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Research Article

Growth Kinetic Effects on MAX Phase Thin-Films Microstructure

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Abstract

In this paper, Ti_3SiC_2, Ti_3AlC_2 and Ti_2AlC thin films were synthesized using a two-step method consisting on $TiAl_2$ magnetron sputtering deposition and post-deposited annealing at 800°C or 1000°C. X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) were used for the phase identification and microstructure studies. We focused on the kinetic effect of MAX phase growth influenced by annealing time of one and several runs. The results obtained show that for one annealing during 30min we synthesized Ti_3AlC_2 or Ti_3SiC_2 respectively for 800°C and 1000°C. Although the total thermal energy provided by annealing steps is equal in each case, one annealing run leads to a very pure 312 MAX phase (Ti_3AlC_2 at 800°C and Ti_3SiC_2 at 1000°C), while the interruption during the annealing and the increase cooling step number for the same total annealing time leads to the 211 MAX phase for 800°C and to a mix between Ti_3AlC_2 and Ti_2AlC for 1000°C.

Keywords: MAX phase; Thin films; Epitaxy; Magnetron sputtering; kinetic effect

Introduction

$M_{n+1}X_n$ phases (n =1-3) consist in a large class of nanolaminated materials where M is an early transition metal element, A is an A-group element and X is either C or N [1-5]. For n = 1,2,3 the MAX phases are respectively called 211, 312 and 413 due to the periodic arrangement of their structure: n M_6X octahedrons separated by a layer of A element in a hexagonal structure. This particular structure gives to the MAX phases a unique combination of metal and ceramic properties, opening the way to a large field of applications [6,7]. The Ti_3SiC_2 and Ti_2AlC MAX phases have been extensively studied due to their excellent properties, including irradiation resistance [8-10], oxidation resistance [11] and electrical properties [12,13]. Several different techniques have been used to synthesize bulk MAX phases. Among these techniques, the most widespread is hot isostatic pressing (HIP) [14] however, various techniques have been developed for the growth of MAX phase thin films using magnetron sputtering technology, either from elemental targets or from compound targets on various substrates [15,16]. As shown on our recent papers, the co-deposition of Ti and Al on SiC-4H substrates leads, depending on annealing conditions, to the formation of either Ti_3SiC_2 or Ti_2AlC [17]. Despite the huge number of studies achieved on MAX phases the formation mechanisms are not well-known. In this paper, we report on correlation between annealing process (temperature, run number, time of run) MAX phase kinetic growth.

Materials and Methods

SiC-4H substrates, single crystal (0001), n-type, supplied by TANKEBLUE, were used in this study. Al and Ti were co-deposited at room temperature onto SiC substrates by magnetron sputtering using pure Al (99.999%) and Ti (99.995%) targets in a high vacuum chamber (Figure 1), the Ar working pressure has been fixed at 0.3 Pa. Before deposition, the substrate was in-situ cleaned by an etching at 60V during 600s. As shown Figure 1 the fresh $TiAl_2$ deposited layer is nanocrystalline. The samples were annealed in a vacuum lamp furnace (heating rate close to 20°C s^{-1}) at 800°C or 1000°C during one run of 30min or 3 runs of 10 min for each temperature under a pressure around 10^{-5}Pa. Composition and thin film thickness have been checked using X-ray reflectometry (3000 Seifert) and SEM techniques (JEOL 7001 TTLS). The structural investigations were performed by using X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). Diffraction experiments were conducted on a D8 Brucker AXS diffractometer operating in the Bragg-Brentano geometry under atmosphere environment. Diffractometer operates with a Cu tube and the Kβ radiation is absorbed by a Ni filter in order to obtain a pure Cu Kα radiation (λ = 0.15418nm). The LynxEye detector is used for ω-2θ scans with a slight offset to avoid SiC reflections (ω-2θ=0.2°). High-Resolution TEM and Scanning Transmission Electron Microscopy (STEM) images were carried out using a JEOL 2200FS (Schottky-FEG, 200kV). TEM samples were prepared by Focused Ion Beam (FIB) using an FEI-HELIOS dual-beam using the standard lift-out method [18].

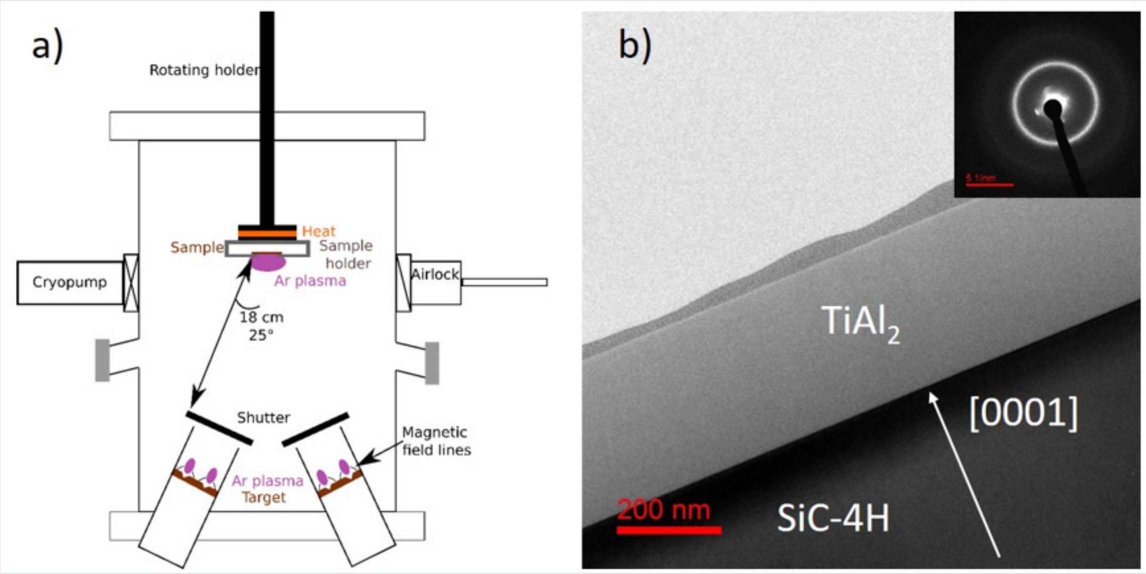

Figure 1: a) PUMA chamber scheme. b) TEM micrography of fresh of fresh $TiAl_2$ deposited layer and associated diffraction pattern. The diffraction pattern clearly indicates the nanocrystalline structure of the $TiAl_2$ layer.

Results

Figure 2 shows X-ray diffractograms of $TiAl_2$, 300nm thick on SiC annealed at 800°C 1 x 30min and 3 x 10min. Both diffractograms exhibit a peak at 39.2° corresponding to $(10\bar{1}4)$ reflection of the Ti_3AlC_2 MAX phase structure. Moreover, the sample annealed during 1 x 30min shows exclusively Ti_3AlC_2 MAX phase diffraction peaks, unlike the 3 x 10min sample also exhibits the (0002) and (0006) diffraction peaks of the Ti_2AlC MAX phase respectively at 9.7° and 39.7°. However, additional peaks could be observed and attributed to secondary phases. For 1 x 30min, peaks at 42.15° and 42.71° are attributed to (300) and (112) reflections of Ti_5Si_3. For 3 x 10min one peak at 46.0° (not shown here) corresponds to (200) reflection of tetragonal $TiAl_2$ phase and one peak at 42.7° corresponds to the (112) reflections of Ti_5Si_3. The diffraction peak at 38.9° corresponds to SiC-4H substrate. Figure 3 shows X-ray diffractograms of $TiAl_2$ 300nm thick on SiC annealed at 1000°C for both annealing strategies. For 1 x 30min, we observed four peaks at 10.05°, 20.12°, 30.37° and 40.82° corresponding to (0002), (0004), (0006) and (0008) reflections of Ti_3SiC_2 MAX phase. Moreover, the only secondary phase presents is the Ti_5Si_3 structure leading to (300) and (112) reflections at 42.15° and 42.71°. The diffractogram of 3 x 10min exhibits two peaks at 9.7° and 39.2° corresponding to the (0002) and $(10\bar{1}4)$ of Ti_3AlC_2 MAX phase, three peaks at 13.0°, 39.7° and 40.2° corresponding to the (0002), $(10\bar{1}3)$ and (0006) of Ti_2AlC MAX phase, one peak at 42.1° corresponding to the (112) of Ti_5Si_3. Figure 4 shows the thin films obtained on SiC-4H for $TiAl_2$ -300nm after annealing at 800°C and 1000°C during 30min. The diffraction patterns obtained and the analysis of HRTEM micrographs reveal Ti_3AlC_2 and Ti_3SiC_2 MAX phase thin film structure consistent with XRD investigations. Moreover the MAX phases grows in epitaxy with SiC - 4H following the relation (0001)MAX // (0001)SiC and $[1\bar{2}10]$ MAX// $[1\bar{2}10]$ SiC. The samples corresponding to 800°C and 1000°C annealed during 3 x 10min (not shown here) exhibit the same epitaxial relationship between the substrate and the layer formed at the interface. However, considering the 1000°C sample the MAX phase isn't Ti_3SiC_2 anymore but Ti_3AlC_2. STEM micrography (Figure 5) clearly indicates the presence of two different structures in the MAX phase layer. Measured spacing between atomic planes are 1.8nm for the interfacial layer and 1.3 nm for the upper layer respectively corresponding to the 312 and 211 MAX phases. As observed on STEM micrographs, all films, whatever kind of MAX phases synthesized, are very flat (Figure 6) and exhibits a very good crystallinity (high chemical homogeneity and almost monocrystalline). The total thickness of the stacking of MAX phase are closed to 30nm and 40nm respectively for 800°C–3 x 10min and 1 x 30min and closed to 80nm and 150nm respectively for 1000°C - 3 x 10min and 1 x 30min.

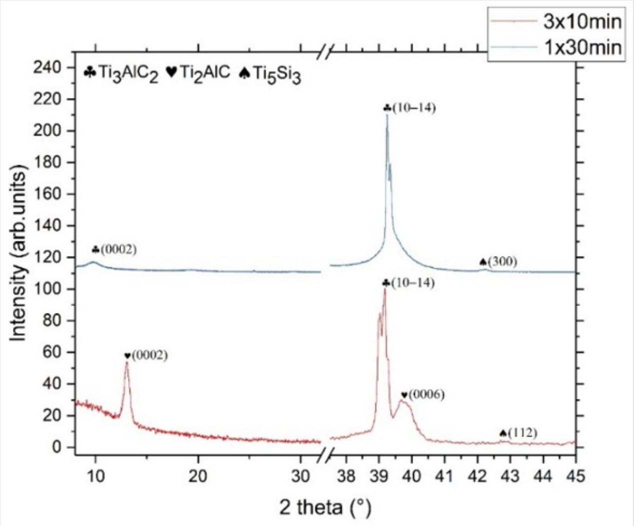

Figure 2: ω - 2θ XRD diffractograms of TiAl$_2$ - 300nm thick onto 4H-SiC annealed at 800°C during 1x30 min and 3x10 min.

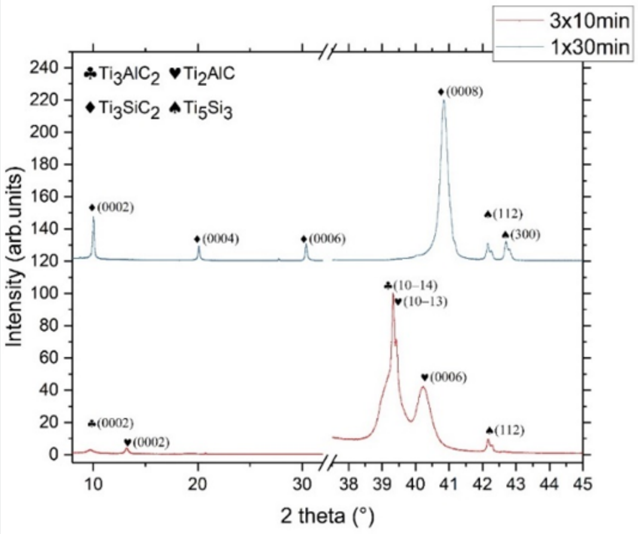

Figure 3: ω - 2θ XRD diffractograms of TiAl$_2$ - 300 nm thick onto 4H-SiC annealed at 1000°C during 1x30 min and 3x10 min.

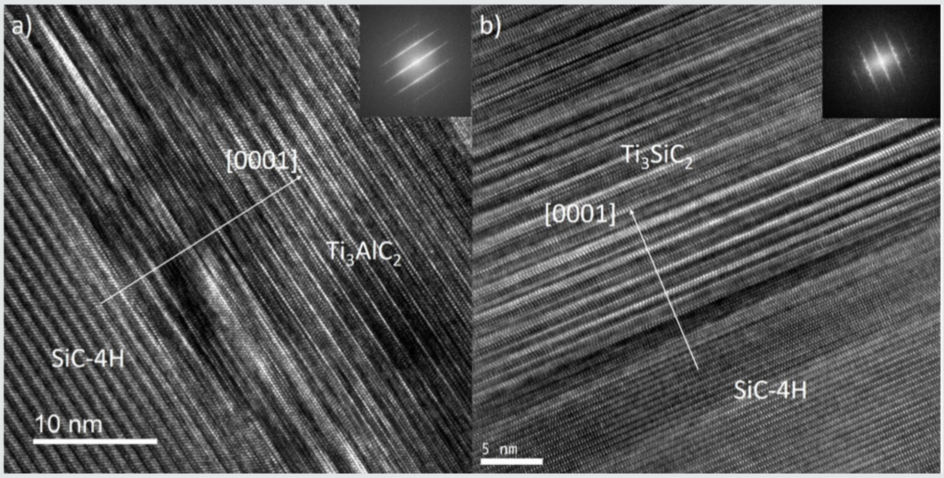

Figure 4: HRTEM micrography of TiAl$_2$-300nm annealed at a) 800°C – 1 x 30 min and b) 1000°C – 1 x 30 min and associated diffraction patterns. The diffraction patterns can be indexed using SiC-4H and respectively Ti$_3$AlC$_2$, Ti$_3$SiC$_2$ structures on [10-10] zone axis.

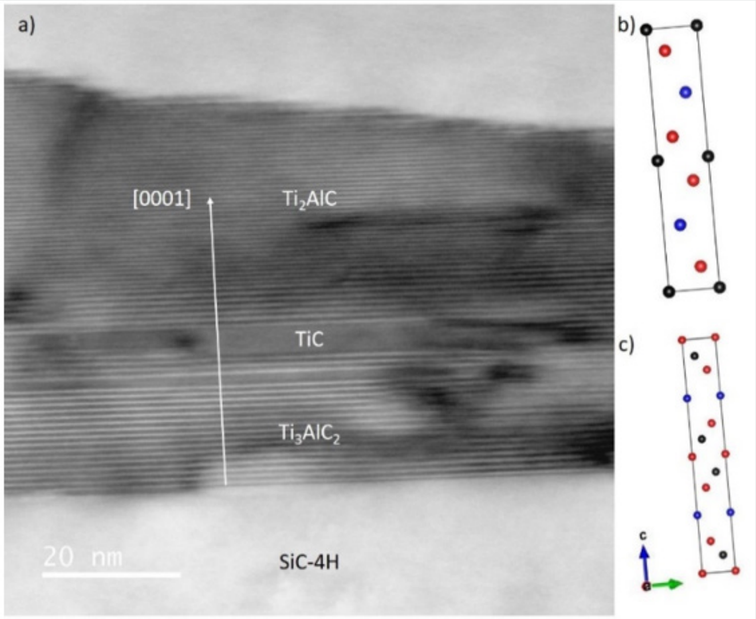

Figure 5: a) HRSTEM micrography of $TiAl_2$ -300nm annealed 1000°C 3x10min, b) and c) represent respectively the Ti_2AlC and Ti_3AlC_2 structure. Black, red and blue dots correspond respectively to C, Ti and Al atoms.

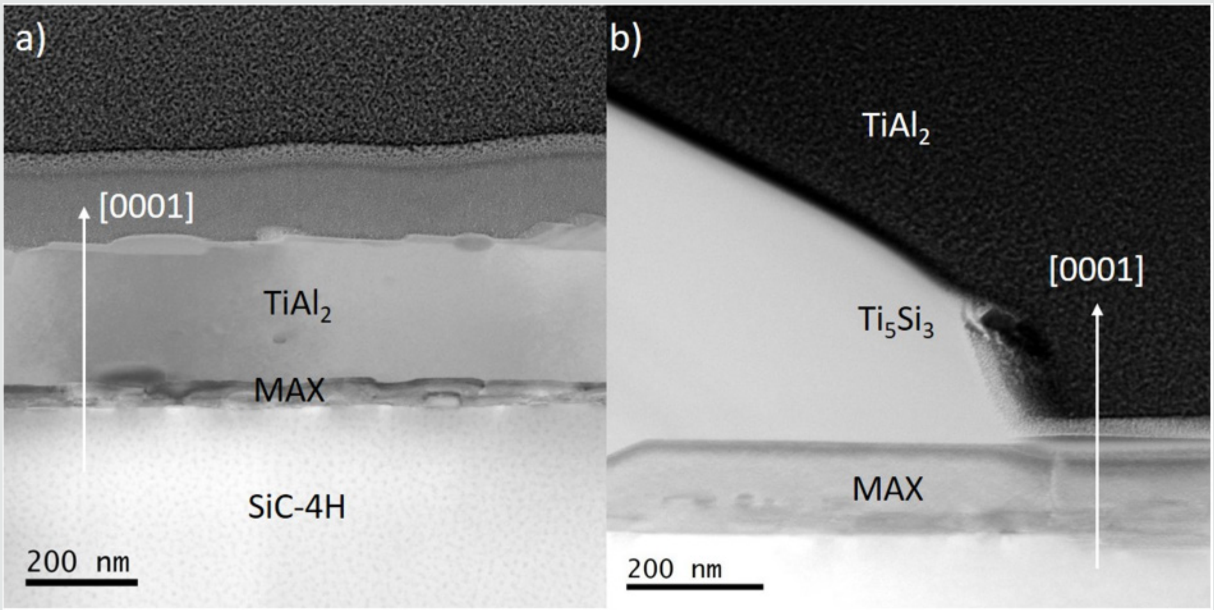

Figure 6: STEM micrographs of TiAl2 - 300nm annealed at 1000°C a) 3x10min and b) 1x30min. The MAX phase stacking layer is respectively 80nm and 150nm thick.

Discussion

As shown Figures 2,3,4 the annealing of the $TiAl_2$ layer leads to the formation of an epitaxial MAX phase thin film onto SiC - 4H whatever successive runs used (long time or several successive short times). For 1 x 30min the structure of this MAX phase is Ti_3AlC_2 or Ti_3SiC_2 depending on annealing temperature, respectively for 800°C and for 1000°C. The formation of 312 MAX phase at low temperature is very interesting and absolutely not expected, indeed, it has been showed that for bulk sample the 312 structure should be formed only at very-high temperature [19,20]. In the case of fast temperature increase, thermodynamical equilibrium isn't respect anymore. Thus, only thermodynamical consideration used in previous studies aren't enough anymore and kinetic effect couldn't be avoid. XRD and TEM experiments indicate that annealing process has an influence on MAX phase structure and properties. Moreover, the MAX phase thickness is also impacted. Indeed, for successive short annealing time, and consequently several cooling temporizations, the layer isn't as thick as the one long run annealing process sample. For multi-step annealing process we assume that the early stages of MAX phase formation have been already explained as follow:

$$SiC + TiAl_2 \rightarrow TiC + (Al,Si)_l \qquad (1)$$

which is in a good agreement with purely thermodynamic considerations [20]. This kind of reaction leads to an epitaxial growth. Then, the reaction continues with the second step:

$$2\ TiC + Al \rightarrow Ti_2AlC + C \qquad (2)$$

leading to the formation of Ti_2AlC and extra silicon atoms (Figure 7). We assume that Si segregates above the Ti_2AlC and stay at the interface between the MAX phase and $TiAl_2$ layer. Indeed, calculations indicate a fast kinetic diffusion of Al atoms in the TiC structure to form Ti_2AlC [21]. Moreover, due to the fact that the $Ti_{n+1}SiC_n$ system does not have the 211 phase, the silicon cannot substitute Al species in the Ti_2AlC MAX phase [22]. During the cooling, the Si reacts with unconsumed $TiAl_2$ to form a very stable Ti_5Si_3 structure. In the same time, we assume that the upper $TiAl_2$, not yet involved in these two previous steps, will crystallize. Thus, the formation of Ti_2AlC MAX phase is a two steps reaction. After cooling, the stacking of all phases is shown (Figure 7), from the top to the interface : polycristalline Ti_3Al_2 / Ti_5Si_3 / Ti_2AlC / SiC. When the annealing is resumed, Ti element has to diffuse toward SiC interface to create TiC, going through MAX phase or MAX phase and Ti_5Si_3 either if Ti become from Ti_3Al or Ti_5Si_3. We assume that the stability of MAX phase is enough strong to unconsidered creation of TiC with Ti originated from MAX Phase. By this way the Ti diffusion process is slow, thus the TiC formation is a very slow process. However, it occurs leading to the following reaction (Figure 7):

$$Ti_2AlC + Ti + SiC \rightarrow Ti_2AlC + TiC + Si \rightarrow Ti_3AlC_2 + Si \qquad (3)$$

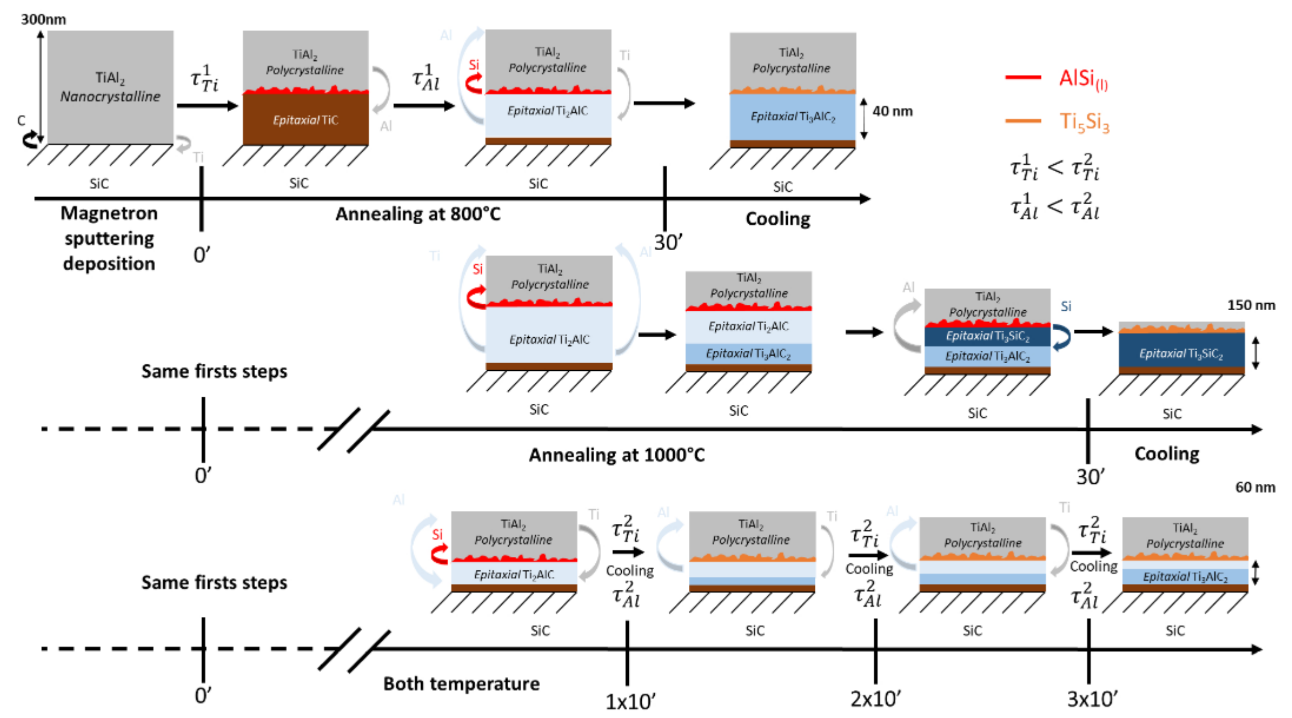

Figure 7: Representation of the mechanisms involved as a function of the temperature and the number of annealing steps (1x30min or 3x10mn), with $\tau^1_{(Ti,Al)}$ and $\tau^2_{(Ti,Al)}$ represent the diffusion time constant of Ti or Al element from the Fick equations for the one annealing step (1x30min) and several steps (3x10min) respectively.

The described mechanisms occur for both, 800°C and 1000°C, but considering that diffusion mechanisms increase with temperature, we assume that Ti diffusion process is higher for 1000°C leading to a thicker Ti_3AlC_2 than for 800°C, which is in a good agreement with XRD (Figure 2). Indeed the 312/211 intensity ratio is much higher for 1000°C than for 800°C. Moreover, considering TEM observations, and due to the high theoretical intensity diffraction of $\left(10\bar{1}4\right)$ MAX phase plane we considered that the formation following this orientation isn't really representative of MAX phase growth mechanisms. For one-single annealing process, we consider that the first reactions are similar. Moreover, considering that the thickness of MAX phase formed is thinner for annealing process having cooling temporization, we can traduce this information by a longer diffusion kinetic (longer diffusion time or lengths) of diffusing species. Without cooling, Ti has to diffuse only in $TiAl_2$ and first MAX phase monolayers in growth indeed Nowadays we don't know if the diffusion of Al is during the cooling or during annealing. If the Al diffuses during cooling only, Ti should diffuse only in $TiAl_2$.Unfortunately, diffusion time and length of Ti in different phases involved is not known. So, the first hypothesis is the increase of Ti diffusion time and length in Ti_5Si_3 + Ti_2AlC than in $TiAl_2$ + Ti_2AlC. The second hypothesis is the same concerning Al diffusion kinetics. Thus, the Ti_2AlC completely turns into Ti_3AlC_2. The XRD and TEM experiments show after 1 x 30min that for 800°C the Ti_3AlC_2 MAX phase is formed while for 1000°C after the MAX phase formed is Ti_3SiC_2. By this way, we assume that at 1000°C the Si can diffuse through the Ti_3AlC_2 structure and can substitutes Al atoms of Ti_3AlC_2 considering the following reaction:

$$Ti_3AlC_2 + Si \rightarrow Ti_3SiC_2 + Al \qquad (4)$$

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This kind of phenomena has been already observed with Au and Ti$_3$SiC$_2$ [23]. Finally during the cooling the Ti$_5$Si$_3$ structure is formed leading to the stacking: SiC /312 MAX phase / Ti$_5$Si$_3$ / TiAl$_2$ (Figure 7) Representation of the mechanisms involved as a function of the temperature and the number of annealing steps (1x30min or 3x10mn), with $\tau^{1}(Ti,Al)$) and $\tau^{2}(Ti,Al)$ represent the diffusion time constant of Ti or Al element from the Fick equations for the one annealing step (1x30min) and several steps (3x10min) respectively.

Conclusion

In this paper we demonstrated the possibility to synthesize Ti$_2$AlC, Ti$_3$AlC$_2$ or Ti$_3$SiC$_2$ thin-film onto SiC - 4H using a common two-steps method by tailoring temperature and time running indeed, for similar thermal cumulative energy (30min at setpoint temperature) the obtained MAX phase structure depends on the annealing process. At low temperature (800°C): one single-step process leads to the formation of Ti$_3$AlC$_2$ MAX phase while multi-step process leads to the formation of Ti$_2$AlC MAX phase with a few quantity of unepitaxial Ti$_3$AlC$_2$. At high temperature (1000°C): one single step leads to the formation of very pure Ti$_3$SiC$_2$ while multi-step process leads to the formation of a Ti$_3$AlC$_2$ - Ti$_2$AlC mixture. We assume that similarly to low temperature the multi-step process decreases the kinetic of the reaction leading to an incomplete transformation of Ti$_3$AlC$_2$- Ti$_2$AlC to Ti$_3$SiC$_2$.

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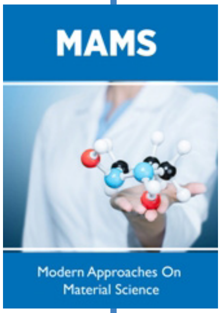

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