Structural and chemical characterization of Al-containing (Ti,Zr)C thin films sputter-deposited from a (Ti,Zr)$_2$AlC target

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Abstract

We report on the synthesis of (Ti,Zr)C containing Al deposited using a compound (Ti,Zr)$_2$:AlC MAX phase target. The structure, chemistry and microstructure of the films are discussed and have shown that Al distorts the crystal structure of the solid solution carbide. Furthermore, depositions of more than 60 min have resulted in films containing MAX phase features. The compositional analysis of these features has shown that the composition varies from a Zr-rich to a Ti-rich MAX phase. Furthermore, we show that there are two steps towards the growth of the MAX phase: first the deposition of a seed layer whose composition varies from Zr-rich to Ti-rich with low Al content and second the growth of the MAX phase-containing carbide.

Keywords: Thin films, mixed carbides, MAX phase
1. Introduction

The carbides based on early transition metals are an important class of materials in applications related to cutting and drilling tools. Particularly cubic carbides, but also nitrides, are very promising because of their high hardness.\textsuperscript{1–4} Beyond the traditional binary carbides, more complex phases exist, including the so-called MAX phases and complex pseudobinaries that sometimes occur as intermediate step.\textsuperscript{5,6} The formation processes of these classes of materials can thus be influenced by the presence of pseudobinary phases which allow the MAX phase to grow by diffusion-controlled processes.

While some MAX phases have been directly deposited without the need of a seed layer at lower temperatures (\textasciitilde 500 °C), in the case for example of Cr$_2$AlC\textsuperscript{7,8}, MAX phases in the Ti-Al-C systems are usually deposited at higher temperatures and often require either a seed layer of TiC$_x$ and/or an annealing step\textsuperscript{9–11}. Indeed, Wilhelmsson et al. have discussed the deposition of ternary films in the Ti-Al-C system, using a seed layer of TiC$_x$.\textsuperscript{11} They have shown that MAX phases are obtained at high temperatures (> 800 °C), while Al starts dissolving in the TiC$_x$ seed layer at temperatures as low as 300 °C. In PVD, nonequilibrium phases can readily occur. For example, in Ti-Al-C films, the dissolved Al content can be much higher than the equilibrium concentration. Furthermore, Frodelius et al. have reported the deposition of a (Ti, Al)C solid solution when attempting to deposit the MAX phase from a Ti$_2$AlC compound target.\textsuperscript{12}

Sputter-deposition from elemental targets is typically preferred for research on growth processes as a finer control of the composition can be attained. However, industrial development requires simpler and faster processes. One way of going about is to use compound targets. While the use of a single target simplifies the deposition conditions, the composition obtained in the film may be different than that of the target at discussed in several cases for Ti$_3$SiC$_2$\textsuperscript{13,14}, Ti$_2$AlC\textsuperscript{12} and Cr$_2$AlC\textsuperscript{15}.

Here, we investigate the carbide phases formed when growing from a (Ti,Zr)$_2$AlC target using sputter-deposition at various substrate temperatures. Initial growth of (Ti,Zr)C carbides was observed for deposition times of 30 min. Longer deposition times at 900 °C have resulted in films containing more than one phase of which the MAX phase.

2. Experimental Details

ZrH$_2$ (<6 \(\mu\)m, >99% purity, Chemetall, Germany), TiH$_2$ (<8 \(\mu\)m; >99% purity; Chemetall, Germany), Al (<5 \(\mu\)m, >99% purity, AEE, United States), and C (<5 \(\mu\)m, >99% purity, Asbury
Graphite Mills, United States) powders were used as starting materials for the MAX phase target synthesis. Ti:Zr:Al:C ratio of 26:28:19:27 were dry mixed for 48 h in air and sintered under vacuum (~10 Pa), using reactive hot pressing (W100/150-2200-50 LAX, FCT Systeme, Frankenblick, Germany) in a graphite die setup with 56 mm diameter. Sintering was done at 1450°C for 1 hour using 30 MPa pressure. Top and bottom surfaces of the sintered disk were removed by grinding and target was machined using electrical discharge machining (EDM).

Films were deposited by magnetron sputtering using the 2-inch (Ti_{0.5}, Zr_{0.5})_{2}AlC compound target. The base pressure in the deposition chamber was kept below 2 × 10^{-7} Torr while the working pressure in presence of Ar was 6 Pa (4.5 mTorr). The target was placed on-axis below the substrate holder at a distance of 180 mm.

The target was operated in constant power mode with a value of 50 W. Rotation was applied to the substrates at 10 RPM. Finally, depositions were carried out at different temperatures from 500 to 900 °C, with increments of 100 °C. Depositions were carried out for 30 min on MgO (111) and Al_{2}O_{3} (0001) substrates which were cleaned prior to deposition in ultrasonic bath of acetone and isopropanol for 5 min each. Depositions of 60 min were carried out on Al_{2}O_{3} (0001) which were also cleaned prior to deposition.

The structural properties of the target and the deposited films were investigated using X-ray diffraction (XRD), using a standard θ-2θ geometry in a Panalytical X’pert MRD with Cu (Kα radiation. Film thicknesses were obtained using X-ray reflectivity (XRR) in a Philips X’Pert MRD system and were confirmed by scanning electron microscopy (Zeiss SEM Leo 1550 Gemini).

The time-of-flight-energy elastic recoil detection analysis (ToF-E ERDA) was measured at the Tandem Accelerator Laboratory of Uppsala University. This technique used 36 MeV $^{127}$I^{8+} ions as incident beam impinging onto the samples at an incoming angle of 67.5° with respect to the surface normal and the induced recoiling particles were detected by two carbon foil time detectors and Silicon p-i-n diode energy detector for energy discrimination at an angle of 45° with respect to the incoming ion beam. The measured ERDA spectra were converted to depth profiles by using the Potku code 16.

Transmission Electron Microscopy (TEM) analysis was performed on an electron transparent, cross-sectional lamella, prepared from the film deposited during 60 min at 900 °C with Focused Ion Beam (FIB), using a Carl Zeiss Cross-Beam 1540 EsB system. TEM was performed at 200
kV using a Tecnai G2 TF20 UT electron microscope. Energy dispersive X-ray spectroscopy (EDXS) was conducted in scanning (STEM) mode.

3. Results and Discussions

The (Ti,Zr)\(_2\)AlC target was analyzed prior to deposition in order to verify the phases present and the homogeneity of the composition. Figure 1(a) shows the XRD pattern of the target before sputtering. One can notice the peaks of the MAX phase along peaks which correspond to aluminides and carbides. While the aluminides and carbides detected were Zr-rich, the peaks are slightly shifted which is due to the presence of Ti in the structures. Furthermore, microstructural analyses have confirmed the presence of different phases. In fact, closer to the outer surface two types of 211 MAX phases appear, a bright phase with a 50:50 Ti to Zr ratio and a darker one with a 70:30 Ti to Zr ratio. Al\(_2\)Zr and (Ti,Zr)C have been detected. The carbide appears to be Zr-rich mostly, however some Ti-rich particles have also been observed. Figure 1(b) shows the elemental distribution of the target’s constituents. The target was coated with graphite to enhance conductivity. The elemental distribution does not vary significantly, therefore, the target is assumed to be homogeneous.

![Figure 1](image)

Figure 1: (a) X-ray diffraction pattern (XRD) of the target before deposition. (b) EDS linescan over the surface of an equivalent MAX phase target.

The target was used to deposit films of various thicknesses on MgO and Al\(_2\)O\(_3\) substrates. Figure 2 shows XRD \(\theta\)-2 \(\theta\) patterns from the films deposited for 30 min on both Al\(_2\)O\(_3\) and MgO substrates at temperatures ranging from 500 to 900 °C. The films consist of 30-to-40-nm thick ternary carbides (Ti\(_x\)Zr\(_{1-x}\))C, as reported in Figure 2. The intensity of the carbide peaks increases with increasing temperature which is directly related to larger grains.
Figure 2: XRD patterns of films deposited during 30 min from a compound target on (a) MgO (111) and (b) Al₂O₃ (0001) substrates.

The compositions and lattice parameters corresponding to each film are given in Table 1. The lattice parameters of the carbides do not follow a particular trend with respect to the substrate temperature. Therefore, one can assume that these differences are related to Al content within the carbide. The shrinkage and subsequent expansion of the lattice can be related to a dissolution of Al within the carbide. To confirm this hypothesis, ERDA measurements were carried out on the films deposited at each temperature on MgO substrates, to be able to extract the Al contribution related to the film. One can notice that the Ti to Zr ratio is very close to 1 : 1 which is also the ratio of the target. The carbon composition seems stable with respect to the temperature. However, it is slightly higher than the 2:1:1 MAX phase composition. Finally, Al is indeed present in the film and constitutes 10 to 15 at.% of the composition, depending on deposition temperature.

Table 1: Lattice parameters and chemical composition of the films deposited at different temperatures on MgO (111) substrates.

| Temperature (°C) | Lattice Parameter a = b = c (Å) | Ti (at.%) | Zr (at.%) | Al (at.%) | C (at.%) |
|-----------------|--------------------------------|-----------|-----------|-----------|---------|
| 500             | 4.50470                        | 26.2 ± 0.8| 25.4 ± 0.7| 16.5 ± 0.7| 32.0 ± 1.1|
| 600             | 4.51788                        | 26.2 ± 0.6| 23.4 ± 0.6| 13.9 ± 0.6| 36.5 ± 1.0|
| 700             | 4.50723                        | 26.8 ± 0.8| 24.7 ± 0.6| 14.6 ± 0.6| 33.9 ± 1.0|
Table:

| Temperature | Ti Concentration | Zr Concentration | Al Concentration | C Concentration |
|-------------|-----------------|-----------------|-----------------|----------------|
| 800 °C      | 4.53135         | 29.3 ± 0.7      | 28.6 ± 0.6      | 9.2 ± 0.5      |
| 900 °C      | 4.52366         | 27.9 ± 0.6      | 25.7 ± 0.5      | 12.2 ± 0.5     |

**Figure 3** shows compositional depth profiles obtained using ERDA on the films deposited on MgO (111) at 800 and 900 °C. One can notice that the distribution of Al is homogeneous throughout the thickness of the films.

**Figure 3**: Compositional depth profile of the films deposited on MgO (111) substrates at (a) 800 °C and (b) 900 °C.

In order to obtain thicker films for further analyses, 60 min long depositions were carried out and resulted in 80-90 nm thick films. The XRD patterns collected for these films are reported in **Figure 4**. One can notice that the (Ti<sub>x</sub>Zr<sub>1-x</sub>)C carbide is still present and seems to be the only constituent phase in the films deposited at 500 and 600 °C. As seen in **Figure 4,(b)**, a peak appears at ~ 38 ° which could correspond to an intermediate and defect-rich TiC<sub>x</sub>. At a temperature of 900 °C, one can notice the presence of the 002 peak of the 211 MAX phase at ~ 12.8 °, as well as some other contributions, which are less obvious, at ~ 25.8 ° (004) and ~ 39.2 ° (006). However, these peaks fit quite poorly with the reported peak positions of Tunca et al. for the case of 1 : 1 ratio of Ti : Zr. Therefore, the MAX phase identified here is not the (Ti<sub>0.5</sub>, Zr<sub>0.5</sub>)<sub>2</sub>AlC ones, but rather a Ti-rich MAX phase such as the (Ti<sub>0.8</sub>, Zr<sub>0.2</sub>)<sub>2</sub>AlC MAX phase reported in the same work. One can then assume that the peaks appearing between 700 and 800 °C, corresponds to a Ti-rich carbide which is transitioning into the MAX phase, while the (Ti<sub>x</sub>Zr<sub>1-x</sub>)C carbide becomes richer in Zr. We can therefore say with confidence, that the 1:1 ratio in the case of the Ti:Zr solid solution is not favorable and the MAX phase cannot be generated. Furthermore, we are able to synthesize this MAX phase at a different metal to metal ratio, however, a thick enough carbide interlayer is required.
Figure 4: XRD patterns of films deposited on Al₂O₃ (0001) at various temperatures using the compound target.

The microstructures of the films were then observed using scanning electron microscopy, of which a representative micrograph of each is given in Figure 5. One can notice how the grains increase in size with increasing substrate temperature from 500 to 700 °C. One can also observe that at 700 and 800 °C, the microstructure looks a bit more defined in terms of grain shape. Also, the larger grains seem to be surrounded by non-uniform smaller grains.

Figure 5: SEM micrographs of the surface of the 80 nm-thick films deposited for 60 min on Al₂O₃ (0001) substrates at (a) 500, (b) 600, (c) 700, (d) 800 and (e) 900 °C, and (f) cross-section of a film deposited on Al₂O₃ (0001) at 900 °C for 90 min.

Finally, at 900 °C, one can observe the presence of at least two phases and two different morphologies of grains. The lighter grains exceed from the surface, causing the roughness of
the film to increase, and result from stacking of smaller plate-like grains. The darker grains correspond to a very typical carbide-like microstructure with randomly oriented grains and exposed 111 faces. Finally, we assume that the protrusions correspond to the MAX phase, while the rest of the film seems to be the \((\text{Ti}_{x}\text{Zr}_{1-x})\text{C}\) carbide. Furthermore, Figure 5(f) shows the cross-section of a \(~160\ \mu\text{m}\)-thick film where one can observe that the microstructure is not homogeneous throughout the thickness. Indeed, closer to the substrate, small and randomly oriented grains are observed. Then the film seems to follow a columnar growth. One can see the presence of a grain exceeding the surface which could correspond to the MAX phase.

In order to confirm this theory, transmission electron microscopy was performed on an electron transparent lamella of the film deposited at 900 °C on \(\text{Al}_2\text{O}_3\) prepared by focused ion beam. A low magnification HAADF STEM image of the film presented in Figure 7 (a). At first glance, there are three distinct microstructural features in the deposited film: (i) The darker, prismatic-like features, which correspond to the protrusions observed in the SEM, (ii) the brighter contrast continuous film, and (iii) the interface between the film and the \(\text{Al}_2\text{O}_3\) substrate. A closer look into these features reveals further information about their composition. The brighter regions in these STEM images correspond to heavier elements. The uneven contrast throughout the blown-up regions shown in the inset suggests that neither the continuous film nor the interface is elementally homogeneous. EDXS maps show that the brighter parts in the film is rich in Zr whereas the darker parts are rich in Ti. Protrusions also have two different microstructures, an anisotropic/columnar structure and a more isotropic/circular structure. The quantification results obtained from each feature is summarized in Table 2. Although slightly deficient in Al, the columnar structures seem to have the right stoichiometric Transition Metal : Aluminium ratio. The continuous film seems to be predominantly \((\text{Ti},\text{Zr})\text{C}\) with some Al dissolved in the structure. The substrate and the film seem to react under the deposition conditions summarized above, probably due to the elevated temperature, evidenced by the different chemistry and the structure of the interface.
**Figure 6:** (a) Overall dark field STEM image of the film. The regions further investigated for compositional analysis is shown with dashed squares. In the insets, blown up versions of these regions are shown. STEM HAADF detector intensity maps are given in (b), (c) and (d). Maps are labelled with the elements they correspond to.

**Table 2:** Elemental analysis of the microstructures observed in the film.

| Microstructural Feature  | Total Transition Metal Concentration (at%) | Ti (at%) | Zr (at%) | Al (at%) |
|-------------------------|------------------------------------------|----------|----------|----------|
| Film                    | 98.15                                    | 30.40    | 67.75    | 1.84     |
| Protrusions-Columnar    | 69.14                                    | 48.48    | 20.66    | 30.85    |
| Protrusions-Circular    | 35.53                                    | 8.79     | 26.74    | 64.47    |
| Interface-Zr Rich      | 35.35                                    | 9.51 ± 1 | 25.84 ± 1.5 | 64.64 ± 2 |
| Interface-Ti Rich      | 66.13                                    | 60.60 ± 3 | 5.53 ± 1 | 33.86 ± 3 |

In order to understand the crystal structure of the aforementioned microstructural features, TEM micrographs and SAED patterns of the film and the interface were investigated **Figure 7 (b), (c) and (d).** The diffraction pattern of the film matches nicely with [112] zone axis of TiZrC₂.
(ICSD code: 618971), which is in good agreement with our previous elemental analysis. Owing to its narrow, sandwiched nature it was not possible to isolate the interface, therefore, we collected the diffraction pattern from all three areas of interest (Figure 7(c)). FFT performed along the HRTEM micrograph (Figure 7(d)) of the interface shows that the interface is not crystallographically uniform, which correlates with the elemental analysis results. The analysis of the crystal structure of the interface is still under investigation and will make the object of further studies to come.

![Figure 7](image.png)

**Figure 7:** (a) TEM micrographs of the film deposited at 900 °C for 60 min on an Al₂O₃ (0001) substrate. SAED patterns taken from (b) the substrate, (c) the substrate-interface-film and (d) the film. (e) The HRTEM micrograph of the three areas of interest.

**4. Conclusions**

We have successfully deposited the mixed (Ti,Zr)C carbide containing up to 15 at.% of Al from a compound (Ti,Zr)₂AlC target as evidenced by ion beam analysis. Higher substrate temperatures and longer deposition times have resulted in films containing both the mixed carbide and MAX phase protrusions. The identified MAX phase, however, did not correspond to the MAX phase of the target, which is attributed to the composition difference observed using compound targets. Furthermore, we evidenced the presence of an interlayer between the Al₂O₃ substrate and the film deposited at 900 °C. Indeed, the interlayer appears to be separated in two compositionally different layers, one of them being Ti-rich (close to the substrate) and the other Zr-rich. Being unable to conclude on the interface structure, further investigations are carried out. Finally, the growth of the MAX phase seems to be affected by the presence of the
interlayer but also by the temperature. Indeed, an intermediate phase between the carbide and the MAX phase has been detected at temperatures between 700 to 800 °C.

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References

1. A. Hoerling, J. Sjölen, H. Willmann, T. Larsson, M. Odén, and L. Hultman, Thin Solid Films 516, 6421 (2008).

2. V. V. Uglov, V.M. Anishchik, V. V. Khodasevich, Z.L. Prihodko, S. V. Zlotski, G. Abadias, and S.N. Dub, Surf. Coatings Technol. 180–181, 519 (2004).

3. T. Ma, P. Hedström, V. Ström, A. Masood, I. Borgh, A. Blomqvist, and J. Odqvist, Int. J. Refract. Met. Hard Mater. 51, 25 (2015).

4. E.A. Levashov, V. V. Kurbatkina, A.A. Zaitsev, S.I. Rupasov, E.I. Patsera, A.A. Chernyshev, Y. V. Zubavichus, and A.A. Velizhanin, Phys. Met. Metallogr. 109, 95 (2010).

5. A. Abdulkadhim, M. to Baben, T. Takahashi, V. Schnabel, M. Hans, C. Polzer, P. Polcik, and J.M. Schneider, Surf. Coatings Technol. 206, 599 (2011).

6. T. Cabioch, M. Alkazaz, M.F. Beaufort, J. Nicolai, D. Eyidi, and P. Eklund, Mater. Res. Bull. 80, 58 (2016).

7. J.J. Li, L.F. Hu, F.Z. Li, M.S. Li, and Y.C. Zhou, Surf. Coatings Technol. 204, 3838 (2010).

8. R. Mertens, Z. Sun, D. Music, and J.M. Schneider, Adv. Eng. Mater. 6, 903 (2004).

9. A. V. Pshyk, E. Coy, M. Kempiński, B. Scheibe, and S. Jurga, Mater. Res. Lett. 7, 244 (2019).

10. J. Nicolaï, C. Furgeaud, B.W. Fonrose, C. Bail, and M.F. Beaufort, Mater. Des. 144, 209 (2018).
11 O. Wilhelmsson, J.P. Palmquist, E. Lewin, J. Emmerlich, P. Eklund, P.O., Persson, H. Högberg, S. Li, R. Ahuja, O. Eriksson, L. Hultman, and U. Jansson, J. Cryst. Growth 291, 290 (2006).

12 J. Frodelius, P. Eklund, M. Beckers, P.O., Persson, H. Högberg, and L. Hultman, Thin Solid Films 518, 1621 (2010).

13 P. Eklund, M. Beckers, J. Frodelius, H. Högberg, and L. Hultman, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 25, 1381 (2007).

14 J.P. Palmquist, U. Jansson, T. Seppänen, P.O.A. Persson, J. Birch, L. Hultman, and P. Isberg, Appl. Phys. Lett. 81, 835 (2002).

15 C. Walter, D.P. Sigumonrong, T. El-Raghy, and J.M. Schneider, Thin Solid Films 515, 389 (2006).

16 K. Arstila, J. Julin, M.I. Laitinen, J. Aalto, T. Konu, S. Kärkkäinen, S. Rahkonen, M. Raunio, J. Itkonen, J.P. Santanen, T. Tuovinen, and T. Sajavaara, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 331, 34 (2014).

17 B. Tunca, T. Lapauw, O.M. Karakulina, M. Batuk, T. Cabioe’h, J. Hadermann, R. Delville, K. Lambrinou, and J. Vleugels, Inorg. Chem. 56, 3489 (2017).