spectra. The number of configurations to be considered is then related to degree of disorder of the considered material (~ 100000 for glasses and ~ 10 for disordered crystals) [37, 38, 33]. This last approach has been used in the present study to simulate the effect of antisite defects in the irradiated structure and propose a structural model for the irradiated final state.

We thus focus on EELS and XAS, combined to *ab initio* calculations, to probe the electronic structure modifications induced by a 240 keV Ar^{2+} ion beam irradiation in a Ti_3AlC_2 thin film. The C K and Al K edges were acquired in the irradiated state in order to bring new insights in the irradiation damages, in complement to TEM and XRD data. The paper is organized as follows: the first two sections are devoted to experimental and computational details respectively. Next, results obtained from XRD and TEM are summarized before focussing on the C K and Al K edges. Finally the structure of the irradiated sample is discussed and a structural model is proposed for the irradiated state.

Figure 2: Experimental X-Ray Diffraction pattern of the Ti_3AlC_2 thin film recorded in θ - 2θ geometry. An offset of $+0.4^\circ$ is applied to the incident beam to avoid a major contribution of the substrate.

2. Experimental details

The sample was a Ti_3AlC_2 thin film epitaxially grown by sputter-deposition from elemental Ti, Al, and C targets onto $\text{Al}_2\text{O}_3(0001)$ with a $\text{TiC}(111)$ seed layer at a substrate temperature of 770°C . More details about the synthesis and the deposition setup can be found in Refs. [39, 40, 41]. Fig. 2 displays the θ - 2θ XRD pattern of the film. It shows that a single-phase film of Ti_3AlC_2 was deposited and that a nearly purely basal plane growth was then achieved with $\text{Al}_2\text{O}_3(0001)//\text{TiC}(111)//\text{Ti}_3\text{AlC}_2(0001)$ orientation relationship, as commonly observed for these nanolaminated materials [42]. However, a small contribution of diffracted intensity from $(10\bar{1}4)$ planes oriented parallel to the surface could also be detected in the θ - 2θ diffraction pattern (cf. the observations in Refs. [39, 43, 44]). The Ti_3AlC_2 film was ~ 160 nm thick, as measured from TEM observations.

Irradiation experiments were carried out in a medium current 180 kV EATON ion implanter, at room temperature, with 240 keV Ar^{2+} ions. The beam current was set below $1 \mu\text{A}\cdot\text{cm}^{-2}$ in order to minimize heating of the specimen during the irradiation process. The ion energy was selected to obtain a damage profile over the whole thickness of the film, as shown in Fig. 3 and so that the ions lose their energy in a nuclear loss regime, as predicted by SRIM simulations [45]. The fluences and corresponding displacements per atom (dpa)

Table 1: Irradiation fluences and displacements per atom (dpa). The mean number of dpa is averaged over the thickness of the film.

fluence (ion.cm ⁻²)	dpa (mean)	dpa (maximum)
1.5×10^{13}	0.017	0.022
3×10^{13}	0.034	0.044
7.5×10^{13}	0.085	0.11
1.5×10^{14}	0.17	0.22
3×10^{14}	0.34	0.44
5.25×10^{14}	0.6	0.77
7.5×10^{14}	0.85	1.1
1.5×10^{15}	1.7	2.2

are reported in table 1.

The evolution of the microstructure of the film was monitored after each irradiation fluence in a D8-Bruker X-ray diffractometer (Cu-K α , 40 kV-40 mA) operating in the θ - 2θ geometry. A slight incidence offset ($\omega = + 0.4^\circ$) was applied to avoid a major contribution of the substrate in the diffractograms. For a given system and irradiation parameters, the temperature has an essential role in the induced damage. It is of interest to mention that the structural materials will be facing temperatures in the range 600–1200°C in the future gas-cooled fast-spectrum nuclear reactors, under normal working conditions [5]. In order to investigate the stability of the irradiation induced structural modifications in this temperature range, thermal annealing of the irradiated specimen was performed. The irradiated Ti₃AlC₂ thin film was annealed from 300°C to 800°C under vacuum (2×10^{-5} mbar), *in situ* in a Philips XPert (45 kV-40 mA) X-ray diffractometer.

Transmission electron microscopy cross-sectional thin foils were prepared by tripod polishing down to a thickness of $\sim 10 \mu\text{m}$. Electron transparency was achieved by ion milling in a Gatan Precision Ion Polishing System (2.5 keV Ar⁺, incidence angle of 8°). A final step at a lower incidence angle (4°) was applied. Electron micrographs and electron energy

Figure 3: Damage profile (full line) and implantation profile of argon atoms (symbols) during 240 keV Ar^{2+} irradiation at a fluence of $1.5 \times 10^{13} \text{ Ar.cm}^{-2}$ in the Ti_3AlC_2 thin film, as predicted from SRIM simulations.[45]

Table 2: Structural parameters of Ti_3AlC_2 .

lattice parameters	canonical atomic coordinates	non-canonical atomic coordinates [46]
$a=3.072 \text{ \AA}$	$\text{Ti}_1 (0,0,0)$	$\text{Ti}_1 (0,0,0)$
$c=18.56 \text{ \AA}$	$\text{Ti}_2 (\frac{2}{3}, \frac{1}{3}, z_{\text{Ti}} = \frac{1}{8})$	$\text{Ti}_2 (\frac{2}{3}, \frac{1}{3}, z_{\text{Ti}} = 0.127)$
	$\text{Al} (0,0,1/4)$	$\text{Al} (0,0,\frac{1}{4})$
	$\text{C} (\frac{1}{3}, \frac{2}{3}, z_{\text{C}} = \frac{1}{16})$	$\text{C} (\frac{1}{3}, \frac{2}{3}, z_{\text{C}} = 0.068)$

loss spectra were acquired in a JEOL 2200FS transmission electron microscope operated at 200 kV. The energy resolution was ~ 1.2 eV, as measured by the full width half maximum (FWHM) of the zero loss peak recorded in vacuum. EEL spectra were acquired at the C K edge in image mode, with parallel illumination and a collection angle of 13.5 mrad.

Polarized X-ray absorption experiments were performed at the SOLEIL synchrotron, on the soft X-ray LUCIA Beamline [47]. Two KTiOPO_4 (011) single crystals are used as a monochromator ; the energy resolution is approximately 0.5 eV at the Al K edge. To avoid as much as possible the contribution from the sapphire substrate, the sample was oriented such that the incident beam hits the sample in grazing incidence ($\sim 3.1^\circ$). For each acquisition the influence of the incidence angle was carefully verified to ensure that no significant contribution from the substrate was detected, and that the signal to noise ratio was high enough, while keeping grazing incidence conditions. To suppress charging effects, the sample was carefully grounded using a lacquer charged with silver for sticking it on the sample's holder. Two different geometries were used to probe the anisotropy of the charge distribution along the c -axis and within the $\{a, b\}$ planes. In the first one, called in-plane geometry, the sample was set parallel to X-ray sheet: the incident electric field is then parallel to the sample's surface and one thus probe the $\{a, b\}$ planes. In the second one, the out-of-plane geometry, the sample is rotated from 90° with respect to the X-ray beam, the electric field is then along the c axis and we probe this direction. All spectra were recorded by monitoring the fluorescence yield under vacuum (10^{-2} mbar) at room temperature. The XANES spectra were acquired with an energy step of 0.2 eV and a collection time of 10 s per data point. In the extended range (EXAFS), the energy step is 1 eV and the acquisition time per point 2 s. No post-acquisition treatment was applied to the experimental data for comparison with simulations because self-absorption effect is very limited in the here probed energy range. In order to gain information about the local atomic order around the Al atoms after irradiation, analysis of the EXAFS signal were performed before and after the highest irradiation fluence, with the graphic interface [48] of the IFEFFIT code [49]. EXAFS being now a well-established technique, details of the analysis will not be presented here, many tutorials can be found on the web server of the xafs society (xafs.org).

3. Computational details

Ti₃AlC₂ crystallizes in an hexagonal structure with P6₃/mmc spacegroup: the structural parameters are displayed in table 2. In particular, Ti₂ and C atomic coordinates have free parameters along the *c*-axis. Both canonical, *i.e.* from geometrical considerations, and non-canonical [46] sets of coordinates, *i.e.* from *ab initio* calculations, were considered. The lattice parameters were determined from the X-ray diffraction pattern shown in Fig.2.

The simulations of the C *K* ELNES and Al-*K* XANES were performed with the FEFF code [50, 51]. FEFF is an *ab initio* self-consistent multiple-scattering code for simultaneous calculations of excitation spectra and electronic structure within the Muffin-Tin approximation. For EEL spectra, the code includes relativistic corrections [51]. Historically, FEFF uses a real space Green function approach to obtain spectra related to an atomic cluster of finite size without being restricted to periodicity. Recently, FEFF has been extended to *ab initio* calculations of EELS and XAS spectra in periodic systems using an impurity Green's function formalism without the need for a supercell.[52] This reciprocal, or *k* space, approach accounts for core-hole effects in deep-core spectroscopies of periodic systems while circumventing the supercell convergence issues encountered with conventional band-structure codes. Furthermore, FEFF includes an *ab initio* determination of the energy-loss function $-1/\pi \text{Im} \epsilon(E)$ that is the central ingredient in the many-pole self-energy model (MPSE) [53], which is a generalization of the Hedin-Lundqvist plasmon-pole model [54]. All calculations were performed considering a core-hole within the random phase approximation [50]. Self-energy effects, known to improve the agreement with the experiment [55, 56], are included into the calculations using the MPSE obtained from optical constants calculated *ab initio* by FEFF [57]. In order to analyze the fine structures in terms of scattering paths among the different coordination shells and to investigate the effect of disorder, the C *K* edge was simulated considering the real space approach. For the Al *K* edge, the reciprocal space approach was used. The converged parameters used in the FEFF calculations are displayed in table 3.

In order to test the possible structural disorder induced by irradiation and particularly antisite defects, calculations were also performed at the C *K* edge, using a random substitu-

Table 3: Parameters of the FEFF calculations. E_F shift is the shift with respect to the Fermi level allowing for the best agreement with experiment, and ℓ_{max} is the maximum orbital momentum.

edge	Orientation	acceleration voltage	collection angle	core-hole	E_F shift (eV)	ℓ_{max}	cluster size	K-points
C K	$[1\bar{1}00]$	$E_0 = 200$ keV	$\beta = 13.50$ mrad	RPA	0	4	13 layers, 6.9 Å	
Al K	$\{a, b\}$			RPA	-6.0	4		SCF: 200
Al K	c			RPA	-3.7	4		XANES: 2000

tion of the Al atoms on Ti sites or on C sites in the MAX phase structure or in a fcc cubic system. For the cubic system, calculations were performed conserving the 312 stoichiometry of the MAX phase: $(\text{Ti}_{0.75}, \text{Al}_{0.25})\text{C}_{0.5}$ or $\text{Ti}(\text{Al}_{0.33}, \text{C}_{0.66})$. The transformation into a cubic phase is a possible mechanism evidenced from XRD and TEM results. For each type of defect ($\text{Al} \leftrightarrow \text{Ti}$ or $\text{Al} \leftrightarrow \text{C}$), the final spectrum is obtained from the average of spectra computed from structures where the Al were randomly distributed on the M or X sublattice. Average spectra were converged for 10 to 13 configurations, values in good agreement with those obtained by Vitova *et al.* for similar calculations [38]. Finally, for the particular case of the fcc $\text{Ti}(\text{Al}_{0.33}, \text{C}_{0.66})$ cubic system, the effect of structural relaxation on the C K ELNES was investigated. This configuration was studied in more details since it was found to be the more realistic one when comparing to the experimental spectra. In brief, we used the following procedure (details are given in appendix):

- choose one configuration representative of the average among the ten necessary to obtain a converged average spectrum.
- build from this configuration a periodic system using a reduced cluster of 5.2 Å (short range approximation).
- perform a structural relaxation on this periodic system.
- compute the C K edge of the relaxed system with FEFF.

For comparison, the C K edge of the perovskite Ti_3AlC and cubic TiC structure were also performed.

The structural relaxations were performed using the Vienna *ab-initio* simulation package (VASP) [58] with projector augmented wave pseudopotentials [59]. Exchange and correlation effects were treated in the generalized gradient approximation using the Perdew-Burke-Ernzerhof functional [60]. A 400 eV plane-wave cutoff was used for C, Ti and Al potentials and a $9 \times 9 \times 9$ Monkhorst-Pack grid was used. The $3p$ semicore states of the titanium atoms were considered in the calculation. The potentials and basis set convergence were tested on Ti_3AlC_2 and led to optimized structural parameters in reasonable agreement with all electron calculation (less than 2% different) [46]. Concerning the cubic phase, the structural relaxation was performed on atomic positions, unit cell parameters and volume. Given the important number of atoms to be considered only a crude relaxation was performed with forces converged down to 0.1 eV/Å.

4. X-ray diffraction and Transmission Electron Microscopy

4.1. Evolution as a function of the irradiation dose

The evolution of the microstructure of the film was monitored by X-ray diffraction after each fluence around 0002, 0004 and 0008 Bragg diffraction peaks of Ti_3AlC_2 (Fig. 4). These peaks shift continuously towards lower 2θ angles, from $1.5 \times 10^{13} \text{ Ar.cm}^{-2}$ up to $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$. A decrease in intensity as well as a FWHM broadening of 0002 and 0004 peaks are also observed. This broadening is likely to be attributed to microstrains induced by irradiation. The lattice stretching along the c -axis as well as the intensity drop of 000 ℓ peaks are in good agreement with results already reported in the literature [9, 11, 12]. The evolution of the XRD patterns with the fluence first suggests a loss of chemical order along the c -axis because of the progressive extinction of the 0002, 0004 and 0006 peaks. However the intensity drop and FWHM broadening are more difficult to evaluate around the 0008 peak because an additional diffraction peak appears from the lowest fluence, $1.5 \times 10^{13} \text{ Ar.cm}^{-2}$ (arrow in Fig. 4). It is first visible as a shoulder at lower angle of the 0008 peak for low fluences. The 0008 shift is accompanied with a higher intensity of this additional peak up to $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$. The diffraction at a higher order is also visible, as indicated in Fig.

Figure 4: (a) Evolution of XRD patterns around the 0002, 0004 and 0008 Bragg peaks of Ti_3AlC_2 as a function of the irradiation fluence. (b) XRD patterns around the first and second orders of diffractions of the γ -structure after irradiation at $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$.

4 (b). It can be interpreted as a phase transformation induced by ion irradiation because the 0008 peak and the one indicated by the arrow in Fig. 4 (a) are observed simultaneously. From a change in relative intensities of X-ray diffraction peaks, Liu *et al.* suggested the formation of the β - Ti_3SiC_2 polymorph during Xe 92 MeV irradiation of α - Ti_3SiC_2 [9]. In the present case, not only the relative intensities evolve but a supplementary peak is induced by the irradiation process. In the following, the crystal structure associated to this peak will be named γ .

The irradiation induces a shift of the TiC 111 peak towards lower angles. It corresponds to a swelling of the TiC lattice, which may be related to the creation of defects, such as large amounts of argon atoms in interstitial position, the projected range of implanted ions being maximum at the seed layer (Fig. 3). Nevertheless the TiC seed layer remains very stable up to $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$. This is in good agreement with the fact that, to our knowledge, no evidence of important damage of this compound has been reported in the literature. This can be related to the similar behavior of the binary carbide ZrC under ion and neutron

irradiation, in which weak structural modifications and evolution of mechanical properties have been demonstrated.[61, 62]

In order to determine the crystal structure of the γ phase, cross-sectional TEM observations were performed on the irradiated film. A SAED pattern of the film before and after irradiation at 1.5×10^{15} Ar.cm⁻² is presented in Fig. 5. Some diffraction orders extinct, indicating a loss of chemical order along the c -axis. Only diffraction spots are observable in the SAED pattern after irradiation, signature of a crystalline material, and without an amorphous contribution, in good agreement with the results of Whittle *et al.* [14] and Wang *et al.* [15]. The dark field micrographs (a) and (b) show that the corresponding diffraction spots originate from the film and the substrate. Separating their contributions by tilting the specimen was not succesful, hence highlighting that the epitaxy between the film and the seed layer is conserved. High resolution micrographs of the specimen after irradiation at the highest fluence are presented in Fig. 6. The distance between atomic planes is even ($\sim 2.5 \pm 0.1$ Å) and corresponds to the one obtained from XRD (~ 2.42 Å). Although the damage profile calculated from the SRIM code is not even (cf. Fig. 3), this contrast of atomic planes is over the entire thickness of the film and is very similar to the one observed in Ti₃SiC₂ after irradiation at 3 dpa [12]. The contrast typical of the nanolayered structure of MAX phases could not be identified, while acquisitions at different focus were attempted but could not reveal the MAX phase nanolayered structure. Fourier transforms of the film and of the seed layer are almost identical, and suggest that the γ phase possesses a crystal structure comparable to TiC along a direction orthogonal to the film surface. Unfortunately it is not possible to obtain more information from these TEM micrographs in the directions perpendicular to the growth axis, *i.e.* within the basal planes. These experiments confirm the outstanding stability of Ti₃AlC₂ under ion irradiation at room temperature.

4.2. Post-irradiation annealing

The evolution of the XRD patterns around Ti₃AlC₂ 0008 and 0002 peaks is presented in Fig. 7 for different annealing temperatures. At 300°C, no major modification is visible concerning the peak attributed to the γ phase. However, at 600°C, this peak shifts towards

Figure 5: SAED patterns of the film before and after Ar^{2+} irradiation ($1.5 \times 10^{15} \text{ Ar.cm}^{-2}$). The dark field micrographs of the irradiated specimen are obtained from the circled spots (a) and (b).

higher angles and broadens. In parallel, a growing intensity of the 0002 peak is clearly evidenced. These evolutions are interpreted as a recovery of the MAX phase structure, which is in good agreement with the beginning of defect annealing from 300°C reported in Ti_3SiC_2 [12] and $\text{Ti}_3\text{Si}_{0.90}\text{Al}_{0.10}\text{C}_2$ [9]. Up to 800°C , this peak keeps on shifting till a position ($2\theta = 39.91^\circ$) close to the 0008 peak of Ti_3AlC_2 in the initial state ($2\theta_i = 38.66^\circ$ for the non-irradiated film). It narrows when further increasing the temperature. These results suggest that the recovery of the MAX phase structure is almost total at 800°C , in good agreement with recent work on $\text{Ti}_3\text{Si}_{1-x}\text{Al}_x\text{C}_2$ [7] and Ti_3SiC_2 [10]. The lattice parameter after recovery ($c_r = 18.50 \text{ \AA}$) is closer to the theoretical value for a powder ($c_t = 18.501 \text{ \AA}$) [68] than the value at the initial state ($c_i = 18.56 \text{ \AA}$). Different states of stress could be at the origin of these discrepancies, the crystal structure being relaxed after recovery. In the case of the 0002 peak, continuous intensity increase is evidenced with the temperature above 600°C , in good agreement with the evolution of the 0008 peak. It is worth noting that no effect of the steady time was evidenced, because the 0002 peaks acquired just after the centering and height adjustment of the specimen (15 minutes), and after 35-50 minutes maintaining are

Figure 6: Bright field high resolution micrographs in cross section view of the Ti_3AlC_2 film (a), and around the TiC seed layer (b), after irradiation at $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$. The inset in (a) is an intensity profile corresponding to the area in dashed line, and the computed diffraction patterns in (b) correspond to the γ phase and the TiC seed layer.

Figure 7: XRD patterns (Bragg-Brentano geometry) acquired during post-irradiation *in situ* annealing around (a) the 0008 peak and (b) the 0002 peak.

similar (not shown). Therefore the recovery of the MAX phase structure is kinematically fast, in agreement with the work of Whittle *et al.* [14], who indicate that the defects and the structure created under ion irradiation have a low stability from a thermodynamic point of view. The FWHM of rocking-curves acquired on the diffraction peak of the γ structure, and on the Ti_3AlC_2 0008 and 0002 diffraction peaks, do not evolve during the annealing (not shown). Hence the recovery of the structure Ti_3AlC_2 does not lead to the nucleation of grains with a different orientation. This is accompanied with a shift of TiC diffraction peak towards larger angles, from $2\theta_{\text{irradiated}}=35.78^\circ$ to $2\theta_{\text{annealed}}=36.04^\circ$. The position after annealing is almost identical to the initial state, and therefore irradiation induced defect annealing in the TiC seed layer is very likely. The decrease of the TiC lattice parameter could originate from the elimination of argon interstitials.

5. Electron energy loss spectroscopy and X-ray absorption spectroscopy

With the aim of understanding the microstructural modifications induced by ion irradiation at a local scale, the C K and Al- K edges of the initial state were first studied, both experimentally and theoretically, before focussing on the electronic structure of the irradiated sample.

5.1. Initial state

5.1.1. C K ELNES

The C K edge of Ti_3AlC_2 acquired in $[1\bar{1}00]$ zone axis for a collection angle of 13.5 mrad is presented in Fig.8, in addition to the theoretical results obtained from FEFF considering either canonical or non-canonical positions for the Ti_2 and C atoms [46]. All fine structures are reproduced by the calculations, with comparable intensity ratios, highlighting the rather good agreement of the theory with the experimental data at this edge. Nevertheless we note that the width of the first oscillation is narrower in the theory as well as a shift of the calculated spectra towards lower energies around 310 and 325 eV. These discrepancies may originate in part from the fact that we do not include any disorder (thermal or static) into the calculations, disorder known to damp and shift slightly fine structures.

In order to obtain a quantitative analysis of the fine structures, the decomposition of the C K edge among the successive coordination shells around the excited atom is presented in Fig. 9 (a). One can notice several points. First, as previously mentioned, the fine structures are converged for a cluster size of 6.9 Å, which means that the C K edge gives an information of the local order in the structure up to a distance corresponding to approximately $c/3$. Second, the fine structures are completely insensitive to the aluminum layer: whatever the corresponding coordination shell, the addition of an Al layer in the decomposition do not modify the calculated ELNES. As a consequence, the C K edge gives a direct probe of the local order in the Ti_6C octahedra layers of the MAX phase. It is interesting to notice that the first peak at the edge onset is mainly due to the presence of the six Ti first neighbors forming the octahedral cage around the excited carbon atom (indicated by an arrow in Fig. 9 (b)). Finally, the decomposition shows that the fine structure J appears when considering the sixth coordination shell constituted of three carbon atoms located in the joint octahedra layer as shown in Fig. 9 (b). The sensitivity of the C K edge to these three C atoms is particular to the Ti_3AlC_2 structure. Indeed, the fine structure J corresponds to scattering paths involving three aligned atoms: C-Ti₁-C. The Ti₁ atom located at the middle of the C-C distance (4.35 Å) acts as a lens and amplify the forward and backward scattering amplitudes that are already maximum: this is the well-known focussing effect [63]. It also explains why

Figure 8: C K ELNES acquired along $[1\bar{1}00]$ zone axis (full line) and corresponding FEFF calculation (dashed line - 1.2 eV convolution) using canonical and non canonical positions ($z_{Ti} = 0.127$ and $z_C = 0.068$).

J is so sensitive to z_C : as soon as it varies, the C-C distance does, as well as the scattering phase-shift and thus J energy position. Hence the structure J is characteristic of a crystal structure containing two joint Ti_6C octahedra layers.

5.1.2. Al-K XANES

The experimental Al- K edges, acquired for an electric field polarization within the basal planes $\{a,b\}$ and parallel to the c -axis, are presented (thick black lines) in Fig. 10 and 11, respectively. Contrary to the C K ELNES, the experimental Al- K XANES evidences a strong anisotropy of the charge distribution around the aluminum atoms, the edge jumps being very different for both geometries.

At first let us discuss the in-plane results shown in Fig.10 where the experiment has been offset for clarity (top). The related FEFF spectrum (top: red line) has to be shifted by -6 eV to align the maximum at 1566.3 eV. This spectrum is obtained considering contributions of (0001) planes (80%, dashed blue line) and $(10\bar{1}4)$ planes (20%, dotted blue line). Indeed, considering only the (0001) planes does not match the experiment beyond ~ 1562 eV and one must therefore add the contribution of the $(10\bar{1}4)$ planes, evidenced from XRD (Fig. 2) that are at about 60° from the basal planes. Nevertheless one remarks that the fine structure labelled A is missing in the calculation as well as the bump noted B. It is more obvious when comparing the experimental result with the theoretical one without broadening (bottom). Excepted for A and B, all experimentally observed fine structures are reproduced

Figure 9: Decomposition of the C K ELNES among the different coordination shells (a) (convolution 1.2 eV). The experimental C K edge acquired by EELS along the $[1\bar{1}00]$ zone axis is added at the top as a comparison and the structure J is indicated by a vertical dashed line. Ti_3AlC_2 unit cell (b) ; a central carbon atom is indicated by an arrow, and the three atoms at the origin of structure J are linked to the central atom by full lines.

by the theory but with energy positions and amplitudes more or less in agreement. The discrepancy is particularly important for the first EXAFS fine structure that is predicted at 1586 eV and observed at 1588.6 eV. The main origin of these discrepancies is the Muffin-Tin approximation that will be discussed latter. Concerning missing fine structures A and B they can be attributed to a small contribution of the substrate as evidenced by the XAS $\text{Al}_2\text{O}_3(0001)$ spectrum recorded for the same in-plane geometry (dashed line, bottom in Fig. 10). Structures A and B correspond to the most intense fine structures. It likely comes from the edge of the sample that may be not covered by a thick enough silver lacquer layer so that the underneath sapphire is partly lighted by the incident X-ray beam for the low incidence we used.

Focussing now on the out-of-plane geometry as well as the related FEFF results (Fig. 11), similar observations can be drawn (here the theoretical spectra have to be shifted only by +3.7 eV to align the maximum at 1568.7 eV). All observed fine structures are predicted by the theory when no broadening is applied (bottom), excepted for those labelled A, B

and C. Here again, these structures can be attributed to the Al_2O_3 substrate (dashed line, bottom in Fig. 11). The substrate may also contribute to the intensity at the top of the edge (1568.7 eV), but it is mixed with the Ti_3AlC_2 contribution predicted to be at maximum for this energy. It should be noted that the $(10\bar{1}4)$ planes contribution (20%) is not as visible as it is for the in-plane geometry, the related spectrum being very close to the one related to (0001) planes in that geometry. Opposite to what was observed for the in-plane geometry, it should be pointed out that the first EXAFS fine structure is here predicted at the observed experimental energy position (1587.4 eV).

If the overall shape of the experimental data is well reproduced by the calculations, therefore reflecting the structural anisotropy of the MAX phase, the discrepancies noted above (fine structures amplitudes and energy positions are more or less off compared to experiment) are mainly due to the Muffin-Tin failure to reproduce the electronic structure anisotropy. This last point is evidenced in Fig. 12 showing that the in-plane and out-of-plane Al K edges seem to be shifted in energy. Taking the usual criterion using the inflexion point (first derivative maximum) as energy reference for the Fermi level, one get 1559 eV in the former case and 1559.8 eV in the latter. This difference cannot be due to an experimental artefact because nothing has been changed in the beam line optics between the in- and out-of-plane measurements: the sample has just been rotated in the X-ray beam. Such an energy difference at the Al K edge onset reflects the electronic structure anisotropy, which has been suggested from pseudopotential band-structure calculations [64].

A strong support for this assumption can be found in full potential calculations obtained from the well known band structure code WIEN2k [65]. The calculated empty local density of states (LDOS that are those probed by XAS) Al_{pz} are non zero at higher energy with respect to the Fermi level than the Al_{px-py} ones (dots in Fig. 12). For comparison with the experiment, the LDOS have been convoluted with a gaussian (FWHM: 0.5 eV). In spite we do not put a core-hole into the LDOS calculation, effect that has to be considered in the present case [32], one notes a fairly good agreement between the experimental fine structures and the LDOS. This analysis clearly shows that the charge density, as well as the potential, is far from spherical around the Al atoms. Of course, non spherical effect

does not exist in a Muffin-Tin approach, it is partly imitated by adding different constant energy for the potentials (and different energy shifts to align with the experimental data) in the FEFF calculations, but it also explains the discrepancies quoted previously. Thus, the Muffin-Tin approximation as used in FEFF is not sufficiently accurate to account for the strong anisotropy effects of the electronic structure of Ti_3AlC_2 . This effect has already been evidenced in strongly anisotropic systems like hexagonal boron nitride,[66] for which the Muffin-Tin approximation is too restrictive. On the other hand, we have previously shown that the agreement between experiment and calculation is satisfactory at the C K edge, for which the octahedral site leads to an overall more isotropic chemical bonding and the Muffin-Tin approximation thus adapted. To end, let us mention that, like at the C K edge, we do not include any disorder in the FEFF calculation, disorder that is known to be significant: a corrugation of Al planes could also contribute to increase the disagreement in the case of the Al K edge [67, 4].

5.2. Final state

5.2.1. C K ELNES

The C K edges acquired for the virgin state, irradiated at 5.25×10^{14} Ar.cm $^{-2}$, and at the highest fluence 1.5×10^{15} Ar.cm $^{-2}$, are presented in Fig. 13. The ELNES remains almost identical with the fluence. As it has been shown from the decomposition among the different coordination shells around a central carbon atom (Fig.9), the C K edge represents essentially the Ti_6C octahedra characterized by the fine structure J, a fingerprint of two joint octahedra layers. It is clearly evidenced from Fig. 13 that the octahedra layers are extremely stable under ion irradiation up to a dose of 1.7 dpa, J remaining unchanged. Hence, we can conclude that the stacking of joint octahedra layers is not affected by the ion irradiation.

5.2.2. Al K XANES

The octahedra layers are strongly damaged tolerant to ion irradiation induced damage, and as a consequence, the aluminum layers are likely to be more damaged to account for the

Figure 10: Top: Al-K XANES (black) and related FEFF calculations (red) for the in-plane geometry. Dashed and dotted blue lines are the contributions of the (0001) and (10 $\bar{1}$ 4) planes, respectively. Double arrows indicate the missing fine structures A and B. Bottom: Comparison between the experiment (top) and FEFF(bottom) without broadening showing that all fine structures are present expected for A and B that are attributed to the Al₂O₃ substrate (dashed line).

Figure 11: Top: Al- K XANES (black) and related FEFF calculations (red) for the out-of-plane geometry. Dashed and dotted blue lines are the contributions of the (0001) and (10 $\bar{1}4$) planes, respectively. Double arrows indicate the missing fine structures A, B and C. Bottom: Comparison between the experiment (top) and FEFF(bottom) without broadening showing that all fine structures are present expected for A, B and C that are attributed to the Al₂O₃ substrate (dashed line).

Figure 12: Enlarged view of the Al- K edge of Ti_3AlC_2 (top and left axis) for in-plane (red line) and out-of-plane (blue line) geometry compared to Al_{px-py} (red dots) and Al_{pz} (blue dots) LDOS (bottom and right axis) calculated with WIEN2k. The fermi level is set at 1559 eV

Figure 13: C K ELNES for the virgin state (bottom), irradiated at $5.25 \times 10^{14} \text{ Ar.cm}^{-2}$ (middle), and at $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$ (top). The spectra are offset for clarity.

Figure 14: Al K XANES for the virgin state (bottom), and irradiated at $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$ (top) for $\{a,b\}$ and c polarizations. The spectra are offset for clarity.

structural modifications highlighted from XRD and TEM. The Al K edge acquired before and after irradiation at the highest fluence are presented in Fig. 14. After irradiation, the XANES is strongly modified for both probed geometries, the most salient result being that spectra are nearly undistinguishable. Fine structures are clearly less visible than for the initial state, the edge is smoother, and the first EXAFS energy position is the same, confirming that ion induced modifications of the Ti_3AlC_2 crystal structure occur in the aluminum planes. Of particular interest, the XANES after irradiation is, contrary to the initial state, isotropic in shape. Thus the charge distribution around an aluminum atom is now more isotropic. This can be interpreted as follows: the aluminum atoms were displaced from a highly anisotropic trigonal prismatic site to a more isotropic atomic site. Another possible assumption is that the aluminum atoms are organized in a completely random matter, and the Al K edge represents an average of all these positions, hence isotropic. To summarize, from EELS and XAS spectroscopies, the γ phase can be viewed as constituted of a ceramic component analogous to the one existing in the parent MAX phase (two joint Ti_6C octahedral layers) and a metallic one where the aluminum atoms seem to be in a cubic symmetry.

6. Discussion

The XRD, TEM, EELS and XAS results raise questions regarding the nature of the γ phase and the location of aluminum atoms. In addition the restoration of the structure during thermal annealing indicates that the defects created during ion irradiation are less stable than a MAX phase structure. A phase transformation is evidenced in Ti_3AlC_2 from the earliest stages of irradiation. Considering the angular positions of the two diffraction orders of the γ -phase (Fig. 4 (b)), and accounting for the fact that the initial prismatic planes are compact with a hexagonal pattern, different crystalline structures can be proposed. The first hypothesis would be hexagonal structures, the β - Ti_3AlC_2 polymorph, or a deformed α - Ti_3AlC_2 with Ti-Al and C-Al substitutions, with a diffraction on $\{0008\}$ and $\{00016\}$ planes and a lattice parameter $c \sim 19.324 \text{ \AA}$ in that case. A second set of possible structures would be of cubic symmetry, with a diffraction on $\{111\}$ and $\{222\}$ planes and a lattice parameter of $\sim 4.19 \text{ \AA}$, like a rock-salt type structure TiC with substitutions of aluminum on titanium and carbon sites, and hence a lower lattice parameter than the seed layer. The hypothesis of a perovskite structure Ti_3AlC can also be considered. The validity of these assumptions can be tested by computing the C K edge spectra related to these structures.

For the evoked hexagonal structures, the calculations' results are displayed in Fig. 15. The hypothesis β - Ti_3AlC_2 does not agree with the EELS experiments (Fig.14), the structure J being hardly visible for that phase. Although the position of the structure J is dependent of the free parameters z_C and z_{Ti} , they are not accessible from our experiments. Here, the canonical positions have been used, but it is worth noting that the experimental position of the structure J cannot be reproduced by considering different values of z_C and z_{Ti} . Moreover, the hypothesis of a β - Ti_3AlC_2 phase is hardly conceivable given the isotropic charge distribution around aluminum atoms as evidenced from the Al K edges recorded after irradiation (see Fig. 14). The effect of substitutions Ti-Al and C-Al on the C K edge of a deformed α - Ti_3AlC_2 ($a = 2.98 \text{ \AA}$ and $c = 19.324 \text{ \AA}$) highlights that the C K ELNES is very sensitive to Ti-Al and C-Al substitutions. For Ti-Al, this result is not surprising since the titanium atoms are the nearest neighbors of carbon, determining therefore the overall shape of the C

K edge. In particular, $\text{Ti} \leftrightarrow \text{Al}$ substitutions clearly affect the intensity of the first peak, in agreement with the interpretation of the C K ELNES decomposition discussed previously. This disagrees with the hypothesis of Nappé *et al.* [12], who suggested Ti-Si substitutions in Ti_3SiC_2 . In the case of substitutions of aluminum atoms on carbon sites, the overall shape of the edge is not as drastically different, but the structure J is no more observable. Of course the EEL spectra presented provide chemical information at a short distance, but averaged over a large probed volume, and small amounts of these substitutions (i.e. below the EELS detection threshold, typically a few percents) cannot be excluded.

Concerning the cubic structures, the FEFF calculations are represented in Fig. 16 and compared to the experimental edge. For TiC , the main difference with the experimental ELNES arises from the structure J at higher energy in the cubic phase, whereas the fine structures above 295 eV are well reproduced. This similarity is due to the fact that C atoms occupy octahedral sites defined by Ti atoms in both structures. For a perovskite structure, the disagreement is even more pronounced: the structure J is at higher energy in the calculated edge, the double structure at 300 eV and 305 eV does not have the appropriate intensity ratio, and the structure at 310 eV does not reproduce the double structure observed in the experimental spectrum. Given the global stoichiometry of the film, $\text{Ti}_3\text{:Al}_1\text{:C}_2$, a transformation in a phase $(\text{Ti}_{0.75}\text{Al}_{0.25})\text{C}_{0.5}$ would be more likely, in which aluminum atoms are on one fourth of titanium sites and half of the carbon sites are empty. It is clear that this structure does not give a correct simulation of the experimental C K ELNES, and it highlights the strong sensitivity of the C K edge to substitutions on the Ti sites, for the same reason given above in the case of the hexagonal structure. Interestingly, the calculation of the C K edge of $\text{Ti}(\text{Al}_{0.33}\text{C}_{0.66})$ reproduces the structure J with a good agreement with the experiment, as shown in Fig.16. Therefore, based on this simulation, the substitution of Al atoms on C sites cannot be excluded for the cubic structure assumption. It is important to note that for the particular case of $\text{Ti}(\text{Al}_{0.33}\text{C}_{0.66})$, an *ab initio* structural relaxation has been performed on the disordered structure before calculating the C K edge. This structural relaxation was mandatory to obtain a good agreement with the experiment (details of the approach used to perform such a relaxation are given in section 9). It is also important to

Figure 15: C K ELNES calculated with the FEFF code for the deformed structure α - Ti_3AlC_2 (convolution 1.5 eV) including Ti-Al or C-Al substitutions, and for the hexagonal polymorph β - Ti_3AlC_2 . The experimental spectrum acquired by EELS after irradiation at $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$ is plotted for comparison (top).

notice that the system is not really cubic after *ab initio* geometrical relaxation. Indeed the important damage tolerance of Ti_6C octahedra in Ti_3AlC_2 under irradiation does not agree with a transformation toward a cubic phase: it will require a de-twinning of the octahedra layers to go from an hexagonal to a rocksalt cubic structure [3]. Such a transformation is hardly conceivable even under ion irradiation.

From the loss of most fine structures in the Al K XANES, and its isotropic character, the possibility of aluminum layers being an amorphous-like medium (a kind of one dimension metallic glass) separating the two joint Ti_6C octahedra layers could also be considered. The

Figure 16: C *K* ELNES calculated with the FEFF code for TiC, Ti_3AlC , $(\text{Ti}_{0.75}, \text{Al}_{0.25})\text{C}_{0.5}$, and $\text{Ti}(\text{Al}_{0.33}, \text{C}_{0.66})$ relaxed cubic structures. The experimental spectrum acquired by EELS after irradiation at $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$ is plotted for comparison (top).

Figure 17: Fourier Transforms (amplitude: full line, imaginary part: dashed line) of the EXAFS signals for the virgin state (bottom), and after irradiation at $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$ (top).

simulation of the C K edge of such a structure is hardly doable for most simulation packages. However, the EXAFS is a method of choice in such a situation, in particular it is easy to show if a sample is amorphous or not just looking at the Fast Fourier Transform (FFT) of the data. We therefore record the EXAFS signal for the in-plane geometry both for the initial (virgin) and final (after irradiation) states. It turns out that the EXAFS oscillations are quite weak (the constituting atoms are all light atoms, i.e. weak scattering centers) and limited in energy range because of the presence of the Si-K edge (1839 eV) coming from the beam line optics (interdiffusion of Si through the Ni coating of the silicon mirrors). The Si-K edge acts as a cut-off and limits the available wavenumber range to $2 \text{ \AA}^{-1} \leq k \leq 7.5 \text{ \AA}^{-1}$ for the analysis. The amplitude and imaginary part of the FFT of the EXAFS data within this range is presented in Fig. 17. The FFT related to the irradiated state presents few clearly defined peaks, meaning that there is a local order characteristic of a crystalline state and not of an amorphous medium around the Al atoms. This is in agreement with the SAED patterns of the Ar-irradiated sample at $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$ (Fig. 5) in which no amorphous contribution can be observed. It is also obvious that the distances between the first neighbors are different from the virgin state ones with apparition of a peak at a short apparent distance around 1.5 $\text{\AA}$ while the apparent distance related to the main peak is larger. Unfortunately it is not possible to perform a reliable analysis of these EXAFS data because of the too limited energy range. Indeed, the first peak of the FFT includes the contributions of the three first neighboring shells: 6 Ti₂ (2.92 $\text{\AA}$), 6 Al (3.07 $\text{\AA}$) and 6 C (3.9 $\text{\AA}$). An EXAFS analysis requires to search for two parameters (one distance, one Debye-Waller factor) per shell and at least one energy origin parameter: a number of parameters therefore far exceeding the one allowed by the Nyquist criteria [49]. If we consider that the apparent distance at 2.5 $\text{\AA}$ corresponds to a true distance $\sim 3 \text{ \AA}$ (Fig.17: bottom), we can have an estimate of the real distance corresponding to the FFT peak observed at 1.5 $\text{\AA}$ (Fig.17: top): the phase shift correction of 0.5 $\text{\AA}$ would lead to a real distance Al-nearest neighbors of $\sim 2 \text{ \AA}$. In MAX phases, such a distance in between atoms is found in the M-X bonds, *i.e.* within the octahedra layers [3], hence strengthening the hypothesis of aluminum atoms in an octahedral site, as in Ti(Al_{0.33},C_{0.66}).

From XRD, TEM, EELS and XAS, the irradiation induces a phase transformation of α - Ti_3AlC_2 into an ordered structure in the direction perpendicular to the surface of the film, with an interplanar distance of 2.42 Å, in which octahedra layers are conserved. Few reasons could account for this difference, such as the fact that the only one study devoted to study ion irradiation effects in Ti_3AlC_2 has been followed by electron diffraction in a [0001] zone axis, *i.e.* along the c axis, which does not enable to evidence any change in the diffraction pattern. Our observations suggest that the hexagonal diffraction pattern observed along the c axis highlights the compact arrangement in the basal planes of the octahedra layers. To end, it also has to be mentioned that the residual stress level inherent to any thin film growth process, and not present in hot pressed materials, could also contribute to the here evidenced ion induced phase transformation in Ti_3AlC_2 thin film.

7. Conclusion

The structural damage induced by 150 keV Ar^{2+} in a Ti_3AlC_2 thin film was investigated by EELS, XAS and first principle calculations, in addition to XRD and TEM. It is evidenced that Ti_3AlC_2 is highly tolerant to ion irradiation damage, with no sign of amorphization for fluences up to $1.5 \times 10^{15} \text{ Ar.cm}^{-2}$ (~ 1.7 dpa). In addition to a loss of chemical order along the c axis, a phase transformation is evidenced by Ar irradiation. The interpretation of the C K and Al K edges acquired by EELS and XAS respectively, demonstrates that the Ti_6C octahedra layers remain, like the binary buffer layer TiC , unperturbed after irradiation whereas the aluminum layers are strongly disordered. From this point of view, the MAX phase can be seen as an ultimate superlattice built from the stacking of ceramic and metallic layers, a behavior already reported to give a good description of the bulk plasmon excitation in these systems [70]. A fast recovery of the MAX phase structure by thermal annealing is shown from 600°C, and is complete at 800°C. The successful use of near edge fine structure analysis to interpret structural evolution in Ti_3AlC_2 demonstrates the strong interest in further utilizing EELS and XAS for irradiation-related investigations. Beyond the potential of fine analysis of spectroscopy signals, this work brings further insight in the understanding

of the behavior of MAX phases under ion irradiation, and highlights the potential of these compounds as possible structural materials in future nuclear reactors.

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9. Appendix

In this appendix the method to obtain the C K edge corresponding to the relaxed structure obtained from a disordered $\text{Ti}(\text{Al}_{0.33}\text{C}_{0.66})$ cubic solid solution is described.

The starting point is a fcc cubic TiC unit cell with a unit cell parameter $a = 4.19$ Å as determined from XRD (see section 4). Several configurations are then generated by randomly substituting Al on C sites in the cluster, respecting the 312 stoichiometry. For each configuration, a complete SCF calculation of the potentials is performed before simulating the C K edge. We checked that this point is not mandatory in our case: calculating the C K edge from potentials determined from a single configuration led to equivalent results. The final C K edge, representative of the complete solid solution, is obtained from the average of the spectra obtained for several configurations. The average is converged when adding the signal corresponding to a new configuration does not change the final spectrum: in our case 10 configurations were sufficient. To compute the average, all spectra were shifted to have their edge onset at the same energy. This approach was globally used for all the solid solutions calculations performed in this study.

The complete set of calculated spectra as well as their average is shown in Fig. 18 (a). To estimate the effect of structural relaxation on these fine structures within a reasonable

Figure 18: (a) C K edges obtained for the ten random structures corresponding to the fcc cubic $\text{TiAl}_{0.33}\text{C}_{0.66}$, top curve: average of the ten curves. (b) Hellinger distance calculated from equation 2 between each configuration and the average. (c) Comparison between the fourth configuration and the average spectrum.

computation time, the configuration closest to the average one was selected. To do so, the Hellinger distance between each configuration and the average spectrum, given by:

$$H_i = \frac{1}{\sqrt{2}} \sqrt{\sum_n (\sqrt{\sigma_i(n)} - \sqrt{\sigma_{av}(n)})^2} \quad (2)$$

was calculated, this approach has been used by Gao *et al.* in order to quantify core-hole effects on light elements K edges [69]. The closest configuration from this point of view was kept. In equation 2, each spectrum is considered as a discrete set of data: $\sigma_i(n)$ is the cross section of the i^{th} configuration, $\sigma_{av}(n)$ the average and n is the energy. As evidenced by Fig. 18 (b) the fourth configuration is the one closest to the average: direct comparison between the two simulations is given in Fig. 18 (c). In principle, one could go to even closer configurations by generating as many new structures as necessary to have the Hellinger distance reduced below a given criterion.

The calculations are performed for a cluster size of 6.9 Å which involves 146 atoms. It would be very time consuming to perform a complete structural relaxation on a periodic system built from such a cluster. In order to get a tracktable system, a short range approx-

Figure 19: Importance of the different coordination shells in the fine structure calculations for clusters ranging from 2.1 Å to 6 Å around the excited atom: the influence is estimated from their normalized Hellinger distance with respect to the reference calculation (Rfms = 6.9 Å).

Figure 20: (a) View of the non-relaxed and relaxed $\text{TiAl}_{0.33}\text{C}_{0.66}$ structure along the $[0-11]$ direction. (b) Comparison of the C K edges computed from these structures with the experimental spectrum obtained after irradiation.

imation has been used: the cluster size has been reduced to 5.2 Å (leading to a 80 atoms cluster). The choice for such cluster size was determined so as to minimize the impact on the C *K* edge fine structures. Fig. 19 gives the Hellinger distance between the converged spectrum ($R_{fms} = 6.9$ Å) and the spectra obtained considering the different coordinations shells ($R_{fms} = 2.1, 3, 3.7, 4.2, 4.7, 5.2$, and 6 Å), normalized to the sum of all distances. It appears from Fig. 19 that beyond 5.2 Å the difference in terms of fine structures modifications is clearly very small (less than 5 % of the total difference). In addition, the C *K* edge obtained with $R_{fms}=5.2$ Å is compared to the reference spectrum in Fig. 19: the two spectra are indeed very close. A 5.2 Å cluster obtained from the fourth random configuration was thus used to build a unit cell in which the environment of the central C carbon is representative, in terms of C *K* edge ELNES, of that in the completely desordered solid solution.

A crude structural relaxation of atomic positions, unit cell parameters, and volume was then performed. No symmetry constraints were added and the relaxation was performed for forces converged down to 0.1 eV/Å. The final unit cell is not cubic anymore: $a=9.1150$ Å, $b=9.12850$ Å, $c=9.13530$ Å, $\alpha=95.61^\circ$, $\beta=86.64^\circ$ and $\gamma=93.22^\circ$. This unit cell is clearly not cubic, but observed along a direction perpendicular to the [111] direction of the cubic lattice (the [0-11] in the present case), the stacking looks very similar to that of the initial cubic system (see Fig. 16). This is in agreement with the TEM observation. The C *K* edge of the central carbon atom is then computed using FEFF. The effect of the structural relaxation is illustrated in Fig. 20 where the experimental spectrum corresponding the irradiated final state is compared to the solid solution averaged spectrum and that obtained from the relaxed structure: the agreement is clearly better in the latter case. In particular, the J structure is found at the good energy position with respect the the first main peak when compared to the experiment and the double structure between 295 and 305 eV is also recovered, however their amplitude is too low compared to the experiment.

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