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A comparative study of (TiZr)C and (CuSiTiYZr)C films microstructure deposited by magnetron sputtering

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Carbide coatings of (TiZr)C and (CuSiTiYZr)C on C45 substrates are prepared by magnetron reactive co-sputtering of Ti, Zr, Si, Ti, Y targets in an atmosphere of Ar+CH_4. Thus obtained films are investigated for phase composition and morphology using XRD (X-Ray Diffraction), SEM (Scanning electron microscopy) and AFM (Atomic Force Microscopy). Primary investigations revealed that the (TiZr)C coating consist of a crystalline structure, mainly FCC, while the (CuSiTiYZr)C coating is mainly amorphous, several FCC crystallites embedded in the matrix are to be observed.

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1. Introduction

HEA (high entropy alloys) are a new trend in recent years. Comprising 5 to 13 elements, mostly with equiatomic or near equiatomic concentrations, these alloys show remarkable properties: an increased hardness value, even after heat treatments such as annealing, a higher strength, and fatigue and corrosion resistance, increased thermal stability when compared to conventional alloys, due to their fine grained structure [1-4].

The scope of this work is to study, by comparison, several structural and morphology aspects of two potentially protective coatings, comprising 3 and 6 elements, obtained by magnetron reactive sputtering in an Ar+CH_4 mixed atmosphere.

2. Experimental details

The films are obtained by magnetron sputtering on C45 substrate using an AJA's ATC ORION unit with five cathodes: Cu, Si, Ti, Y and Zr, about 50mm in diameter.

The deposition parameters are as follow: the pressure in the deposition chamber was at 5×10^{-5}Torr, the pressure of CH_4+Ar was 5×10^{-1}Pa, the distance between the substrate and cathodes was 17cm, substrate voltage bias was set to -100V and the deposition temperature set to 300°C. The total deposition time was 1 hour.

Prior to deposition the substrate was cleaned by placing it on a holder and sputtered with argon ions for about 300s [5].

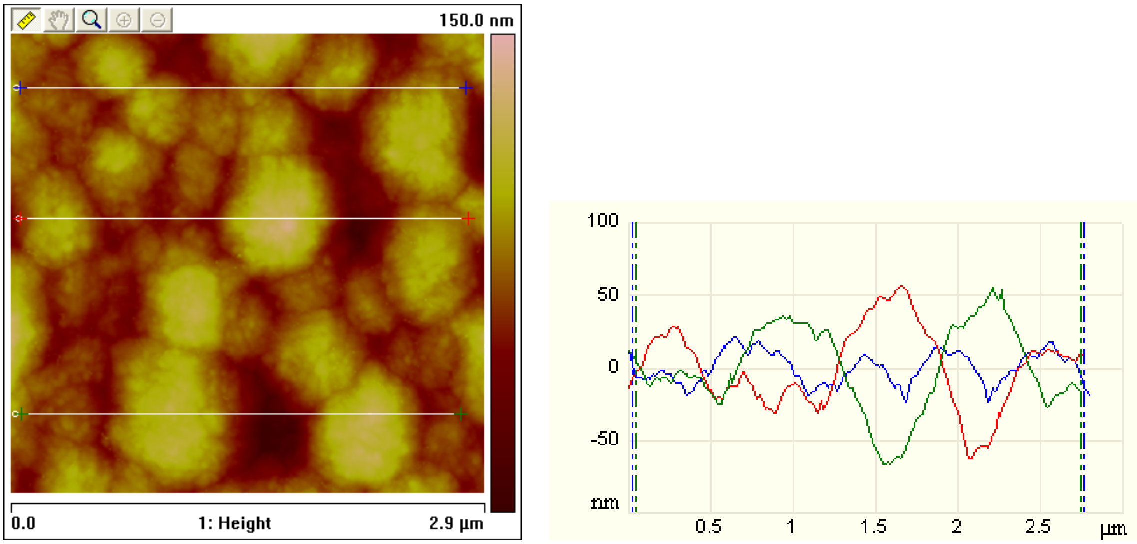
Surface topography was investigated by SEM, using an electronic microscope FEI Quanta Inspect F, a HRTEM Tecnai G F30 S-Twin, AFM using an INNOVA microscope in tapping mode, while the phase composition and crystalline structure was determined by PANalytical X-Ray diffractometer with Cu_α radiation.

3. Results and discussion

The film thickness, measured on HRTEM images, averaged 2.73μm for (TiZr)C and 1.80μm for (CuSiTiYZr)C.

3.1 Surface topography

The AFM image shown in Fig. 1 a. exhibits dome shaped structures, with various sizes and heights, and a random distribution on the surface. The surface roughness on a 9μm^2 area was around 4.32 nm.



a b

Fig. 1. a. AFM topography of the (CuSiTiYZr)C film with b. height profile on three lines.

Analyzing the height profiles on the three scanned lines shows a rugged dome surface. The height variation interval, the difference between the highest point, mountain, and lowest point, valley, are found as 21.14 nm for line 1, 27.08 nm for line 2 and 24.49 nm for line 3.

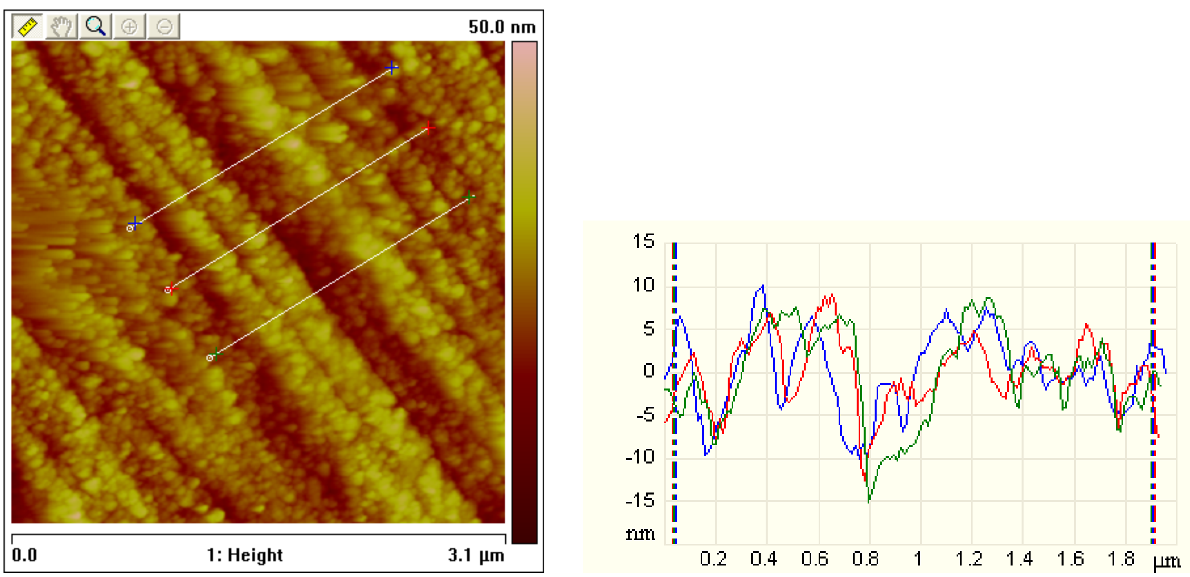


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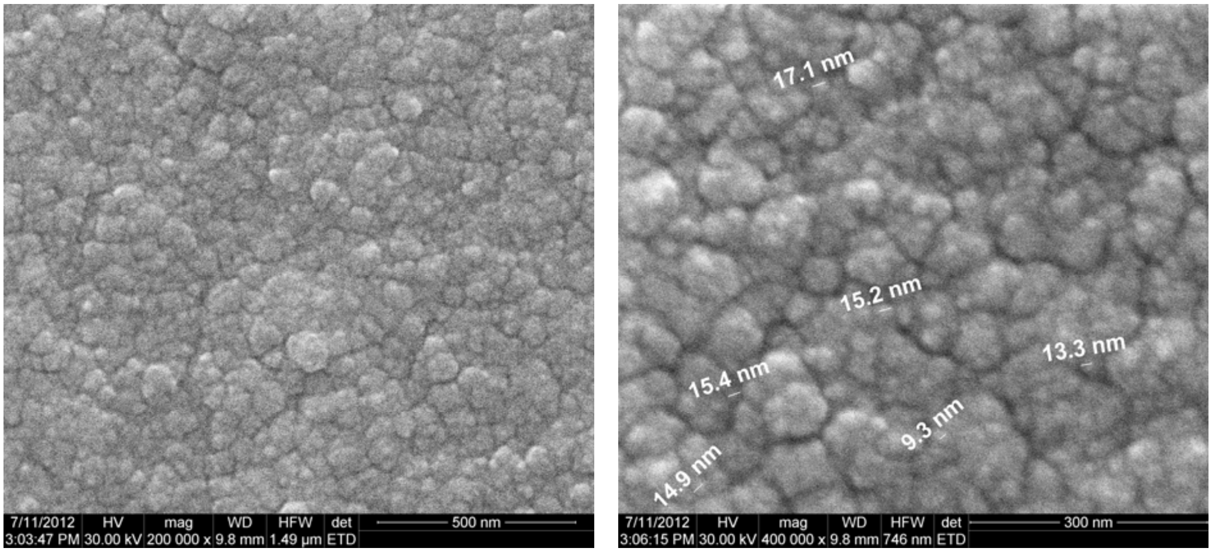
Fig. 2 a. AFM topography of the (TiZr)C film with b. height profile on three lines.

The film for the (TiZr)C shows a columnar morphology, as seen in Fig. 2.a., conformed in parallel strips. The surface roughness on a 9µm^2 area is found to be 8.79nm.

On the height profiles obtained from three lines, Fig. 2.b. the maximum heights are close in values, while the height variation shows an interval of 40.09nm for line1, 42.42nm for line 2 and 48.49nm for line 3.

The columns top surfaces are rough.

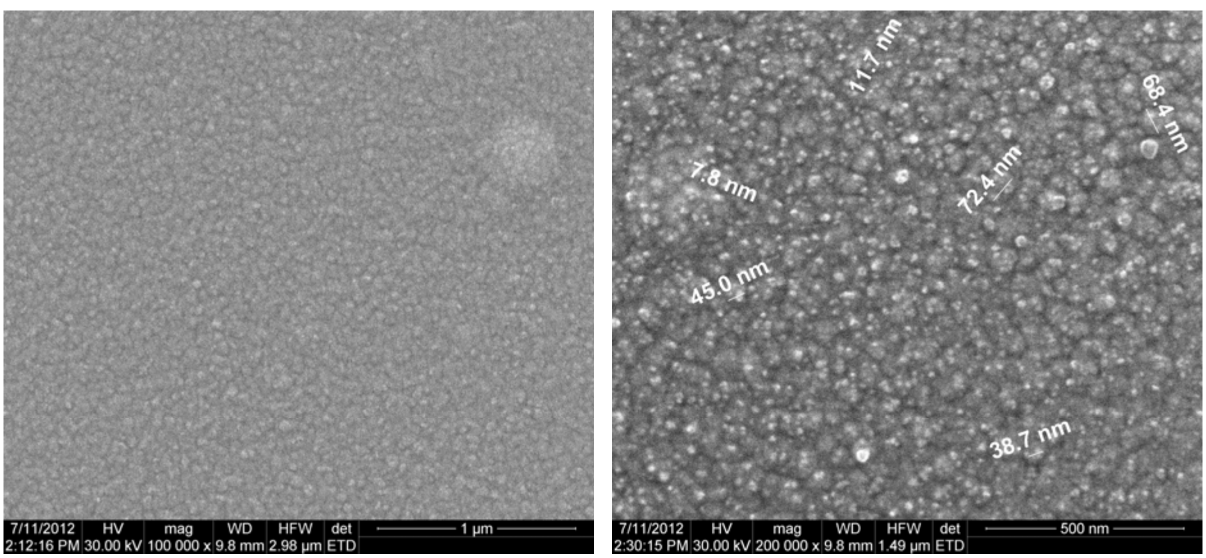


a. 200000X b. 400000X

Fig. 3. SEM image (secondary electrons) of (TiZr)C topography.

The surface topography of the samples, Fig. 3, shows equal size fine grains covering the investigated surface. The measured large particles show a variation of size from 45 to 65nm, while the nano-sized grains indicate sizes from 9 to 20nm.

The investigated sample shows in Fig. 4.a. uniform distribution of surface formations, ranging from 7.8 to 72.4nm, covering the entire investigated area.



a. 100000X b. 200000X

Fig. 4. SEM image (secondary electrons) of (CuSiTiYZr)C topography.

The presence of a nodule can also be observed in Fig. 4.a. The nodule is circular in shape, with a mean diameter of 0.3435µm and a mean area of 0.1215 µm^2.

3.2 Phase composition and crystalline structure

From Fig. 5 it can be seen that the (TiZr)C shows a crystalline structure, with a cubic crystal system and an

Fm-3m space group. The phase was identified as titanium zirconium carbide, $TiZrC_2$, with a lattice parameter of 4.56 Å.

If we compare the peaks detected with the indexed peak list a slight shift to the left is noticeable, which may indicate a tension in the structure, occurred during deposition.

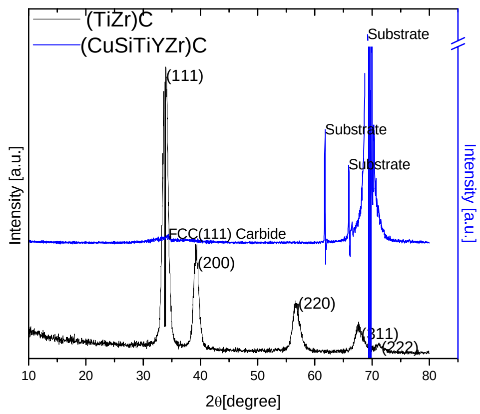


Fig. 5. Ray diffraction of the coatings.

The (CuSiTiYZr)C film shows a single FCC carbide phase, observed at 34°, and at higher angles substrate characteristic peaks are to be observed. The FCC carbide phase could be zirconium carbide, $ZrC_{0.966}$, with a cubic Fm-3m structure.

Approximating crystallite size by Scherrer formula we noticed few nanometer sized (2-6nm) grains in (CuSiTiYZr)C coating embedded in an amorphous matrix, while the (TiZr)C indicated a wide range of crystallite size, also in nanometer range.

Similar structures were observed by Braic et al. [6-8] in their studies.

The enthalpy, entropy and atomic size difference values for our studied materials when compared with literature data suggested a solid solution phase for the 3 element film and a transition between solid solution and amorphous structure for the 6 element film, observations confirmed during experimental investigations.

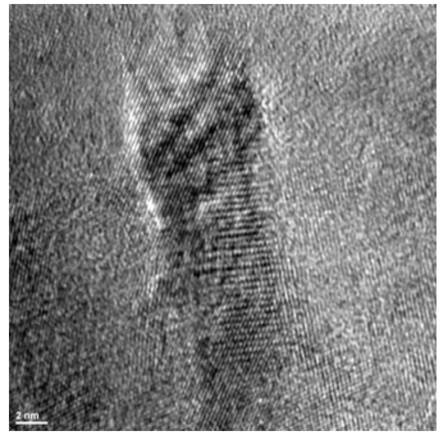


Fig. 6. Crystallite observed in (TiZr)C.

The HRTEM studies confirmed nanometer sized crystallites; the grain observed in Fig. 6 is about 8nm wide and 24nm long.

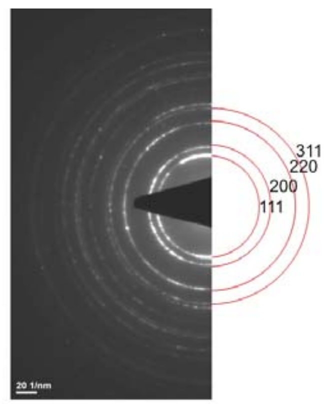
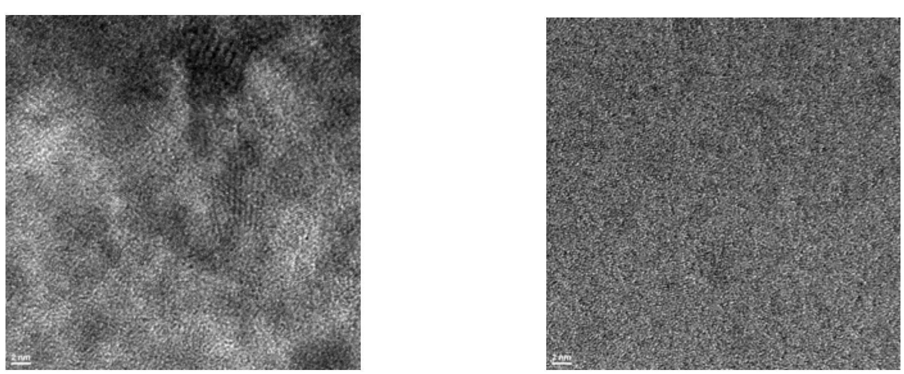


Fig. 7. SAED on (TiZr)C.

The SAED pattern, Fig. 7, on (TiZr)C indicates a polycrystalline material with grain size ranging from 0.5 - 10µm, the 111, 200 and 220 rings are brighter and correspond to $TiZrC_2$ compound.



a b

Fig. 8. HRTEM observed sections of (CuSiTiYZr)C coating.

4. Conclusions

Six and three element thin films are obtained by reactive magnetron sputtering in an Ar+CH_4 mixed atmosphere.

The XRD and HRTEM analysis showed a crystalline structure for the (TiZr)C coating, while the (CuSiTiYZr)C was mainly amorphous with several crystallites embedded in this matrix.

The competition on vertical build-up and lateral diffusion are key factors on surface morphology.

The columnar morphology is a consequence of geometrical defects and the shadowing effect [9] and can be found in high energetic compounds, like carbides, nitrides, fluorides and sulfides.

The nodules formed are caused mostly by impurities and are specific to sputtering process; a more thorough cleaning process should avoid their formation.

The height variation between peaks and valleys is almost double when columnar structures are formed.

Due to its structure, better mechanical properties are to be expected from the 6 element film, investigations are currently performed.

Acknowledgements

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