Incipient low-temperature formation of MAX phase in Cr–Al–C films

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Abstract: Ceramic-metallic MAX phase of chromium aluminium carbide ternary compounds was successfully obtained through deposition by DC sputtering onto Si substrates. A study of the influence of substrate temperature and in-air post-annealing on the film crystallinity and oxidation was undertaken. Scanning electron microscopy (SEM), wavelength-dispersive X-ray analysis (WDSX), and X-ray diffraction (XRD) were used for film characterization. It is shown that, at substrate temperature of about 450 °C, as-deposited films are amorphous with small nanocrystals. Subsequent annealing in air at 700 °C leads to film crystallization and partial oxidation. WDSX spectroscopy shows that the films oxidise to a depth of around 120 nm, or 5% of total film thickness which amounts at around 2.68 µm. As a novelty, this demonstrates the possibility of in-air crystallization of Cr₂AlC films without significant oxidation. Materials Analysis Using Diffraction (MAUD) software package for a full-profile analysis of the XRD patterns (Rietveld-type) was used to determine that, as a result of annealing, the average crystallite size changes from 7 to 34 nm, while microstrain decreases from 0.79% to 0.24%. A slight tendency of preferential growth along the (10 $\bar{1}$ 0) direction has been observed. Such texturing of the microstructure has the potential of inducing beneficial anisotropic fracture behaviour in the coatings, potentially interesting for several industrial applications in load-bearing devices.

Keywords: ternary carbides; DC sputtering; annealing; crystallization; X-ray diffraction (XRD); wavelength-dispersive X-ray analysis (WDSX)

1 Introduction

The ternary ceramic compounds known as MAX phases have recently attracted considerable attention due to their nano-laminate atomic structure. Although discovered in the 1960s by Jeitschko *et al.* [1], the class of compounds M_{n+1}AX_n where $n = 1, 2, 3$, has lately generated great scientific interest. Barsoum and El-Raghy [2] synthesized single-phase bulk Ti₃SiC₂ and found it to exhibit high

electric and thermal conductivities, to be easy to machine, extremely stiff, and highly resistant to oxidation and thermal shock. In the form of thin films, these compounds are attractive due to their potential applications as ceramic coatings with unique properties in the areas stretching from nuclear industry to microelectronics. A review of thin film MAX phases has been published by Eklund *et al.* [3]. Some reviews on Cr₂AlC compounds were also published recently [4,5]. The main obstacle for utilising MAX phase films is perceived to be the high temperature required for synthesis of the crystalline matrix, which, for many MAX phase materials, is above 650 °C and severely limits the choice of substrate

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materials to be stable at this temperature.

Thin films of Cr_2AlC composition have reportedly been synthesized using magnetron sputtering techniques from elemental targets [6,7] and from compound targets [8,9]. In particular, using DC magnetron sputtering from a compound target, Walter *et al.* [8] have reported formation of single-phase Cr_2AlC thin films on stainless steel substrates heated at temperatures around 650 °C.

Very recent work emphasizes the surge of interest for this compound [10–22]. Due to its nano-laminate structure, Cr_2AlC has low hardness, high Young's modulus, and good compression strength; it is a good electrical and thermal conductor and has very good oxidation resistance. Among possible applications of Cr_2AlC , one can count protective coatings for turbine propellers in avionics [2] or self-healing materials [19]. Berger *et al.* [10] have studied the influence of the substrate temperature on the formation of the Cr_2AlC stable phase; however, their coatings had a mixed phase structure composed of $(\text{Cr,Al})_2\text{C}_x$ solid solution and ordered Cr_2AlC . Interesting studies on the effect of tuning of the sputtering powers [11] and of the substrate bias voltages [12] on the morphological and structural features of the Cr_2AlC coatings have also been recently published. Again, in these cases, a mixture of crystalline phases are found in the coatings, namely, Cr_2AlC , AlCr_2 as well as binary carbide phase Cr_7C_3 [11,12]. Further approaches towards the industrial applicability of such coatings have been reported in Refs. [13,14]. Smialek *et al.* [13] undertook studies of hot corrosion and low cycle fatigue on Cr_2AlC -coated high refractory alloys. It has been shown that the coating successfully prevents the hot corrosion pitting occurring in the uncoated samples. It has also been revealed that the presence of undesirable Cr_7C_3 phase diminishes the protection capability of the coating by promoting internal oxidation and favouring embrittlement of the coating. Other recent studies of MAX phase coatings [16–18] have also shown that the outcome of the obtained phase composition in the MAX coatings is highly influenced by the synthesis methods. For instance, sputtering from a Cr–Al–C hot-pressed composite target [17] was reported to yield crystalline Cr_2AlC coating; however, the synthesis implied hot pressing at 800 °C of the target followed by long time (20 h) annealing procedures at high temperature (620 °C) of the coating.

Another possible way to form the Cr_2AlC crystalline coatings could be to deposit the films at room temperature and to anneal them in air in order to promote the

crystallisation. For industrial application, it is of interest to minimise the complexity of technological steps for obtaining stable Cr_2AlC coatings and this includes the possibility of annealing in ambient conditions instead of controlled atmosphere. It is of interest to check whether this process oxidises the film and to characterise the resulting crystalline structures. The present work attempts to address these issues. As compared to previously cited research [10–12], our work shows that almost single-phase Cr_2AlC coating can be synthesized by DC sputtering via re-crystallization from amorphous-like precursor at rather low annealing temperatures (starting with 450 °C) with low oxygen contamination (only about 5% of the total film thickness) and induced (10 $\bar{1}$ 0) texture, a feature which may induce a beneficial anisotropic fracture behaviour in the coatings [20].

2 Experimental

For the Cr_2AlC thin film deposition, DC sputtering was performed in the S16 UHV/PVD ultra high vacuum chamber, from Intercovamex, Mexico (base pressure 2×10^{-4} Pa) with 3 DC power sputtering sources. The sputtering targets were made of elemental Cr (Alfa Aesar™, 99.95%), Al (Alfa Aesar™, 99.99%), and carbon (Alfa Aesar™, 99.999%). The power sources were adjustable in order to finely tune the desired chemical composition. For achieving the stoichiometry needed for the Cr_2AlC MAX phase, the cathode power has been settled at 85 W for Cr, 58 W for Al, and 155 W for C. The thin films were deposited onto Si (100) substrates (around 2 cm × 3 cm) in an Ar pressure of 0.02 Pa in the chamber. Before deposition, the substrates were Ar^+ sputter-cleaned for 45 min with the substrates heated at 100 °C. The deposition mode was static with the sample holder in fixed position. Deposition time was fixed at 150 min. Two samples at different temperatures were synthesized. Sample 1 was deposited on a substrate resistively heated to 450 °C using a resistive heater placed under the holder. Sample 2 has been deposited on the non-heated substrate at 150 °C (temperature reached inside the UHV chamber during deposition). The temperature was measured on the sample holder using a Pt resistance probe.

Post-deposition annealing treatments have been performed *ex situ* (in air) in a temperature-controlled oven with a 40 K/min heating rate. Pieces from as-deposited samples 1 and 2 were annealed at 650 °C

for 20 min (samples denoted with suffix “b”, e.g., 1b and 2b respectively) and 700 °C for 30 min (suffix “a”).

The chemical composition was measured by wavelength-dispersive X-ray spectroscopy (WDSX), while the phase structure and morphology have been investigated using grazing incidence X-ray diffraction (GIXRD) and scanning electron microscopy (SEM). A Bruker Advance D8 diffractometer has been used for the XRD studies, while SEM images were obtained using a Tescan Lyra field-emission gun scanning electron microscope with WDSX module. The XRD analysis was performed using the Cu K α radiation (operating voltage 40 kV and current 40 mA) in grazing incidence mode, typical for thin films, with an angle of incidence of the X-ray beam of 2°. XRD scans were performed with a 0.05° angle step between 10° and 85° (in 2 θ). Besides giving information about the chemical composition of the sample, WDSX has the advantage that it may quantify well the content of oxygen in the sample.

3 Results and discussion

3.1 Scanning electron microscopy

The surface of the thin films is uniform and relatively flat as shown in the SEM images in Figs. 1 and 2. The film is homogeneous throughout its whole thickness as can be seen in the cross-section image of the as-deposited sample 2 (Fig. 1). Both SEM images show an apparent thickness of around 1.9 μm . However, as the electron beam in SEM is perpendicular to the sample plane and therefore parallel to the coating edge of the sample, imaging the cross-section requires inclination of the sample holder at 45°. Therefore, SEM images presented show the thickness of the film which is a projection of the edge (real thickness) itself, inclined at 45°. To obtain the actual thickness of the film, the value measured on the image has to be multiplied by a factor 1.414 to give a real thickness of about 2.68 μm . It is worthwhile mentioning that the thickness has been measured also using X-ray reflectivity (XRR) and the measurements on the as-deposited sample 2 yield a value of 2.556 μm , quite close to the values determined by direct observation in SEM. For the as-cast sample 1, the value obtained by XRR (2.37 μm) is also quite close to that derived from the direct observation, which is about 2.49 μm (around 5% difference in the estimation by the two different techniques).

Fig. 1 SEM image of as-deposited film without substrate heating (sample 2). Film/substrate interface is marked on the image.

Figure 2 shows that there is little change after annealing at 700 °C. The surface of the coating preserves its uniformity after the annealing procedure and the thickness is almost the same.

3.2 Energy-dispersive and wavelength-dispersive X-ray spectroscopy analysis

The chemical composition of the as-deposited films has been found by EDX to be close to the nominal Cr₂AlC single-phase composition. The values for the Cr:Al:C relative composition were found by EDX to be 51 at%: 25 at%: 24 at%. The samples deposited onto the unheated substrate and onto the substrate heated to 450 °C show almost the same composition, within the error range of the experimental EDX technique. It is clear from the EDX data that the Cr L-lines significantly overlap with the oxygen K-line due to insufficient resolution of the EDX detector. This makes accurate assessment of oxygen concentration impossible by the deconvolution of EDX spectra. In order to assess oxygen content in the films, we have therefore used WDSX spectroscopy. In this case, deconvolution of X-ray spectra with three main line components allows a small oxygen peak to be seen in the as-deposited

Fig. 2 SEM image of the film annealed at 700 °C (sample 2). Film/substrate interface is marked on the image.

sample 1 (Fig. 3). After annealing, the area of the oxygen peak significantly increases (Fig. 4) due to oxidation of the film.

It is possible to utilise different electron energies for assessment of the oxide layer thickness and thereby to analyse how oxygen is distributed in the thin film after annealing. Results arising from the quantitative analysis of WDSX spectra are presented in Table 1.

Fig. 3 WDSX spectrum of the as-deposited sample 1. Peak deconvolution shows (shaded areas) the relative proportion of oxygen and chromium.

Fig. 4 WDSX spectrum of sample 1 annealed at 700 °C (sample 1a).

Table 1 Peak area and O:Cr relative content in the annealed sample at different electron beam energies

Beam energy (keV)	WDSX peak area integral			O Kα/Cr Lα
	Cr LI	Cr Lα	O Kα	
4	7374	2232	6684	3.0
6	7652	4833	7634	1.6
8	1116	7519	6647	0.9
10	13720	9259	6695	0.7
12	15361	10810	6798	0.6
14	16664	11395	6855	0.6
16	16635	12195	6340	0.5

In order to interpret the WDSX data, we have employed the modelling program Monte Carlo Simulation of Electron Trajectory in Solids (CASINO version 3.3). It was assumed that Cr_2O_3 is the only oxide form, as traces of Cr_2O_3 were found by full-profile MAUD analysis of the XRD pattern of the annealed sample 2. It was also assumed that the X-ray collection efficiency functions for both Cr Lα and O Kα are the same, which is a reasonable approximation as the line energies are quite close. The modelling shows that, to satisfy line integral ratios, the oxide layer should be approximately 120 nm thick, which is less than 5% of the whole film thickness. The integral ratio saturation at energies above 10 keV is explained by strong Cr Lα X-ray absorption in the material as X-ray of this energy can hardly escape from a depth larger than 300 nm.

3.3 X-ray diffraction patterns

The sample deposited without additional substrate heating (sample 2) appears to be amorphous. The part of this same sample annealed at 650 °C for 20 min (sample 2b) is also amorphous. The corresponding XRD patterns are presented in Fig. 5.

The XRD pattern of the sample deposited onto the heated substrate, sample 1, is presented in Fig. 5 together with the patterns corresponding to pieces from the same as-deposited sample annealed at 650 °C for 20 min and 700 °C for 30 min, respectively. The grazing-incidence 2θ geometry was chosen for the XRD analysis in order to minimize the strong signals arising from the Si (100) Bragg lines. The as-deposited film and the film annealed at 650 °C for 20 min show

Fig. 5 Grazing-incidence XRD patterns of the samples: as-deposited (sample 1), annealed at 650 °C for 20 min (sample 1b), and 700 °C for 30 min (sample 1a).

patterns with broad Bragg lines, centred at about 42° (in 2θ). In most alloys, such patterns are characteristic of a material structure made of small nanocrystals [23–25] with topological disorder [26,27] and dominant amorphous-like structure [28]. The broad Bragg lines observed in the patterns suggest the existence of a Cr–Al–C solid solution. The maximum of the broad Bragg line has the same value (42.2°) as the $(10\bar{1}3)$ Bragg peak of the hexagonal Cr_2AlC structure. It seems that the Cr–Al–C solid solution is the precursor from which the hexagonal Cr_2AlC phase may be formed after appropriate annealing.

The XRD pattern of the sample 1b, annealed at 650°C for 20 min shows a pronounced Bragg peak centred at about 40.6° seen as an appendix on the broad feature centred at $\sim 42^\circ$. The origin of this peak is uncertain. It appears in our several Cr_2AlC samples, always after intermediate stages of annealing (not complete crystallization) and disappears when full crystallization has occurred. We suggest that it may belong to a metastable phase that forms after intermediate annealing. Recent reports on crystallization kinetics of amorphous Cr_2AlC [29] show that annealing at intermediate temperatures (between 560 and 610°C) promotes formation of a metastable phase $(\text{Cr,Al})_2\text{C}_x$, distorted hexagonal, space group $P63/mmc$. A recent report by Berger *et al.* [10] confirmed that an XRD peak appearing at 40.6° in 2θ may belong to the (002) reflection of the $(\text{Cr,Al})_2\text{C}_x$ distorted hexagonal phase, therefore confirming our assumption. After annealing further at 650°C , the Cr_2AlC single phase is stabilized and the distorted hexagonal metastable phase disappears. In previous papers [11,12] it has been argued that proper identification of Cr_2AlC must consider also the presence of the (0002) reflections (at around 13.8° in 2θ). There are however some authors claiming the existence of Cr_2AlC phase without the occurrence of (0002) peak (*hkl* Bragg–Bravais notations) [8,18,20, 21,29]. With that said, we have however identified unambiguously both the (0002) and (0004) peaks in the all-crystalline sample, as analyzed hereafter.

The XRD pattern of the sample 1a annealed at 700°C for 30 min presents very sharp, well-defined Bragg lines that are all attributed to Cr_2AlC . It follows that, in this case, the film is completely crystallized. The only phase identified by XRD pattern analysis is the Cr_2AlC hexagonal structure, with the $P63/mmc$ space group. This finding is in agreement with previous reports [8] on crystallization behaviour of Cr_2AlC . It has been

shown by differential scanning calorimetry that the crystallization temperature of the bulk Cr_2AlC is between 670 and 680°C , a fact that explains the occurrence of the full crystalline structure only after annealing at 700°C [8].

A more detailed XRD pattern is found in the case of the sample 2a annealed at 700°C for 30 min (Fig. 6). In this case, the less intense Bragg reflections of (0002) , (0004) , and $(10\bar{1}6)$ of the hexagonal structure of Cr_2AlC are also observable. For this sample, the hexagonal Cr_2AlC is found to be the main phase observed (more than 95% of the total intensity of the Bragg reflections). Small, non-indexed peaks in Fig. 6 are possibly attributed to Cr_2O_3 . The full-profile detailed analysis of the spectrum (see the next section) confirms the presence of a small amount of Cr_2O_3 suggesting that the oxygen uptake is mainly restricted to the surface of the film. This finding confirms the results from the detailed WDSX analysis reported in Section 3.2.

3.4 XRD analysis procedure

We have applied full-profile refinement procedure on the XRD patterns in order to obtain with accuracy the phase composition as well as structural parameters such as lattice parameters, unit cell volume, average grain size, and lattice microstrain using the integral breadth method as well as the possible crystallographic texture.

The patterns have been fitted using MAUD [30] and Datlab [31] programs. These powder diffraction packages, developed for polycrystalline multiple phase materials, allow deconvolution of complex overlapping Bragg

Fig. 6 Grazing-incidence XRD pattern of the sample 2a annealed at 700°C for 30 min. Peak indexing, as resulted from the full-profile analysis is given on the figure.

peaks, calculation of position and line-width of each individual Bragg reflection, and determination of lattice parameters. Datlab has been used for the peak analysis and calculation of lattice parameters in the as-deposited and annealed samples, while MAUD was used to quantitatively determine the phase composition in the samples.

The deconvolution of complex broadened Bragg peaks typical for amorphous systems requires some additional notes. As it is known, long-range-order (LRO) defines ordered (crystalline) structures while short-range-order (SRO) defines disordered structures. Loss of LRO causes the appearance of disorder in the solid state by mainly two mechanisms [32]: (1) thermodynamic disordering that leads to occurrence of the amorphous phase, characterized (among other models) by the “random close packed” model; (2) kinetic disordering (a continuous disordering process) that leads to occurrence of nanocrystalline materials, solid solutions or glassy states (as in bulk metallic glasses), characterized by the “continuous random network” model. Of most importance is the fact that kinetic disordering preserves the local crystalline symmetry into the glassy state, at a range defined by the SRO. In terms of XRD patterns, both amorphous and glassy states will show broad peaks but with different features. Visually, while in the pure amorphous state the broad line presents a “hill-like” allure, in our as-deposited sample the broad line presents a “mountain-like” allure with a clearly defined tip of the peak.

During crystallization, initially formed nucleation sites continuously grow to form nanocrystals and, furthermore, nanosized grains. Depending on the crystallization mechanism, i.e., nucleation or growth or a combination of both, the microstructure during the crystallization process changes continuously. These changes are visible in the XRD patterns by the sharpening and better resolution of the Bragg peaks. If one sees the process in reverse, as the crystallite size reduces the XRD peak line-widths increase up to a point where Cr_2AlC peaks are convoluted into a large amorphous peak. It is important to note that the position of this broad peak corresponds to the position of the $(10\bar{1}3)$ peak of the hexagonal Cr_2AlC structure. This is no coincidence, as the broad line arises as a convolution of the several broadened Bragg lines (closely positioned) of the hexagonal structure. Some peaks ($(10\bar{1}0)$ at around 36.3° and $(10\bar{1}3)$ are nevertheless visible as kinks or tips on the broad peak feature (Fig. 5). This is the

reason why we consider the as-deposited state as being an amorphous Cr-Al-C solid solution with hexagonal structure since it is the metastable precursor from which the crystalline structure emerges after annealing. A similar metastable precursor with hexagonal symmetry has also been reported for early stages of crystallization for amorphous Cr_2AlC in Ref. [29]. Our fitting method is based on the full-profile Rietveld-type analysis extended towards kinetically disordered materials by including the pair distribution function.

MAUD numerical fitting (line) of the XRD pattern (symbols) for the crystallized sample 2a shows that, apart from the Cr_2AlC hexagonal phase, the presence of rhomb-centred hexagonal Cr_2O_3 phase has been confirmed in the XRD pattern by indexation of several observed peaks that do not belong to the main ternary phase. For instance, the main Bragg line (104) of the rhomb-centred hexagonal Cr_2O_3 (PDF file No. 38-1479) at around 33.6° (in 2θ) is clearly observed and cannot be attributed to other phases, neither ternary (Cr-Al-C) nor binary (Cr_7C_3 or AlCr_2). The indexation of that peak is provided in Fig. 6.

Quantitative analysis based on whole profile fitting shows that, in the crystallized sample 2a, the Cr_2AlC represents 95.5 wt% of the sample while the Cr_2O_3 represents 4.5 wt%, a finding that is confirmed by WDSX results, depicted in Section 3.2.

The Bragg peaks of the diagrams have been fitted to a pseudo-Voigt line profile. The Voigt profile is a spectral line that can account for peak broadening by two mechanisms. The first one is strain-related and would produce a Gaussian profile, and the other is related to the size of the grains and would produce a Lorentzian profile.

By using the lattice parameters, line-widths, and mixing parameters obtained for each Bragg reflection, we were able to calculate the average grain size which is defined as being the average crystallographic coherent domain size. The method we used is based on the integral breadth algorithm.

The integral breadth β is defined as the peak area divided by the maximum height of the peak. The integral breadth method summarized in Ref. [33], calculates the root-mean-square strain (RMSS) and both surface- and volume-weighted domain sizes according to the “double-Voigt” method [34,35], which is equivalent to the Warren–Averbach approach [36].

In sputtered films, due to different diffusion mechanisms as well as the influence of the preferential

growth direction imposed by the alignment of the substrate lattice, stress is expected to be induced during deposition and, consequently, the lattice microstrain between the atomic planes should be significant. RMMS is defined as the amount (change in size or volume) by which a crystal lattice deforms under stress or force and is given as a ratio of the deformation to the initial dimension of the lattice.

The results of the fittings are given in Table 2. The lattice parameters resulted from the fit as well as the unit cell volume are quite close to the values for the bulk Cr_2AlC . While a changes slightly upon annealing, c parameter shows a 5% decrease upon annealing. The unit cell volume is also bigger for the as-deposited sample compared to the annealed samples. This behaviour may be explained by an atomic structure refinement effect [37] during material crystallisation. The obtained lattice parameters are affected by the errors due to the numerical fitting of the XRD patterns, and therefore this lattice evolution upon annealing is to be considered only qualitatively. It is observable that the grain size increases with increase in the annealing temperature from 6.6 nm, in the case of the as-deposited sample, to 14 nm in the case of the sample annealed at 650 °C while, for the two completely crystallized samples, the Cr_2AlC crystallites increase in size up to average values of about 23 and 32 nm, respectively. The reliability of the fitting is proven by the difference between experimental and fitted points and also by providing the chi-square (or goodness of fit $GofF$) and R_{wp} factor of each fitting (Table 2).

We have compared our lattice parameter data with the *ab-initio* data from Mertens *et al.* [7] and Schneider *et al.* [6]. According to Mertens' calculations, our results for the annealed (crystallized) films do not match a perfect Cr_2AlC hexagonal structure but a $\text{Cr}_2\text{Al}_{1.1}\text{C}$ hexagonal structure with stacking faults, as calculated using the VASP code. Our results are also close to those determined by Schneider *et al.* for paramagnetic configuration of Cr_2AlC , with slight deviations due

perhaps to the presence of oxygen impurities in the hexagonal lattice of the annealed samples, as a consequence of the in-air annealing procedure.

In general, growth of coatings occurs with preferential spatial orientation. There are several theories that try to explain this preferential growth during sputtering. The minimization of the surface energy and deposition parameters are among the factors invoked to explain preferential growth of coatings on substrates [21]. It has been shown that, in the early stages of deposition, surface energy dominates the preferential growth and the tendency is for in-plane growth anisotropy [38,39]. With increase in film thickness, strain energy predominates and the growth may be preferential in the out-of-plane directions. It is possible from XRD measurements of the fully crystalline samples to estimate the preferential orientation of growth by investigating the texture coefficient which can be calculated using the following formula [21,39]:

$$T_{hkl} = n \cdot (I_{hkl} / I_{hkl}^0) \cdot \sum_n I_{hkl} / I_{hkl}^0 \quad (1)$$

T_{hkl} is the texture coefficient of the corresponding Bragg reflection, I_{hkl} is the integral intensity as determined by numerical fitting of XRD patterns, I_{hkl}^0 corresponds to the bulk Cr_2AlC Bragg peak intensity (from the ICDD file), and n is the number of Bragg peaks observed.

The texture results for the $(10\bar{1}0)$, $(10\bar{1}3)$, and $(11\bar{2}0)$ Bragg lines are presented in Table 3. One may notice that the texture coefficient for the $(10\bar{1}3)$ Bragg line is < 1 while the highest texture coefficient is observed for the $(10\bar{1}0)$ Bragg line. It may be concluded that there is a slight preferential growth of the Cr_2AlC coating in the $(10\bar{1}0)$ direction.

Studying the effect of the composition on the structure of Cr–Al–C, Mertens *et al.* [7] correctly pointed out that, while deviations from stoichiometry in MAX phases have been experimentally observed, XRD patterns do not indicate the presence of a second phase. According to the ternary phase diagrams, deviations from stoichiometry should result in formation of

Table 2 Lattice parameters, average crystal size, and microstrain for the investigated samples. R_{wp} and χ^2 (goodness of fit) are also provided

Sample	Lattice parameter			Crystal size (nm)	Microstrain (%)	R_{wp}	χ^2
	a (Å)	c (Å)	V (nm ³)				
1	2.86±0.08	13.6±0.07	0.095	6.6±2.8	0.79±0.08	2.12	3.86
1b	2.84±0.006	13.18±0.01	0.092	14.2±3.2	0.37±0.05	1.05	2.27
1a	2.83±0.02	12.92±0.01	0.088	34.3±2.6	0.24±0.03	0.67	1.15
2a	2.84±0.02	12.95±0.02	0.088	23.6±2.2	0.35±0.01	0.58	1.23

Table 3 Texture coefficient results for the two fully crystalline thin films

Sample	Texture coefficient		
	(10 $\bar{1}0$)	(10 $\bar{1}3$)	(11 $\bar{2}0$)
1a	1.34	0.43	1.08
2a	1.23	0.79	1.03

supplemental binary phases. Based on XRD results and *ab-initio* calculations, they conclude that deviations from stoichiometry of up to 6.3 at% Al (or Cr/C ratio between 1.72 and 1.93, Cr/Al ratio between 1.42 and 2.03) still result in occurrence of only a single Cr₂AlC phase, in the XRD patterns. Possible pathways for accommodating these deviations were presented by Mertens *et al.* [7] under a model that explains these extended compositional ranges by “segregation of material which escapes detection by XRD, segregation of an amorphous phase or another phase that cannot be detected by XRD”. They calculate, by *ab-initio* VASP code, various structures including a perfect Cr₂AlC, stacking fault hexagonal structure with Al excess and structures obtained by interstitial Al substitutions. As previously mentioned, compared with Mertens *et al.*’ results, our values for the lattice parameters and unit cell volume for fully crystallized samples 1a and 2a, fit within the model of a Cr₂Al_{1.1}C hexagonal structure with stacking faults.

4 Conclusions

Ternary compounds of composition Cr₂AlC belonging to the class of so named MAX phases were deposited by DC sputtering onto Si substrates at 100 °C (substrate not heated) and at 450 °C (substrate heated). The film deposited without additional substrate heating is amorphous. It was shown that, for 450 °C deposition temperature, even if the sample is largely amorphous-like, there is partial crystallisation of the as-deposited film, the small nanocrystals formed having a size of about 6.6 nm and a microstrain value at around 0.79%, as determined from full-profile MAUD analysis of XRD patterns. Annealing of the film in air at 700 °C leads to crystallite growth to a size of 32 nm and reduction of the microstrain to 0.24%. The demonstration of a microstrain reduction is a significant finding, being extremely important for coatings as it allows better adhesion and prevents delamination of the coating in practical applications. There is also partial oxidation

of the film which has been investigated by WDSX spectroscopy with spectra taken at different electron beam energies. WDSX results combined with calculations by means of Monte Carlo Simulation of Electron Trajectory in Solids have shown that the oxide layer is less than 5% of total film thickness. This indicates the possibility that films can be crystallized in air without significant oxygen contamination. A tendency of preferential growth of the films along the (10 $\bar{1}0$) direction was determined by the texture analysis. This preferential growth may induce a beneficial anisotropic fracture behaviour in the coatings as demonstrated in Ref. [20]. The XRD pattern fitting results are consistent with a possible Al excess in the Cr₂AlC hexagonal structure, as revealed by comparing our calculated lattice parameters with *ab-initio* data previously reported [7].

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