

Article

Structural Evolution, Mechanical Properties, and Thermal Stability of Multi-Principal TiZrHf(Ta, Y, Cr) Alloy Films

Yung-I Chen ^{1,*} , Tzu-Yu Ou ¹, Li-Chun Chang ^{2,3}  and Yan-Zhi Liao ¹

¹ Department of Optoelectronics and Materials Technology, National Taiwan Ocean University, Keelung 202301, Taiwan; outzuyu23@gmail.com (T.-Y.O.); 11289034@mail.ntou.edu.tw (Y.-Z.L.)

² Department of Materials Engineering, Ming Chi University of Technology, New Taipei 243303, Taiwan; lcchang@mail.mcut.edu.tw

³ Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, New Taipei 243303, Taiwan

* Correspondence: yichen@mail.ntou.edu.tw

Abstract

Mixing enthalpy (ΔH_{mix}), mixing entropy (ΔS_{mix}), atomic-size difference (δ), and valence electron concentration (VEC) are the indicators determining the phase structures of multi-principal element alloys. Exploring the relationships between the structures and properties of multi-principal element films is a fundamental study. TiZrHf films with a ΔH_{mix} of 0.00 kJ/mol, ΔS_{mix} of 9.11 J/mol·K (1.10R), δ of 3.79%, and VEC of 4.00 formed a hexagonal close-packed (HCP) solid solution. Exploring the characterization of TiZrHf films after solving Ta, Y, and Cr atoms with distinct atomic radii is crucial for realizing multi-principal element alloys. This study fabricated TiZrHf, TiZrHfTa, TiZrHfY, and TiZrHfCr films through co-sputtering. The results indicated that TiZrHfTa films formed a single body-centered cubic (BCC) solid solution. In contrast, TiZrHfY films formed a single HCP solid solution, and TiZrHfCr films formed a nanocrystalline BCC solid solution. The crystallization of TiZrHf(Ta, Y, Cr) films and the four indicators mentioned above for multi-principal element alloy structures were correlated. The mechanical properties and thermal stability of the TiZrHf(Ta, Y, Cr) films were investigated.

Keywords: co-sputtering; crystal structure; mechanical properties; multi-principal element alloys; thermal stability



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1. Introduction

High-entropy alloys (HEAs) and medium-entropy alloys (MEAs) with multiple principal elements have attracted researchers' attention due to their specific effects, namely high entropy, lattice distortion, sluggish diffusion, and cocktail effects, which differ from those of traditional alloys designed with the primary constitution and some additives [1]. With these specific effects, HEAs and MEAs have been developed in versatile applications, such as alloys with high strength and ductility at cryogenic temperatures [2], hydrogen storage materials [3], diffusion barriers [4–6], and biocompatible implants [7,8]. The mixing enthalpy (ΔH_{mix}), mixing entropy (ΔS_{mix}), and atomic-size difference (δ) of multi-component alloys were vital indicators that influenced the phase structures of HEAs and MEAs [9]. For example, the alloys with low δ , high ΔS_{mix} , and not very negative ΔH_{mix} tended to form a compound with a single solid solution crystallizing into a simple structure. Moreover, alloys' valence electron concentration (VEC) determines the solid solutions' phase structures [10,11]. The alloys exhibited hexagonal close-packed (hcp), body-centered cubic

(bcc), and face-centered cubic (fcc) phases as their VEC were <4.09 [11], $4.18\text{--}6.87$ [10,11], and ≥ 8 [10], respectively. Ti, Zr, and Hf, with a VEC of 4, can crystallize into either hcp or bcc structures [12]. In a previous study [13], TiNbTa(Zr) films with a VEC value of $4.40\text{--}4.90$ exhibited a bcc phase, whereas the other TiNbTa(Zr) films with VEC values of $4.17\text{--}4.24$ showed a hcp and bcc mixed phase. Ta and Nb are biocompatible and known as bcc-phase stabilizers in Ti-based alloys [14], and their oxide, Ta_2O_5 and Nb_2O_5 , are recognized as passivation films during corrosion tests [15]. RHEAs primarily comprise refractory metal elements from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W. These alloys have gathered widespread attention due to their suitability for high-temperature applications [16]. According to the Hume-Rothery criteria established for binary alloy systems, a solid solution forms when the solute and solvent elements have an atomic size difference of less than 15%. However, a critical indicator δ of 0.065 distinguished solid solution formation and amorphous structures for HEA systems [17]. Moreover, a more negative ΔH_{mix} favors the formation of an amorphous phase [17]. Ta, with a VEC of 5, has an atomic radius of 0.143 nm, which is slightly lower than those of Ti (0.14615 nm), Zr (0.16025 nm), and Hf (0.15775 nm) [18]. In contrast, Y, with a low VEC value of 3, possesses a large atomic radius of 0.18015 nm, whereas Cr, with a high VEC of 6, has a small atomic radius of 0.12491 nm [18]. Investigating the phase structures and characteristics of TiZrHfM films with distinct metallic atoms ($M = \text{Ta, Y, Cr}$) becomes the topic of this study. Moreover, the thermal stability of these phases through vacuum annealing in the temperature range of $500\text{--}800\text{ }^\circ\text{C}$ was investigated.

2. Materials and Methods

TiZrHfM ($M = \text{Ta, Y, Cr}$) films were prepared through a four-gun co-sputtering system, as illustrated in Figure 1. Direct current (DC) powers applied to the sputter guns are listed in Table 1. Targets of Ti (99.995%), Zr (99.9%), Hf (99.99%), Ta (99.99%), Y (99.99%), and Cr (99.99%) (Ultimate Materials Technology, Jubei, Taiwan) with a diameter and thickness of 50.8 and 6 nm, respectively, were adopted. A Ti interlayer was deposited on the substrates using a DC power of 200 W, an Ar flow rate of 20 sccm, and a substrate holder rotation speed of 30 rpm, which formed a thickness of 90–181 nm. Then, TiZrHf, TiZrHfTa, TiZrHfY, and TiZrHfCr films of 685–1272 nm were deposited on the Ti interlayer. Vacuum annealing was performed in 5.3×10^{-3} Pa at $500\text{--}800\text{ }^\circ\text{C}$ for 1 h. The heating rate was $20\text{ }^\circ\text{C}/\text{min}$, and the annealed sample was furnace cooled to $<50\text{ }^\circ\text{C}$ in 2 h. Film thicknesses and surface morphologies were examined using a field emission scanning electron microscope (JSM-IT700HR, JEOL, Tokyo, Japan). The chemical compositions of the films were determined using a field-emission electron probe microanalyzer (JXA-iHP200F, JEOL, Tokyo, Japan). Three measurements for each sample were used for calculating the standard deviations of thickness and compositions. Phase identification was conducted using grazing incident X-ray diffraction (GIXRD; X'Pert PRO MPD, PANalytical, Almelo, The Netherlands). Lattice constants (a_0) of the films were decided from GIXRD reflections by using the equation [19]:

$$a = a_0 + K \times \frac{\cos^2 \theta}{\sin \theta} \quad (1)$$

where a is the lattice constant for a distinct reflection, K is a constant, and θ is the diffraction angle. Although standard deviations are not provided, the uncertainty in lattice constant estimation is primarily influenced by instrumental resolution, peak fitting accuracy, and alignment. Based on typical GIXRD setups and analysis methods, the relative uncertainty is estimated to be within $\pm 0.5\%$. The hardness and elastic modulus of films were measured using a nanoindentation tester (TI-900 Triboindenter, Hysitron, Minneapolis, MN, USA) equipped with a Berkovich diamond probe tip, and the data calculations were performed

using the Oliver–Pharr method [20]. The indentation depth was controlled at 80 nm to minimize substrate influence. Six measurements for each sample were used to determine the standard deviation. Residual stress in the films was determined using the curvature method [21]. Corrosion experiments of the films prepared on SUS420 substrates were carried out in a 3.5 wt.% NaCl aqueous solution with a pH value of 6.3 using a potentiodynamic polarization test setup (SP-200, BioLogic, Seyssinet-Pariset, France) with an Ag/AgCl reference electrode and a Pt counter electrode. The samples with C and Pt protective layers for transmission electron microscopy (TEM, JEM-2010F, JEOL, Tokyo, Japan) observation were prepared using a focused ion beam system (NX2000, Hitachi, Tokyo, Japan).

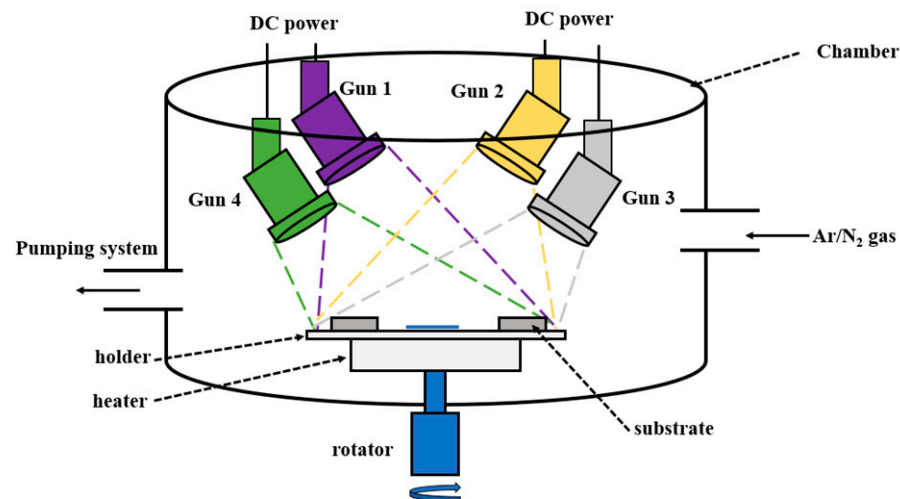


Figure 1. Schematic of the co-sputtering apparatus.

Table 1. Target, power arrangements, and thickness values for co-sputtering TiZrHf (Ta, Y, Cr) films.

Sample	Gun 1	Gun 2	Gun 3	Gun 4	T_F^1 (nm)	T_I^2 (nm)
	P_{Ti}^3	P_{Hf}	P_{Zr}			
Ti ₃₁ Zr ₃₃ Hf ₃₆	120	80	100		796 ± 9	131 ± 0
	P_{Ti}	P_{Hf}	P_{Zr}	P_{Ta}		
Ti ₂₄ Zr ₂₃ Hf ₂₇ Ta ₂₆	120	80	120	80	916 ± 8	143 ± 3
Ti ₃₀ Zr ₂₀ Hf ₂₅ Ta ₂₅	170	80	120	80	1058 ± 10	135 ± 1
Ti ₂₁ Zr ₃₀ Hf ₂₅ Ta ₂₄	120	80	170	80	795 ± 8	181 ± 8
Ti ₂₀ Zr ₁₈ Hf ₃₈ Ta ₂₄	120	130	120	80	923 ± 13	163 ± 3
Ti ₁₇ Zr ₁₇ Hf ₂₆ Ta ₄₀	120	80	120	130	685 ± 5	102 ± 8
	P_{Ti}	P_{Hf}	P_{Zr}	P_Y		
Ti ₂₄ Zr ₂₃ Hf ₂₇ Y ₂₆	130	80	90	100	1046 ± 7	117 ± 1
Ti ₂₉ Zr ₂₁ Hf ₂₆ Y ₂₄	180	80	90	100	1110 ± 10	117 ± 6
Ti ₂₂ Zr ₃₀ Hf ₂₇ Y ₂₁	130	80	140	100	1145 ± 3	115 ± 7
Ti ₂₁ Zr ₁₉ Hf ₄₂ Y ₁₈	130	130	90	100	1189 ± 6	117 ± 6
Ti ₁₉ Zr ₁₈ Hf ₂₆ Y ₃₇	130	80	90	150	1272 ± 2	124 ± 1
	P_{Ti}	P_{Hf}	P_{Zr}	P_{Cr}		
Ti ₂₉ Zr ₁₉ Hf ₂₆ Cr ₂₆	150	90	100	60	1133 ± 7	139 ± 9
Ti ₃₁ Zr ₁₇ Hf ₂₈ Cr ₂₄	200	90	100	60	1129 ± 10	137 ± 0
Ti ₂₄ Zr ₂₆ Hf ₂₇ Cr ₂₃	150	90	150	60	1119 ± 11	90 ± 10
Ti ₂₂ Zr ₁₅ Hf ₄₁ Cr ₂₂	150	140	100	60	1165 ± 5	125 ± 2
Ti ₂₁ Zr ₁₆ Hf ₂₅ Cr ₃₈	150	90	100	110	1200 ± 7	107 ± 0

¹ T_F : film thickness. ² T_I : interlayer thickness. ³ P : powers applied on the targets. Power unit: watts.

3. Results and Discussion

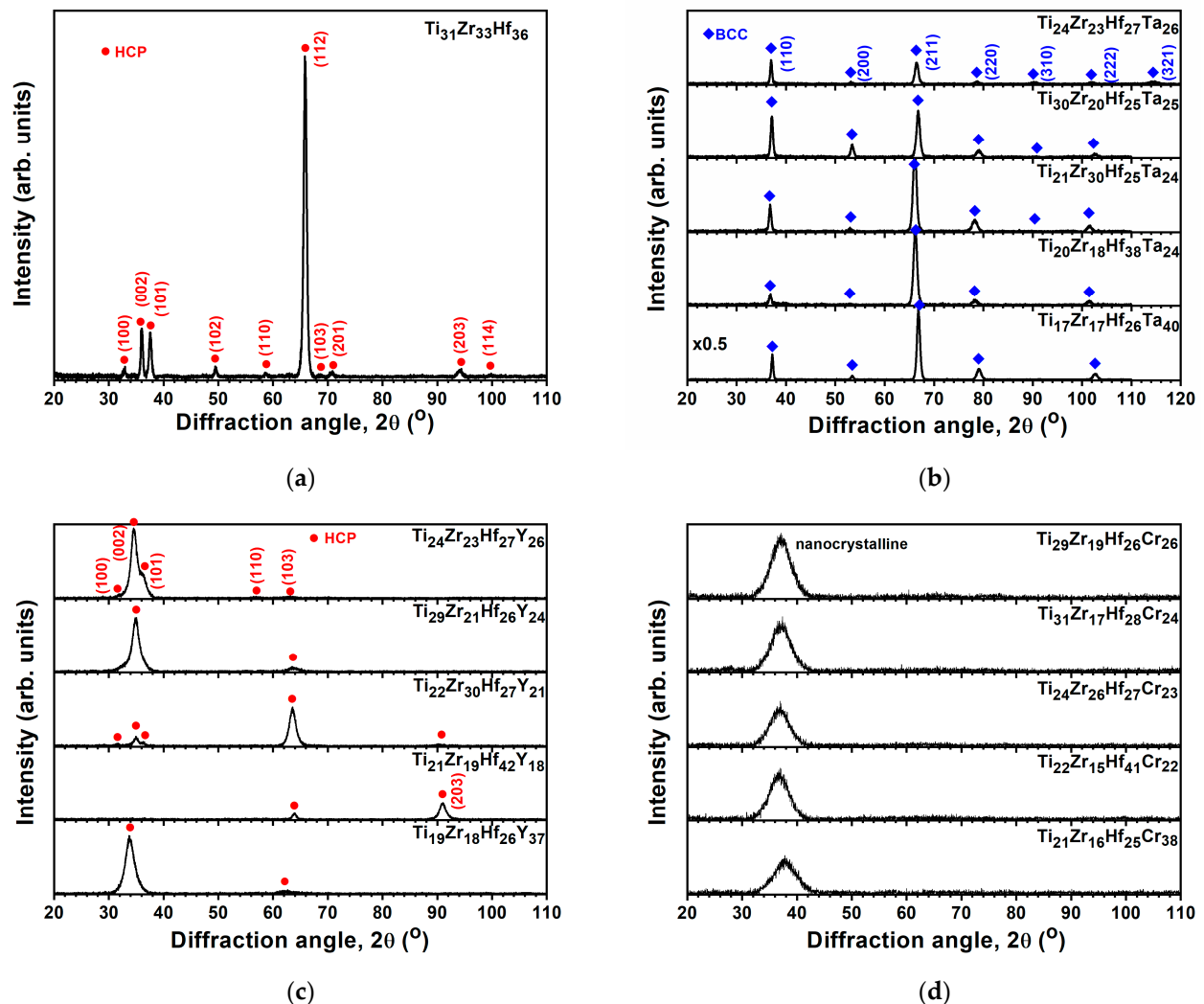
3.1. Chemical Compositions and Phases

Table 2 lists the chemical compositions of the TiZrHf(Ta, Y, Cr) films. The O contents in the TiZrHf, TiZrHfTa, and TiZrHfY films were in the range of 3.4–6.5 at.%, whereas the TiZrHfCr films had a lower O content of 0–2.6 at.%. These TiZrHf(Ta, Y, Cr) films were denoted by their metallic compositions. The calculated VEC, δ , ΔH_{mix} , and ΔS_{mix} values, without considering the oxygen content, are shown in Table 2. The ΔS_{mix} of $\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$ film was 9.11 J/mol K or 1.10 R, whereas the ΔS_{mix} values of all the prepared TiZrHf(Ta, Y, Cr) films were in the range of 1.31–1.38 R, classified as MEAs. The equilibrium state of Ti, Zr, and Hf at room temperature is a close-packed hexagonal (HCP) structure (ICDD 00-044-1294, 00-005-0665, and 00-038-1478). It is expected that the TiZrHf alloys should exhibit a single HCP structure [22]. However, Tsai et al. [23] reported a TiZrHf film exhibiting a body-centered cubic (BCC) structure. This discrepancy may arise due to the non-equilibrium nature of the sputtering process involving high-energy particle collisions, leading to the formation of high-temperature phases for the TiZrHf films. In this study, a co-sputtered $\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$ film exhibited an HCP phase, as shown in Figure 2a. Figure 2b displays that all the surveyed TiZrHfTa films exhibited a single BCC phase, either for the near-equiatomic $\text{Ti}_{24}\text{Zr}_{23}\text{Hf}_{27}\text{Ta}_{26}$ or Ti-enriched $\text{Ti}_{30}\text{Zr}_{20}\text{Hf}_{25}\text{Ta}_{25}$, Zr-enriched $\text{Ti}_{21}\text{Zr}_{30}\text{Hf}_{25}\text{Ta}_{24}$, Hf-enriched $\text{Ti}_{20}\text{Zr}_{18}\text{Hf}_{38}\text{Ta}_{24}$, and Ta-enriched $\text{Ti}_{17}\text{Zr}_{17}\text{Hf}_{26}\text{Ta}_{40}$ films. The presence of (321) reflection, the seventh one, of the $\text{Ti}_{24}\text{Zr}_{23}\text{Hf}_{27}\text{Ta}_{26}$ film indicates that this phase is a BCC phase, not a simple cubic phase. The lattice constants of $\text{Ti}_{24}\text{Zr}_{23}\text{Hf}_{27}\text{Ta}_{26}$, $\text{Ti}_{30}\text{Zr}_{20}\text{Hf}_{25}\text{Ta}_{25}$, $\text{Ti}_{21}\text{Zr}_{30}\text{Hf}_{25}\text{Ta}_{24}$, $\text{Ti}_{20}\text{Zr}_{18}\text{Hf}_{38}\text{Ta}_{24}$, and $\text{Ti}_{17}\text{Zr}_{17}\text{Hf}_{26}\text{Ta}_{40}$ films were determined to be 0.3438, 0.3426, 0.3449, 0.3452, and 0.3426 nm, respectively, which interlaid those of BCC Ti (0.33065 nm, ICDD 00-044-1288), Zr (0.35453 nm, ICDD 00-034-06570), Hf (0.35 nm, ICDD 01-089-5154), and Ta (0.33058 nm, ICDD 00-004-0788). The high-entropy and rapid quenching effects resulted in the high-entropy alloys (HEAs) forming single-phase structures rather than complex intermetallic compounds. The δ values were 3.79% for the $\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$ film and 4.54–4.82% for the TiZrHfTa films, which implied the formation of solid solutions as $\delta < 6.5\%$ [17]. Moreover, the VEC value was 4.00 for the $\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$ film and 4.24–4.40 for the TiZrHfTa films, indicating their solid solutions were HCP and BCC phases [11], respectively. In contrast, the GIXRD patterns of TiZrHfY films exhibited an HCP phase (Figure 2c), whereas the TiZrHfCr films seemed nanocrystalline (Figure 2d). The δ , ΔH_{mix} , and VEC values were 6.81–8.07%, 6.89–10.91 kJ/mol, and 3.63–3.82 for the TiZrHfY films, respectively, whose structures could not be identified according to the δ - ΔH_{mix} phase selection rule proposed in [17] ascribed to limited data. Braic et al. [22] reported that the TiZrHfY film with a δ of 7.6% had two HCP phases, whereas the TiZrY film with a high δ of 8.6% was amorphous. Ti, Zr, Hf, and Y tend to form HCP phases. The large Y atom has a 16% expansion related to the average atom size of Ti, Zr, and Hf, which enlarges the lattice constants of an HCP structure for TiZrHfY films. By contrast, the small Cr atom reveals a −19% shrinkage related to the average atom size of Ti, Zr, and Hf, which makes the lattice unstable and reduces long-range order crystallinity. Therefore, the fabricated TiZrHfCr films were nanocrystalline or X-ray amorphous. The δ , ΔH_{mix} , and VEC values were 8.87–10.41%, 6.19–8.61 kJ/mol, and 4.44–4.77 for the TiZrHfCr films in this study. δ plays a critical role in forming amorphous phases [24]. Regarding kinetics, magnetron sputtering technology's lattice distortion and rapid quenching effects alleviate the diffusion of deposited atoms, promoting the emergence of nanocrystalline and amorphous composite structures in thin films.

Table 2. Chemical compositions, valence electron concentration, atomic-size difference, mixing enthalpy, and mixing entropy of TiZrHf(Ta, Y, Cr) films.

Sample	Chemical Composition (at.%)					VEC ¹	δ ² (%)	ΔH_{mix} ³ (kJ/mol)	ΔS_{mix} ⁴ (J/mol K)
	Ti	Zr	Hf	Ta/Y/Cr	O				
Ti ₃₁ Zr ₃₃ Hf ₃₆	28.9 ± 0.4	31.5 ± 0.6	34.5 ± 0.3	-	5.1 ± 0.1	4.00	3.79	0	9.11
Ti ₂₄ Zr ₂₃ Hf ₂₇ Ta ₂₆	22.7 ± 0.0	21.2 ± 0.4	25.9 ± 0.4	24.9 ± 0.2	5.3 ± 0.4	4.26	4.70	1.82	11.50
Ti ₃₀ Zr ₂₀ Hf ₂₅ Ta ₂₅	28.7 ± 0.3	19.1 ± 0.2	23.9 ± 0.3	23.1 ± 0.3	5.2 ± 0.4	4.24	4.62	1.62	11.44
Ti ₂₁ Zr ₃₀ Hf ₂₅ Ta ₂₄	20.2 ± 0.4	27.8 ± 0.2	23.9 ± 0.1	22.5 ± 0.1	5.6 ± 0.3	4.24	4.74	1.77	11.47
Ti ₂₀ Zr ₁₈ Hf ₃₈ Ta ₂₄	18.6 ± 0.8	16.6 ± 0.5	36.1 ± 0.5	22.7 ± 0.6	6.0 ± 0.4	4.24	4.54	1.82	11.12
Ti ₁₇ Zr ₁₇ Hf ₂₆ Ta ₄₀	15.7 ± 0.8	16.5 ± 0.4	24.9 ± 0.2	37.7 ± 0.4	5.2 ± 0.5	4.40	4.82	2.35	10.97
Ti ₂₄ Zr ₂₃ Hf ₂₇ Y ₂₆	22.0 ± 0.4	21.3 ± 0.5	25.4 ± 0.3	24.8 ± 0.7	6.5 ± 1.7	3.73	7.72	9.09	11.50
Ti ₂₉ Zr ₂₁ Hf ₂₆ Y ₂₄	27.9 ± 0.5	20.0 ± 0.1	24.2 ± 0.2	23.0 ± 0.2	4.9 ± 0.3	3.76	7.85	8.79	11.47
Ti ₂₂ Zr ₃₀ Hf ₂₇ Y ₂₁	20.4 ± 0.9	28.3 ± 0.5	25.8 ± 0.5	20.0 ± 0.8	5.5 ± 0.2	3.79	7.12	7.57	11.43
Ti ₂₁ Zr ₁₉ Hf ₄₂ Y ₁₈	19.9 ± 0.4	18.4 ± 0.2	40.7 ± 1.5	17.6 ± 0.9	3.4 ± 3.0	3.82	6.81	6.89	10.94
Ti ₁₉ Zr ₁₈ Hf ₂₆ Y ₃₇	18.1 ± 0.5	16.5 ± 0.5	24.3 ± 0.0	34.9 ± 0.3	6.2 ± 0.4	3.63	8.07	10.91	10.94
Ti ₂₉ Zr ₁₉ Hf ₂₆ Cr ₂₆	28.4 ± 0.4	18.2 ± 0.6	25.3 ± 0.3	25.7 ± 0.4	2.4 ± 0.5	4.53	9.29	6.96	11.42
Ti ₃₁ Zr ₁₇ Hf ₂₈ Cr ₂₄	30.2 ± 0.2	17.0 ± 0.3	27.8 ± 0.5	23.3 ± 0.1	1.7 ± 0.3	4.47	8.96	6.42	11.34
Ti ₂₄ Zr ₂₆ Hf ₂₇ Cr ₂₃	23.6 ± 0.6	25.3 ± 0.4	26.3 ± 0.3	22.2 ± 0.6	2.6 ± 1.2	4.46	9.10	6.61	11.51
Ti ₂₂ Zr ₁₅ Hf ₄₁ Cr ₂₂	21.7 ± 0.3	14.1 ± 0.2	40.4 ± 0.4	21.6 ± 0.3	2.2 ± 0.2	4.44	8.87	6.19	10.91
Ti ₂₁ Zr ₁₆ Hf ₂₅ Cr ₃₈	20.5 ± 0.1	16.0 ± 0.1	25.2 ± 0.0	38.3 ± 0.2	0.0 ± 0.0	4.77	10.41	8.61	11.08

¹ VEC: valence electron concentration. ² δ : atomic-size difference. ³ ΔH_{mix} : mixing enthalpy. ⁴ ΔS_{mix} : mixing entropy.

**Figure 2.** GIXRD patterns of the (a) TiZrHf, (b) TiZrHfTa, (c) TiZrHfY, and (d) TiZrHfCr films.

Our previous studies have reported the TEM observations of BCC TiZrHfTa [25] and HCP TiZrHfY [26] films, which exhibit coarse columnar structures. Figure 3a depicts the cross-sectional TEM (XTEM) image of the $\text{Ti}_{29}\text{Zr}_{19}\text{Hf}_{26}\text{Cr}_{26}$ film, distinguishing the Ti interlayer and the $\text{Ti}_{29}\text{Zr}_{19}\text{Hf}_{26}\text{Cr}_{26}$ film. The $\text{Ti}_{29}\text{Zr}_{19}\text{Hf}_{26}\text{Cr}_{26}$ film exhibits a featureless morphology, indicating the formation of an almost amorphous or nanocrystalline structure. The selected area electron diffraction (SAED) pattern reveals diffused rings, implying the formation of a nanocrystalline structure (Figure 3b). Figure 3c shows a high-resolution TEM (HRTEM) image with no distinct crystalline regions in which no well-defined crystalline domains are observed, further indicating that the crystallites are extremely fine. Structural characterization, including GIXRD and HRTEM analysis, confirms that the $\text{Ti}_{29}\text{Zr}_{19}\text{Hf}_{26}\text{Cr}_{26}$ thin film possesses a nanocrystalline structure.

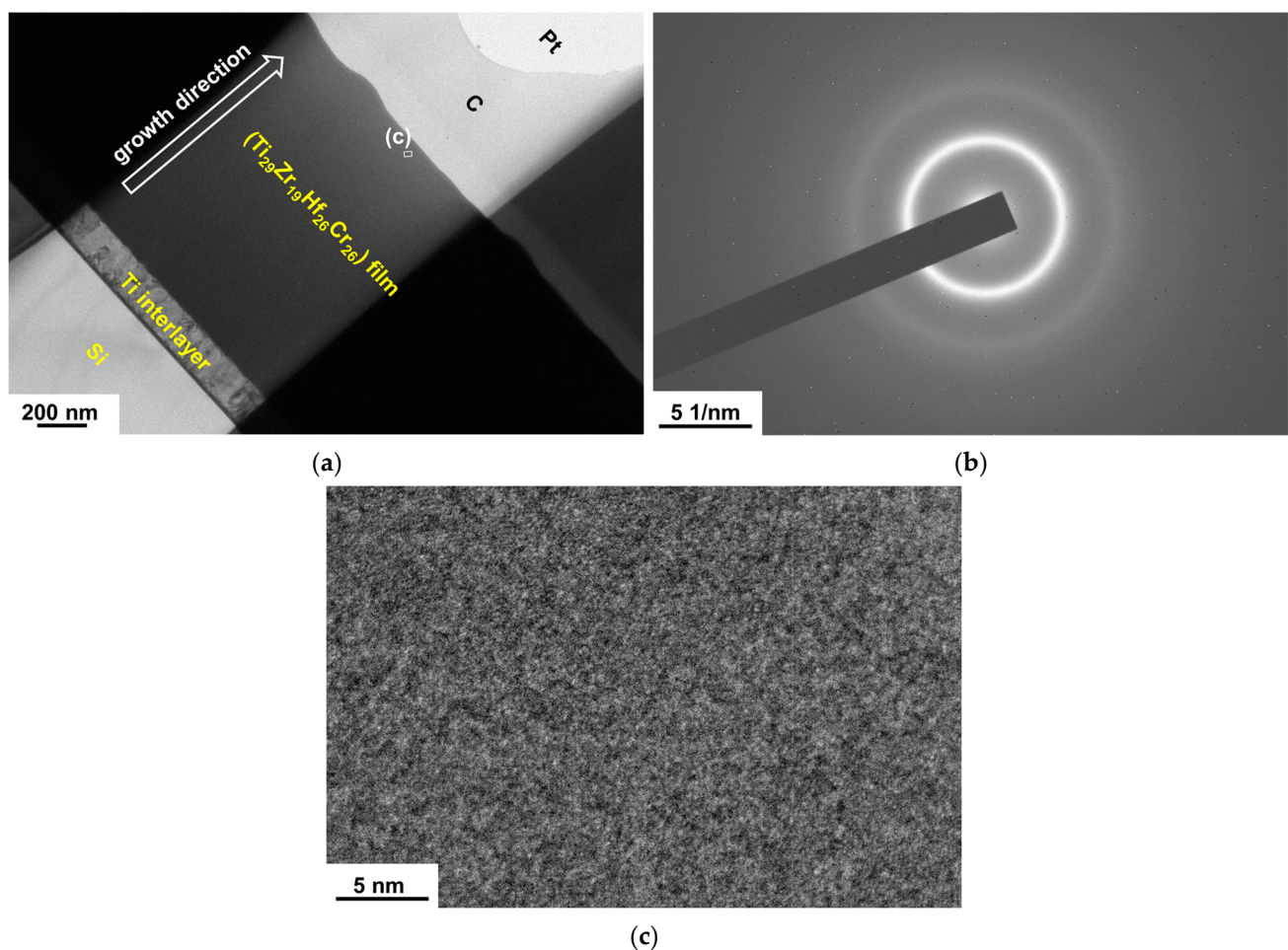


Figure 3. (a) XTEM, (b) SAED, and (c) HRTEM images of the $\text{Ti}_{29}\text{Zr}_{19}\text{Hf}_{26}\text{Cr}_{26}$ film.

3.2. Mechanical and Anticorrosive Properties of TiZrH(Ta, Y, Cr) Films

Table 3 lists the hardness (H) and elastic modulus (E) values of TiZrHf, TiZrHfTa, TiZrHfY, and TiZrHfCr films. The $\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$ film had H and E values of 7.4 and 179 GPa, respectively, an elastic recovery (W_e) of 31%, and a residual stress of -0.13 GPa. The TiZrHfTa films had H and E values of 4.6–5.4 and 100–114 GPa, respectively, lower than those of the $\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$ film. The TiZrHfTa films had W_e values of 28–33% and residual stresses ranging from 0 to -0.23 GPa, comparable to those of the $\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$ film. The TiZrHfY films had H and E values of 6.0–7.9 and 106–134 GPa, respectively. The H values of the TiZrHfY films were comparable to those of the $\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$ film, accompanied by higher W_e values of 33–38% and larger compressive residual stresses between

−0.41 and −0.74 GPa. However, the E values of the TiZrHfY films were at low levels of 106–134 GPa. The TiZrHfCr films had H and E values of 5.3–8.4 and 91–113 GPa, respectively, W_e values of 43–48%, and residual stresses ranging from −0.15 to −0.43 GPa. The TiZrHfY film exhibited enhanced mechanical performance and higher compressive residual stress, primarily attributed to Y's relatively large atomic radius. Incorporating Y atoms increases the lattice parameters of the HCP structure, thereby intensifying lattice mismatch and structural stress. Additionally, the significant atomic size difference between Y and the other constituent elements promotes solid solution strengthening, further contributing to the improved mechanical properties of the TiZrHfY film.

Table 3. Mechanical properties and residual stresses of TiZrHf(Ta, Y, Cr) films.

Sample	H ¹ (GPa)	E ² (GPa)	W_e ³ (%)	σ ⁴ (GPa)
Ti ₃₁ Zr ₃₃ Hf ₃₆	7.4 ± 0.8	179 ± 14	31	−0.13 ± 0.00
Ti ₂₄ Zr ₂₃ Hf ₂₇ Ta ₂₆	4.7 ± 0.6	104 ± 9	32	−0.23 ± 0.00
Ti ₃₀ Zr ₂₀ Hf ₂₅ Ta ₂₅	4.6 ± 0.3	100 ± 4	28	0.00 ± 0.00
Ti ₂₁ Zr ₃₀ Hf ₂₅ Ta ₂₄	5.0 ± 0.3	101 ± 3	33	−0.14 ± 0.24
Ti ₂₀ Zr ₁₈ Hf ₃₈ Ta ₂₄	5.1 ± 0.5	105 ± 6	30	−0.04 ± 0.11
Ti ₁₇ Zr ₁₇ Hf ₂₆ Ta ₄₀	5.4 ± 0.3	114 ± 3	30	−0.14 ± 0.05
Ti ₂₄ Zr ₂₃ Hf ₂₇ Y ₂₆	6.0 ± 0.6	106 ± 6	33	−0.48 ± 0.02
Ti ₂₉ Zr ₂₁ Hf ₂₆ Y ₂₄	7.4 ± 0.5	114 ± 6	37	−0.54 ± 0.01
Ti ₂₂ Zr ₃₀ Hf ₂₇ Y ₂₁	7.9 ± 0.5	131 ± 7	36	−0.41 ± 0.13
Ti ₂₁ Zr ₁₉ Hf ₄₂ Y ₁₈	7.9 ± 0.5	134 ± 9	38	−0.46 ± 0.07
Ti ₁₉ Zr ₁₈ Hf ₂₆ Y ₃₇	6.1 ± 0.3	106 ± 4	37	−0.74 ± 0.04
Ti ₂₉ Zr ₁₉ Hf ₂₆ Cr ₂₆	6.6 ± 0.1	105 ± 3	45	−0.24 ± 0.00
Ti ₃₁ Zr ₁₇ Hf ₂₈ Cr ₂₄	6.8 ± 0.0	104 ± 1	44	−0.27 ± 0.01
Ti ₂₄ Zr ₂₆ Hf ₂₇ Cr ₂₃	5.3 ± 0.4	91 ± 5	44	−0.15 ± 0.00
Ti ₂₂ Zr ₁₅ Hf ₄₁ Cr ₂₂	6.5 ± 0.0	105 ± 1	43	−0.43 ± 0.01
Ti ₂₁ Zr ₁₆ Hf ₂₅ Cr ₃₈	8.4 ± 0.1	113 ± 1	48	−0.28 ± 0.01

¹ H : hardness. ² E : elastic modulus. ³ W_e : elastic recovery. ⁴ σ : residual stress.

Figure 4 depicts the potentiodynamic polarization curves of SUS420 substrate, Ti₃₁Zr₃₃Hf₃₆, TiZrHfTa, TiZrHfY, and TiZrHfCr films tested in a 3.5 wt.% NaCl aqueous solution and the relevant data are summarized in Table 4. While only one specimen was tested per film, possible uncertainties in corrosion parameters may result from variations in surface condition, measurement reproducibility, and reference electrode stability. Based on experience with similar tests, the accuracy of polarization resistance (R_p) values is estimated to be within ±10%. The Ti₃₁Zr₃₃Hf₃₆ film exhibited an I_{corr} value of 0.338 $\mu\text{A}/\text{cm}^2$ and an E_{corr} value of −354 mV, along with a high polarization resistance R_p of $1.9 \times 10^5 \Omega \cdot \text{cm}^2$, indicating excellent corrosion resistance. Numerous studies have reported that refractory metals in TiZr-based refractory high-entropy alloys tend to form dense and highly protective oxide layers on the surface, thereby imparting superior corrosion resistance [27–30]. Compared to the Ti₃₁Zr₃₃Hf₃₆ film, adding Ta did not enhance the corrosion resistance. In contrast, the film with Y addition exhibited the poorest corrosion resistance, likely due to the formation of Y oxides that provide active pathways for corrosive species, thereby facilitating penetration and compromising the film's protective capability [31,32]. The TiZrHfCr film demonstrated significantly improved corrosion resistance, as Cr is known to be one of the most effective elements for enhancing the corrosion resistance of coatings. The incorporation of an appropriate amount of Cr promotes the formation of a continuous and uniform Cr₂O₃ passivation layer on the surface, which effectively protects the coating from corrosion [33,34].

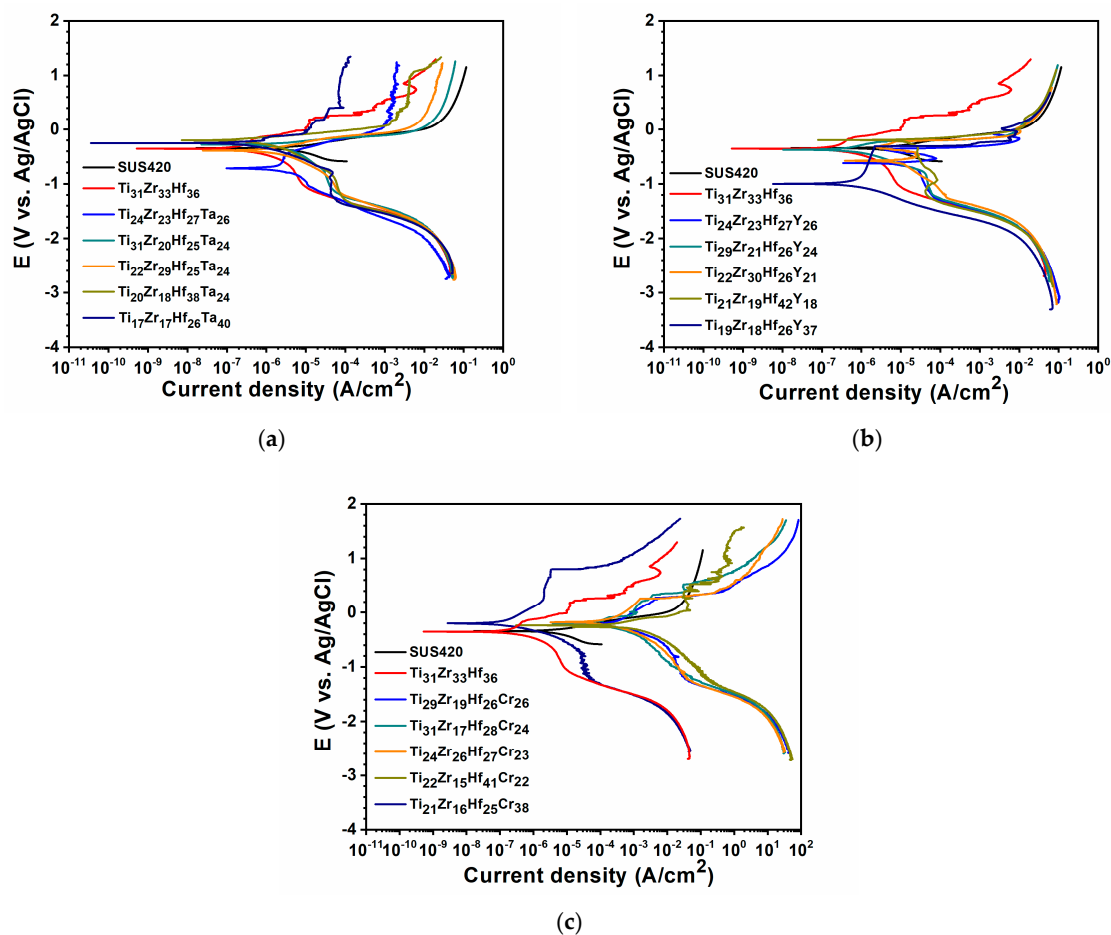


Figure 4. Potentiodynamic polarization curves of SUS420 substrate, $\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$ film, and (a) TiZrHfTa , (b) TiZrHfY , and (c) TiZrHfCr films tested in a 3.5 wt% NaCl aqueous solution.

Table 4. Corrosive characteristics of the bare SUS420 substrate and TiZrHf(Ta, Y, Cr) films.

Sample	E_{corr}^1 (mV)	I_{corr}^2 ($\mu\text{A}/\text{cm}^2$)	R_p^3 ($\Omega \cdot \text{cm}^2$)	β_a^4 (mV)	β_c^5 (mV)	R_p Ratio
SUS420	−345	4.826	7.7×10^3	132.6	238.5	1.0
$\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$	−354	0.338	1.9×10^5	472.3	221.1	25.2
$\text{Ti}_{24}\text{Zr}_{23}\text{Hf}_{27}\text{Ta}_{26}$	−714	2.129	2.4×10^4	169.4	360.1	3.1
$\text{Ti}_{30}\text{Zr}_{20}\text{Hf}_{25}\text{Ta}_{25}$	−281	1.497	1.7×10^4	66.3	443.2	2.2
$\text{Ti}_{21}\text{Zr}_{30}\text{Hf}_{25}\text{Ta}_{24}$	−388	1.330	3.4×10^4	139.6	396.2	4.4
$\text{Ti}_{20}\text{Zr}_{18}\text{Hf}_{38}\text{Ta}_{24}$	−199	0.231	1.0×10^5	65.5	366.7	13.6
$\text{Ti}_{17}\text{Zr}_{17}\text{Hf}_{26}\text{Ta}_{40}$	−251	0.221	1.2×10^5	88.4	178.2	15.1
$\text{Ti}_{24}\text{Zr}_{23}\text{Hf}_{27}\text{Y}_{26}$	−619	6.291	2.9×10^3	47.4	318.8	0.4
$\text{Ti}_{29}\text{Zr}_{21}\text{Hf}_{26}\text{Y}_{24}$	−372	0.418	6.9×10^4	95.3	216.9	9.0
$\text{Ti}_{22}\text{Zr}_{30}\text{Hf}_{27}\text{Y}_{21}$	−578	18.120	3.1×10^3	178.2	470.9	0.4
$\text{Ti}_{21}\text{Zr}_{19}\text{Hf}_{42}\text{Y}_{18}$	−199	15.414	1.2×10^3	46.1	473.2	0.2
$\text{Ti}_{19}\text{Zr}_{18}\text{Hf}_{26}\text{Y}_{37}$	−997	0.551	8.3×10^4	254.3	179.2	10.8
$\text{Ti}_{29}\text{Zr}_{19}\text{Hf}_{26}\text{Cr}_{26}$	−225	0.269	2.0×10^5	359.3	190.1	26.2
$\text{Ti}_{31}\text{Zr}_{17}\text{Hf}_{28}\text{Cr}_{24}$	−202	0.064	4.5×10^5	101.9	184.8	58.1
$\text{Ti}_{24}\text{Zr}_{26}\text{Hf}_{27}\text{Cr}_{23}$	−180	0.140	3.5×10^5	301.6	176.7	45.1
$\text{Ti}_{22}\text{Zr}_{15}\text{Hf}_{41}\text{Cr}_{22}$	−243	0.319	7.8×10^4	78.3	215.1	10.2
$\text{Ti}_{21}\text{Zr}_{16}\text{Hf}_{25}\text{Cr}_{38}$	−201	0.133	3.3×10^5	318.5	146.6	42.7

¹ E_{corr} : corrosion potential. ² I_{corr} : corrosion current density. ³ R_p : polarization resistance. ⁴ β_a : anodic Tafel slope. ⁵ β_c : cathodic Tafel slope.

3.3. Thermal Stability of TiZrHf(Ta, Y, Cr) Films

The thermal stability of TiZrHf(Ta, Y, Cr) films was evaluated by annealing these films in a vacuum tube furnace. Figure 5 displays the GIXRD patterns of the Ti₃₁Zr₃₃Hf₃₆ films annealed at 500, 700, and 800 °C. The structure of the Ti₃₁Zr₃₃Hf₃₆ film annealed at 500 °C maintained an HCP phase, whereas the Ti₃₁Zr₃₃Hf₃₆ films annealed at 700 and 800 °C showed an additional oxide phase (ICDD 00-042-1164). Figure 6 depicts the surface morphologies of the annealed Ti₃₁Zr₃₃Hf₃₆ films. Granular oxide particles were observed on the surfaces of 700 and 800 °C-annealed Ti₃₁Zr₃₃Hf₃₆ films. After annealing at high temperatures, the phase splitting for multi-principal element alloys was not observed for the Ti₃₁Zr₃₃Hf₃₆ films. The hardness value of the Ti₃₁Zr₃₃Hf₃₆ film was 7.4 GPa at the as-deposited state and was increased to 11.6 and 18.8 GPa, and then decreased to 17.6 GPa as the film was annealed at 500, 700, and 800 °C, respectively. The elastic modulus value was 179 GPa at the as-deposited state and was varied to 171, 241, and 226 GPa as the film was annealed at 500, 700, and 800 °C, respectively. The oxide phase formation and randomly disposed geometry increased the mechanical properties of the Ti₃₁Zr₃₃Hf₃₆ films.

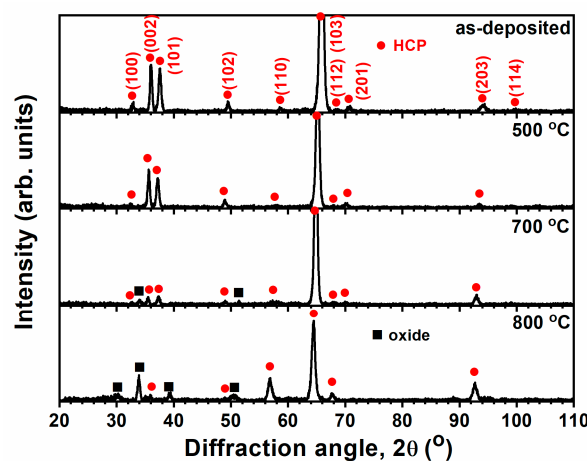


Figure 5. GIXRD patterns of the Ti₃₁Zr₃₃Hf₃₆ films annealed at 500, 700, and 800 °C for 1 h.

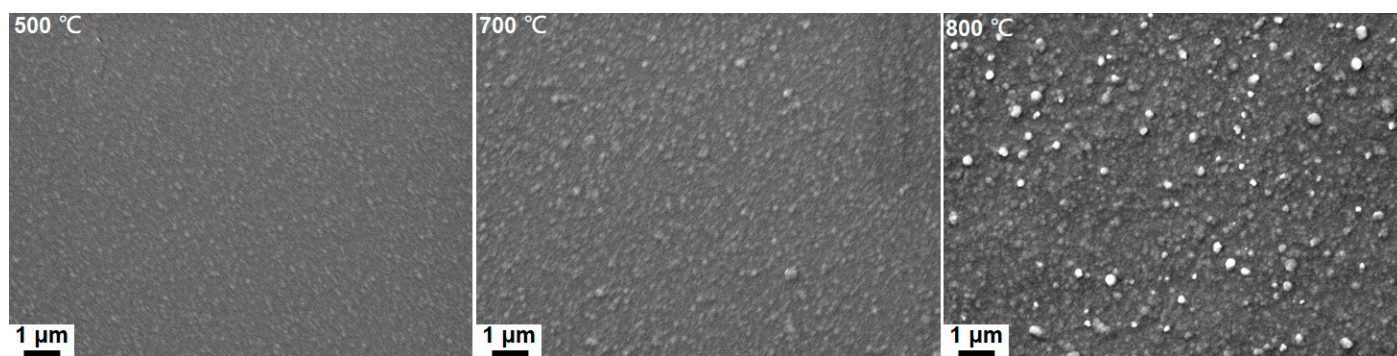


Figure 6. Surface morphologies of the Ti₃₁Zr₃₃Hf₃₆ films annealed at 500, 700, and 800 °C for 1 h.

Figure 7a depicts the GIXRD patterns of the TiZrHfTa films annealed in a vacuum at 500 °C for 1 h. The Ti₁₇Zr₁₇Hf₂₆Ta₄₀ film maintained a BCC phase, namely BCC2; however, the peak widths broadened, implying recrystallization of the film. Figure 8a depicts an XTEM image of the 500 °C-annealed Ti₁₇Zr₁₇Hf₂₆Ta₄₀ film. The SAED pattern reveals a BCC structure with (110), (200), (211), (220), and (310) diffraction rings (Figure 8b). Figure 8c displays the dark-field image related to the (200) diffraction spot shown in Figure 8b, which exhibits a columnar structure with 36–105 nm widths. The HRTEM image shown in Figure 8d reveals lattice fringes with a *d*-spacing of 0.237 nm correlated to the BCC2 (110)

planes. In contrast, all the other TiZrHfTa films exhibited phase separation after annealing at 500 °C. The as-deposited BCC phase split into two BCC phases (Figure 7a); the new BCC phase, namely BCC1, had d -spacings larger than those of BCC2. Moreover, an HCP phase appeared after these TiZrHfTa films were annealed at 700 °C (Figure 7b). Yao et al. [35] and Chen et al. [36] reported that bulk metallic HfNbTaTiZr alloys transformed into a BCC Ta–Nb, an HCP Hf–Zr, and a BCC matrix after annealing at 500–700 °C and 550–700 °C, respectively. The phase separation due to annealing did not occur at 500 and 700 °C for the Ti₁₇Zr₁₇Hf₂₆Ta₄₀ film. Cheng et al. [37] reported that (TiZrHf)_x(NbTa)_{1–x} thin films with 0.55 < x < 0.7 exhibited high resistance to crystallization up to 500 °C. Figure 9a presents an XTEM image of the Ti₂₀Zr₁₈Hf₃₈Ta₂₄ film after annealing at 700 °C for 1 h. The SAED image from the outer part of the film reveals two BCC phases, BCC1 and BCC2, and an HCP phase (Figure 9b). Figure 9c displays a dark-field image related to the BCC2 (110) diffraction spot shown in Figure 9b. The outer part of the annealed films maintained a columnar structure with widths of 72–75 nm. Figure 9d shows an HRTEM image, which reveals lattice fringes with d -spacings of 0.249, 0.235, and 0.268 nm correlating to BCC1 (110), BCC2 (110), and HCP (002) planes, respectively. By contrast, the inner part of the film adjacent to the Ti interlayer consists of a granular structure, as shown in Figure 9e. According to the structure-zone model for sputtered films [38], a columnar structure is familiar. Annealing provides thermal energy that accelerates atomic diffusion. As sputtered films are annealed, energetic atoms could move along grain boundaries, promote grain growth and defect annihilation, and form a coarser columnar structure, accompanied by well-aligned crystallographic orientation. In contrast, recrystallization and grain growth at high temperatures tend to create a granular structure attributed to the driving force of reducing free energy. The hardness values of the TiZrHfTa films increased from 4.6 to 5.4 GPa at the as-deposited state to 6.8–7.9 and 11.2–12.5 GPa after they were annealed at 500 and 700 °C, respectively, as shown in Table 5. The elastic moduli increased from 100–114 GPa at the as-deposited state to 128–144 and 182–196 GPa after 500 and 700 °C annealing, respectively.

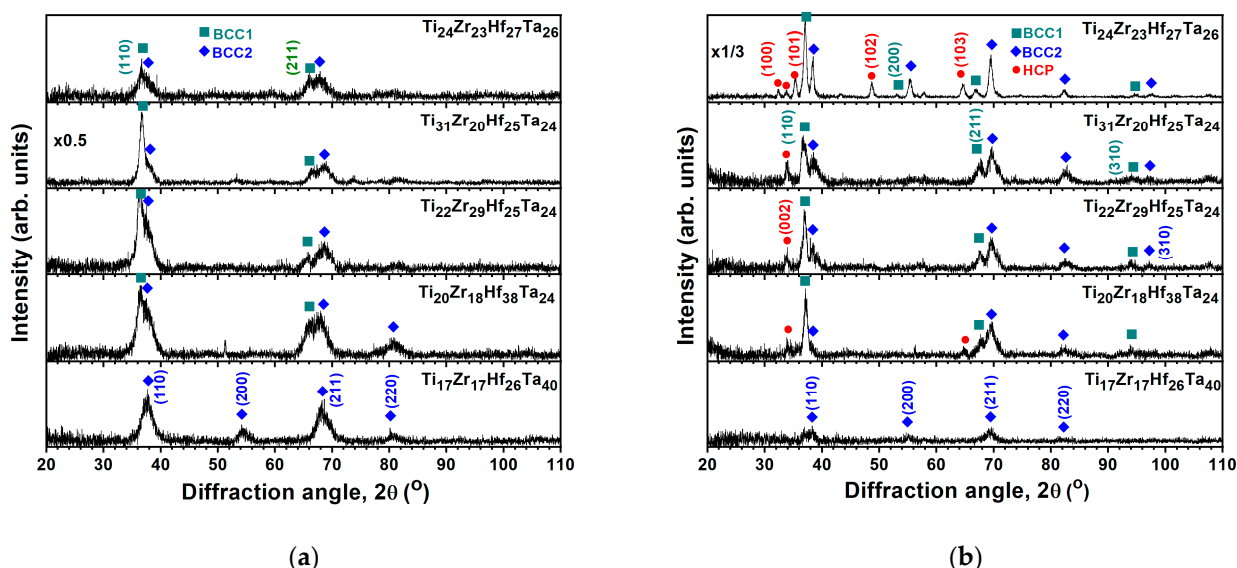


Figure 7. GIXRD patterns of the TiZrHfTa films annealed for 1 h at (a) 500 and (b) 700 °C.

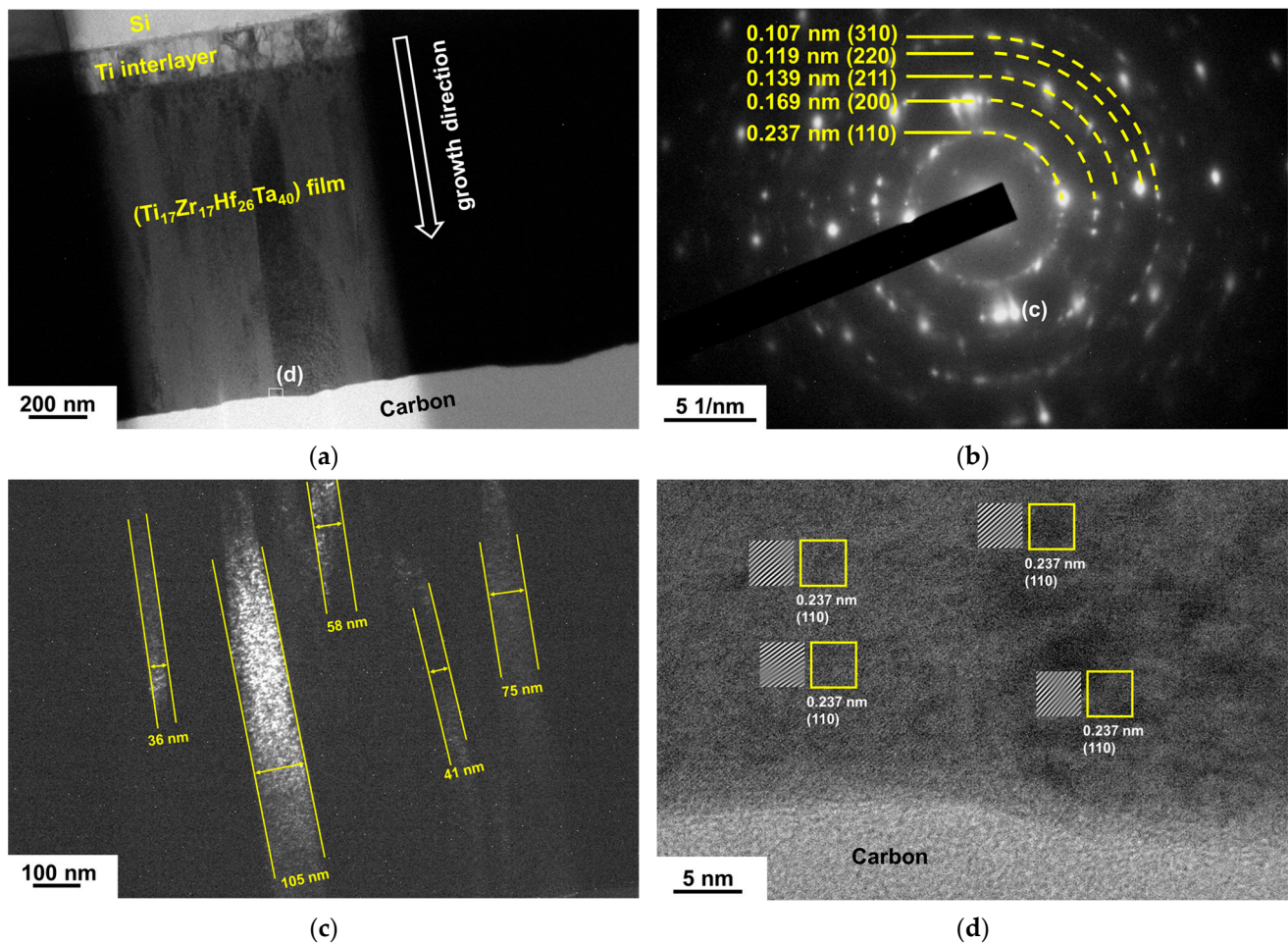


Figure 8. (a) XTEM, (b) SAED, (c) dark-field, and (d) HRTEM images of the $\text{Ti}_{17}\text{Zr}_{17}\text{Hf}_{26}\text{Ta}_{40}$ film after annealing at 500 °C for 1 h.

Table 5. Mechanical properties of as-deposited and annealed TiZrHf(Ta, Y, Cr) films.

Sample	Hardness (GPa)			Elastic Modulus (GPa)		
	RT	500 °C	700 °C	RT	500 °C	700 °C
$\text{Ti}_{31}\text{Zr}_{33}\text{Hf}_{36}$	7.4 ± 0.8	11.6 ± 0.2	18.8 ± 1.7	104 ± 9	171 ± 2	241 ± 14
$\text{Ti}_{24}\text{Zr}_{23}\text{Hf}_{27}\text{Ta}_{26}$	4.7 ± 0.6	7.9 ± 0.6	12.5 ± 0.4	100 ± 4	138 ± 6	182 ± 3
$\text{Ti}_{30}\text{Zr}_{20}\text{Hf}_{25}\text{Ta}_{25}$	4.6 ± 0.3	7.4 ± 0.2	11.4 ± 1.2	101 ± 3	131 ± 3	196 ± 13
$\text{Ti}_{21}\text{Zr}_{30}\text{Hf}_{25}\text{Ta}_{24}$	5.0 ± 0.3	6.9 ± 0.3	12.2 ± 0.5	105 ± 6	128 ± 5	193 ± 4
$\text{Ti}_{20}\text{Zr}_{18}\text{Hf}_{38}\text{Ta}_{24}$	5.1 ± 0.5	6.8 ± 0.6	11.2 ± 0.4	114 ± 3	135 ± 8	188 ± 5
$\text{Ti}_{17}\text{Zr}_{17}\text{Hf}_{26}\text{Ta}_{40}$	5.4 ± 0.3	7.5 ± 0.3	12.1 ± 0.8	106 ± 6	144 ± 5	192 ± 7
$\text{Ti}_{24}\text{Zr}_{23}\text{Hf}_{27}\text{Y}_{26}$	6.0 ± 0.6	9.1 ± 0.5	10.4 ± 0.6	114 ± 6	139 ± 3	184 ± 9
$\text{Ti}_{29}\text{Zr}_{21}\text{Hf}_{26}\text{Y}_{24}$	7.4 ± 0.5	8.4 ± 0.4	10.8 ± 0.5	131 ± 7	141 ± 7	189 ± 7
$\text{Ti}_{22}\text{Zr}_{30}\text{Hf}_{27}\text{Y}_{21}$	7.9 ± 0.5	8.7 ± 0.3	9.3 ± 0.4	134 ± 9	132 ± 3	172 ± 4
$\text{Ti}_{21}\text{Zr}_{19}\text{Hf}_{42}\text{Y}_{18}$	7.9 ± 0.5	11.6 ± 0.4	8.5 ± 0.4	106 ± 4	199 ± 2	170 ± 4
$\text{Ti}_{19}\text{Zr}_{18}\text{Hf}_{26}\text{Y}_{37}$	6.1 ± 0.3	9.8 ± 0.7	15.8 ± 1.1	104 ± 9	165 ± 6	236 ± 10
$\text{Ti}_{29}\text{Zr}_{19}\text{Hf}_{26}\text{Cr}_{26}$	6.6 ± 0.1	10.5 ± 0.6	16.4 ± 3.1	105 ± 3	142 ± 6	202 ± 23
$\text{Ti}_{31}\text{Zr}_{17}\text{Hf}_{28}\text{Cr}_{24}$	6.8 ± 0.0	11.1 ± 0.2	20.6 ± 0.6	104 ± 1	152 ± 2	241 ± 6
$\text{Ti}_{24}\text{Zr}_{26}\text{Hf}_{27}\text{Cr}_{23}$	5.3 ± 0.4	9.0 ± 0.7	15.0 ± 5.2	91 ± 5	139 ± 10	205 ± 43
$\text{Ti}_{22}\text{Zr}_{15}\text{Hf}_{41}\text{Cr}_{22}$	6.5 ± 0.0	11.3 ± 0.4	19.0 ± 0.4	105 ± 1	154 ± 2	223 ± 3
$\text{Ti}_{21}\text{Zr}_{16}\text{Hf}_{25}\text{Cr}_{38}$	8.4 ± 0.1	11.6 ± 0.1	19.5 ± 0.2	113 ± 1	154 ± 1	234 ± 2

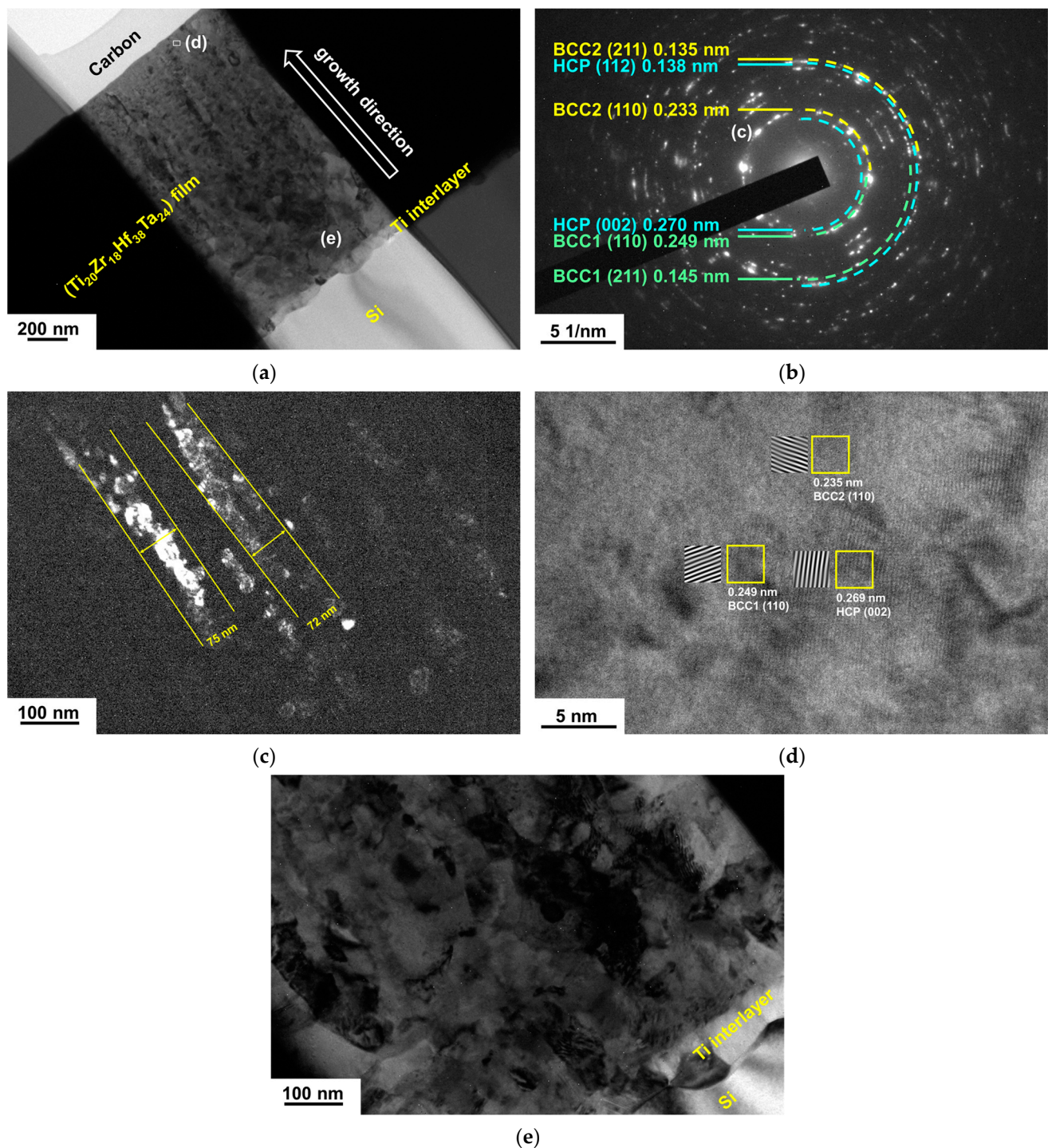


Figure 9. (a) XTEM image of the $\text{Ti}_{20}\text{Zr}_{18}\text{Hf}_{38}\text{Ta}_{24}$ film after annealing at 700 °C for 1 h; (b) SAED, (c) dark-field, and (d) HRTEM images of the outer part of the film; (e) XTEM image of the inner part of the film.

Figure 10 depicts the GIXRD patterns of TiZrHfY thin films after they were annealed at 500 and 700 °C for 1 h. The as-deposited HCP phase of most of the TiZrHfY films splits into a combination of HCP and BCC phases, along with the formation of a cubic Y_2O_3 oxide [ICDD 00-043-0661] after 500 °C annealing. The $\text{Ti}_{21}\text{Zr}_{19}\text{Hf}_{42}\text{Y}_{18}$ film with high Hf and low Y contents maintained the original HCP phase. All the TiZrHfY films exhibited similar XRD reflections after 700 °C annealing. The standard Gibbs free energies of oxide formation at 500 °C are −1119, −803, −950, and −1001 kJ/(mol of O_2) for Y_2O_3 , TiO_2 , ZrO_2 , and HfO_2 [39], respectively. Y_2O_3 is the dominant oxide phase. Figure 11a displays

an XTEM image of the $\text{Ti}_{19}\text{Zr}_{18}\text{Hf}_{26}\text{Y}_{37}$ after annealing at 500 °C for 1 h. Figure 11b shows an SAED pattern with BCC (110), (200), (211), and (220) and Y_2O_3 (111), (200), and (311) signals. The diffraction ring for HCP (100) plans was insignificant, and it lay between Y_2O_3 (111) and (200) signals. Figure 11c shows a dark-field image correlated to the BCC (110) diffraction point in the SAED pattern, which displays a columnar structure with widths of 41–59 nm. Figure 11d exhibits an HRTEM image near the sample's surface, which reveals lattice fringes with a d -spacing of 0.263 nm belonging to Y_2O_3 (200) planes. Figure 11e presents an HRTEM image for the region beneath the sample's surface, as Figure 11a shows, which displays lattice fringes with a d -spacing of 0.252 nm for BCC (110) planes. The hardnesses of the TiZrHfY films increased from 6.0–7.9 GPa at the as-deposited state to 8.4–11.6 and 8.5–15.8 GPa (Table 5) after they were annealed at 500 and 700 °C, respectively. The elastic moduli increased from 104–134 GPa at the as-deposited state to 132–199 and 170–236 GPa after 500 and 700 °C annealing, respectively. The increases in mechanical properties after annealing for the TiZrHfY films were not as significant as those of the annealed TiZrHfTa and TiZrHfCr films. This may be attributed to the influence of Y_2O_3 oxides, which possess a low hardness in the range of 8–9 GPa [40]. Xu et al. [41] reported that cubic Y_2O_3 films exhibited an optimal hardness of 12 GPa after 350 °C annealing, whereas the hardness decreased to 7–9 GPa after 500–650 °C annealing. The improvement on mechanical properties of the annealed TiZrHfY films contributed from oxides was limited.

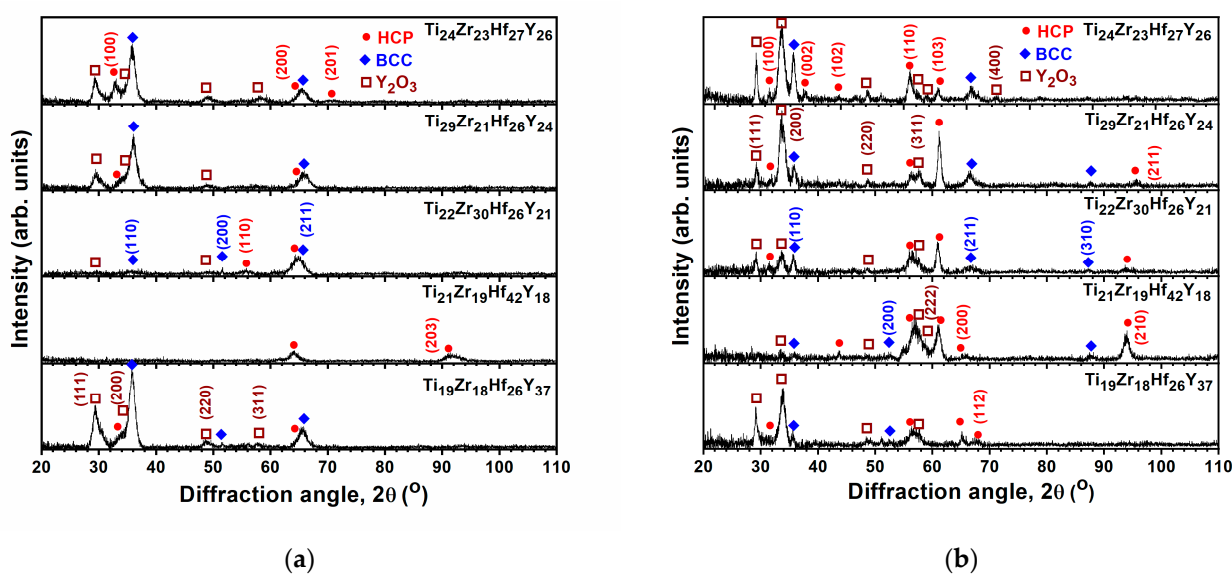


Figure 10. GIXRD patterns of the TiZrHfY films annealed at (a) 500 and (b) 700 °C for 1 h.

Figure 12 displays GIXRD patterns of the TiZrHfCr thin films annealed at 500 and 700 °C for 1 h. BCC and HCP phases were observed, accompanied by the appearance of ZrO_2 oxide phases. The ZrO_2 phases were monoclinic (ICDD 00-037-1484) and tetragonal (ICDD 00-042-1164) at 500 and 700 °C, respectively. The hardnesses of the TiZrHfCr films increased from 5.3–8.4 GPa at the as-deposited state to 9.0–11.6 and 15.0–20.6 GPa (Table 5) after they were annealed at 500 and 700 °C, respectively. The elastic moduli increased from 91–113 GPa at the as-deposited state to 139–154 and 202–241 GPa after 500 and 700 °C annealing, respectively. The mechanical properties of the 700 °C-annealed TiZrHfCr films were the highest values within the studied TiZrHf(Ta, Y, Cr) films. This may be attributed to the structural transformation of the TiZrHfCr film from an amorphous phase in the as-deposited state to a mixed BCC and HCP phase after 1 h of annealing. Moreover, hardness values of 12–19 GPa were reported for ZrO_2 thin films [42–44], which implied the

oxide phase could contribute to the enhancement of mechanical properties for the annealed TiZrHfCr films.

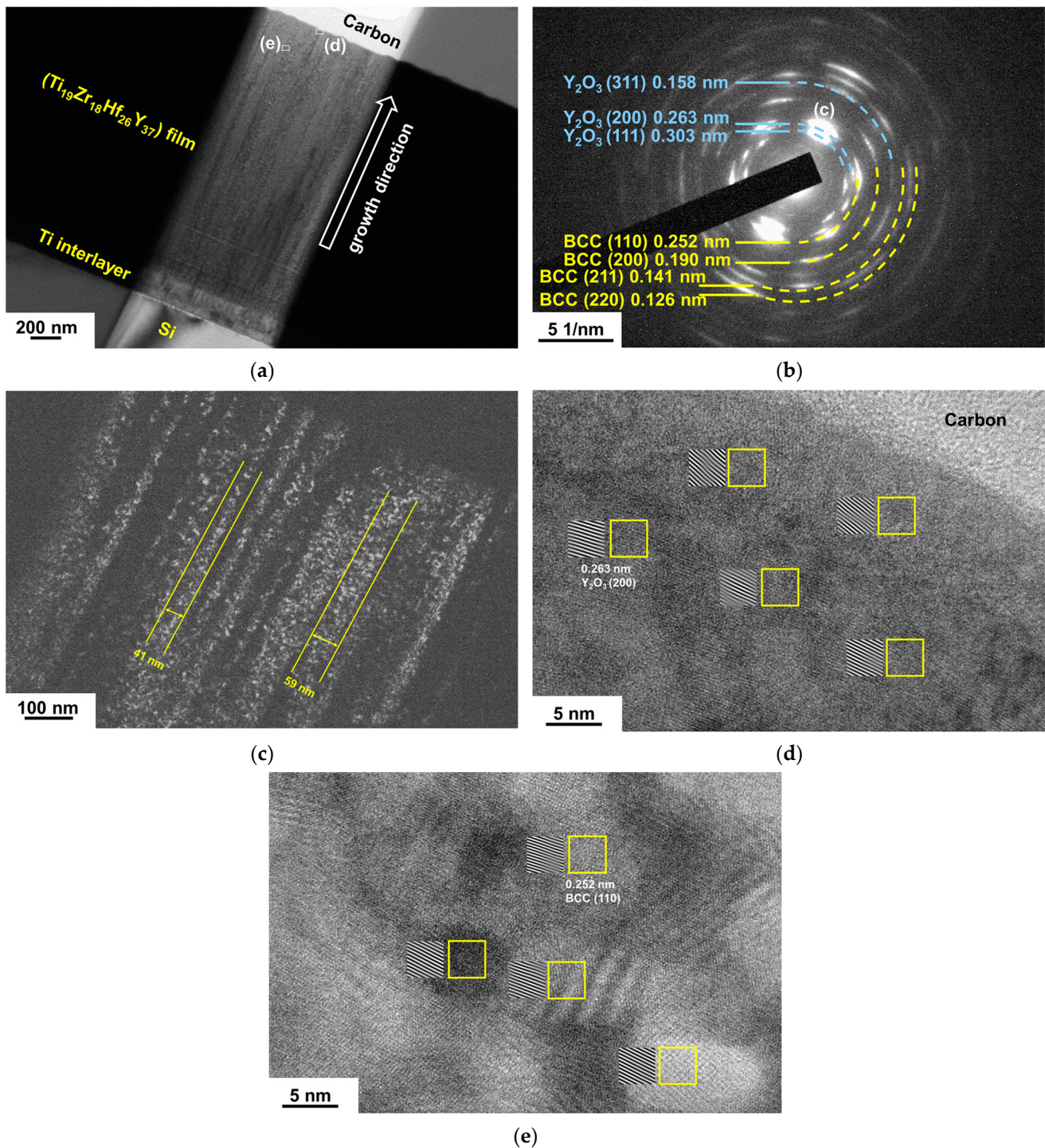


Figure 11. (a) XTEM, (b) SAED, and (c) dark-field images of the $\text{Ti}_{19}\text{Zr}_{18}\text{Hf}_{26}\text{Y}_{37}$ film after annealing at 500 °C for 1 h; HRTEM images at the near-surface region (d) and the inner part (e) of the film.

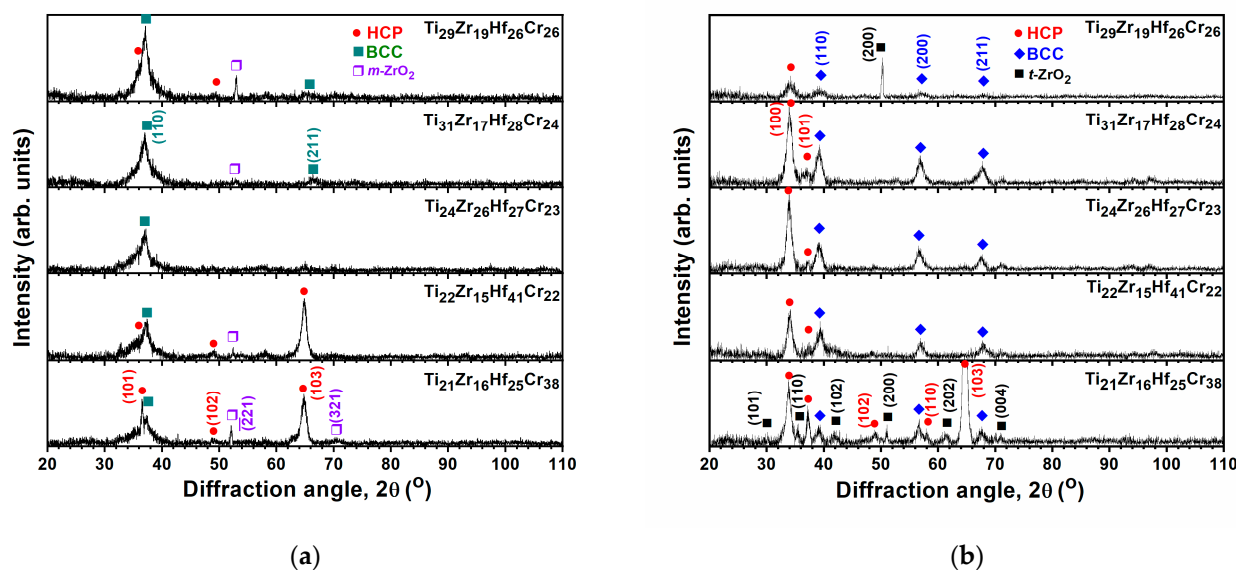


Figure 12. GIXRD patterns of the TiZrHfCr films annealed at (a) 500 and (b) 700 °C for 1 h.

4. Conclusions

In this study, a series of TiZrHf-based multi-principal element alloy thin films were successfully fabricated, and the effects of incorporating Ta, Y, and Cr on their phase structure, mechanical properties, corrosion resistance, and thermal stability were systematically investigated. The TiZrHf film, with appropriate mixing entropy, atomic size mismatch, and valence electron concentration, formed a hexagonal close-packed solid solution, representing a typical medium-entropy alloy thin film system. Adding Ta stabilized the formation of a single-phase body-centered cubic structure, although no significant improvement in corrosion resistance was observed. In contrast, incorporating Y resulted in the poorest corrosion performance, likely due to the formation of porous Y_2O_3 oxides that act as active pathways for corrosive agents. On the other hand, the Cr addition markedly enhanced both corrosion resistance—through forming a dense and continuous Cr_2O_3 passivation layer—and mechanical strength. The $Ti_{31}Zr_{17}Hf_{28}Cr_{24}$ film exhibited an I_{corr} value of $0.064 \mu A/cm^2$ and an E_{corr} value of -202 mV, along with the highest R_p ($4.5 \times 10^5 \Omega \cdot cm^2$), which was 58.1 and 2.3 times higher than that of the SUS420 substrate and $Ti_{31}Zr_{33}Hf_{36}$ film, respectively. Regarding thermal stability, the TiZrHfCr film exhibited the highest hardness and elastic modulus even after annealing at elevated temperatures up to 700 °C. It indicates superior structural integrity and mechanical performance, making it a promising candidate for high-temperature protective coatings. Overall, the results demonstrate that compositional engineering is a practical approach to tailoring the phase formation and functional properties of TiZrHf-based thin films, providing a fundamental basis for developing advanced multi-principal element alloy coatings.

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