

Article

The Effect of Yttrium Addition on Microstructure and Mechanical Properties of Refractory TiTaZrHfW High-Entropy Films

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Abstract: Refractory high-entropy films (RHEFs) are a new type of high-temperature material with great prospects for applications due to their superior properties. They have the potential to replace nickel-based superalloys in order to develop a new generation of materials that can be used under extreme conditions. $(\text{TiTaZrHf})_{100-x}\text{Y}_x$ RHEFs are prepared using the magnetron sputtering technique. The yttrium (Y) content varies from 0 to 56 at.%. XRD analysis indicates the formation of an amorphous phase in Y-free films, while new phases are formed after the addition of Y. The results are confirmed by TEM analysis, revealing the formation of nano-grains with two phases L_{12} and Y-P6/mmm structure. With an increasing Y content, the grain size of the nano-grains increases, which has a significant effect on the mechanical properties of the films. Hardness decreases from 9.7 GPa to 5 GPa when the Y amount increases. A similar trend is observed for the Young's modulus, ranging from 111.6 to 82 GPa. A smooth and featureless morphology is observed on the low Y content films, while those with a larger Y content appear columnar near the substrate. Furthermore, the phase evolution is evaluated by calculating the thermodynamic criteria ΔH_{mix} , ΔS_{mix} , Ω , and δ . The calculation results predict the formation of new phases and are then in good agreement with the experimental characterization.

Keywords: high-entropy alloys; thin films; rare earth; magnetron sputtering; TEM; SEM; simulation



Citation: El Garah, M.; Patout, L.; Bouissil, A.; Charai, A.; Sanchette, F. The Effect of Yttrium Addition on Microstructure and Mechanical Properties of Refractory TiTaZrHfW High-Entropy Films. *Coatings* **2023**, *13*, 1380. <https://doi.org/10.3390/coatings13081380>

Academic Editor: Aivaras Kareiva

Received: 17 July 2023

Revised: 1 August 2023

Accepted: 2 August 2023

Published: 7 August 2023



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1. Introduction

High-entropy alloys (HEAs) are of considerable interest due to their superior properties. Since 2004, they have been defined as quasi- or equimolar alloys, and they consist, at least, of five elementary elements with an atomic percentage ranging from 5 to 35 at.% [1–3]. Various investigations have been carried out to explore the physical and chemical properties of HEAs for potential applications [4,5]. Due to the high-entropy effect, solid solutions can be formed rather than intermetallic compounds. HEAs tend to form FCC [6], BCC [7], and HC [8] crystalline structures. They exhibit interesting mechanical and physical properties [9–12] compared to conventional alloys. Refractory high-entropy alloys (RHEAs) are composed of refractory components and have become more attractive for applications in extreme environmental conditions. Refractory transition metal elements are characterized by a high melting point. They can be used in many areas, such as oxidation [13], wear [14], corrosion [15], and high-temperature mechanical impact [16]. Due to the different properties and performances, researchers are striving to develop manufacturing techniques to obtain RHEAs with superior properties.

In fact, RHEAs have relatively high temperature resistance up to 1600 °C and can be exploited for aerospace applications as potential substitutes for nickel-based superalloys. For examples, Senkov et al. developed high-entropy refractory alloys with near-equiatomic concentrations, Nb₂₅Mo₂₅Ta₂₅W₂₅ and V₂₀Nb₂₀Mo₂₀Ta₂₀W₂₀ [17]. The results reveal that the alloys exhibit high compressive yield strength and high thermal stability. Nb₂₅Mo₂₅Ta₂₅W₂₅ has a yield strength of 477 MPa at 1600 °C with a density of 12.36 g/cm³; however, its toughness is low at room temperature (RT). Refractory alloys could be a good alternative for replacing superalloys.

Compared to bulk alloys, films have also been developed and used in surface coating technology to improve the durability of materials in extreme environments. Various technologies have been used to design and synthesize the films, such as laser cladding [18–20], magnetron sputtering [21–26], and others [27,28]. Among them, magnetron sputtering is the most used technique to synthesize the films in neutral or reactive atmospheres. Good mechanical properties, corrosion resistance, and thermal stability were reported for RHEFs. Alvi et al. [29] have studied TaCuMoW by magnetron sputtering. The films have high hardness and Young's modulus, with measured values of 21.3 and 278.2 GPa, respectively. Generally, alloys or films can have improved properties when doped with other elements [30]. Bachani et al. [31] reported that VNbMoAlTaW can improve the corrosion resistance of 304L stainless steel (SS) substrates in H₂SO₄ solution. These results have been obtained by adding Al with different amount into VNbMoAlTaW. The film containing 2.37 at.% Al showed excellent corrosion resistance compared to 304L SS. As the atomic percentage of Al increases, the film tends to form a porous oxide that can be easily affected by acid.

The addition of elements to RHEFs can then strongly affect their properties. For this purpose, rare earths have excellent physical and chemical properties. They play an interesting role in improving the performance of the products. The irradiation hardening of V-4Cr-4Ti-xY alloys as a function of the yttrium amount has been reported [32]. The study reports a hardening effect of all V-4Cr-4Ti-xY alloys under self-ions V²⁺ irradiation at 550 °C. Moreover, doping materials with rare earth elements can also improve the oxidation resistance. With the appropriate amount, these elements can react with oxygen and hinder the diffusion of the latter [33]. Lu et al. [34] reported the yttrium effect on the oxidation resistance of AlMoNbTaTiZr. The study of the addition of yttrium in small quantities has been carried out at three different temperatures: 800, 900, and 1000 °C. With 0.6 at.% yttrium, the results revealed that the film had better oxidation resistance. The addition of yttrium in a high amount (1 at.%) leads to the formation of local stresses and cracks due to the rapid and aggregate oxidation of Al₃Y₅ [34]. The addition of rare earth elements has also been reported to improve the mechanical properties of refractory alloys. For example, the addition of rare earth in steels or in aluminum alloys is an effective method to adapt the microstructure and improve their mechanical performances [35,36]. The approach can also be exploited to improve the properties of HEAs/HEFs. In particular, yttrium has been used in HEAs to study its effect on their microstructure evolution and mechanical properties. It is important to note that the enthalpy ΔH_{mix} of yttrium is lower than that of other elements; therefore, its combination with other elements can stabilize the film structure. Due to their performances, RHEFs can then have a wide range of applications in surface modification fields. Up to now, limited investigations have been reported in the literature regarding the yttrium effect on the properties of RHEAs. Long et al. [37] and Li et al. [38] reported that the presence of yttrium and boron elements in HEAs can lead to precipitations due to the formation of negative enthalpy. Nano-phases were also formed for AlCoCrFeNiY_x [39], while face-centered cubic (FCC)-phased dendrite and hexagonal (h) interdendrites were reported for YCoCrFeNi [40]. The results showed improved yield strength, toughness, and compressive strength of the alloys after adding yttrium. Hong et al. [41] reported the enhanced solution solid strengthening of CoCrNi medium entropy alloys after increasing the yttrium content.

This study focuses on the influence of Y content from 0 to 56 at.% on the microstructure and the mechanical properties of TiTaZrHfW RHEF. The phase evolution as a function of the yttrium content is predicted by calculating the thermodynamic criteria of the films.

2. Experimental Details

2.1. Deposition Process

TiTaZrHfW_{100-x}Y_x films are deposited on glass and silicon substrates using the magnetron sputtering technique. Two separate targets, pure Y and equimolar TiTaZrHfW, were used for the preparation of the films. Before the deposition process, substrates are cleaned by subsequent ultrasonication in acetone and ethanol (20 min each) followed by a drying process with hot air. Afterward, the substrates are ion etched in argon under a pressure of 0.5 Pa using a radiofrequency (RF) power of 400 watts for 30 min.

Each target is first cleaned in argon under a pressure of 0.5 Pa for 10 min before the deposition. For the TiTaZrHfW target, a discharge current is kept at 1 A while that of the yttrium target is changed from 0 to 2 A. The distance between the target and the substrate is about 10 cm. During the deposition process, the total pressure is kept constant at 0.3 Pa. No bias or substrate heating is performed during the deposition.

2.2. X-ray Diffraction (XRD)

A D8-Advance Bruker diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with CuK α radiation ($\lambda = 1.54 \text{ \AA}$) was used in order to analyze the microstructure of the TiTaZrHfW_{100-x}Y_x films and identify the different present phases. The θ - 2θ angle range was fixed from 30 to 90°. The scan parameters such as step size and scan speed were fixed at 0.02° and 0.5°/s, respectively.

2.3. Scanning Electron Microscopy (SEM)

The cross-sectional morphology of all films was carried out using a TESCAN SEM (TESCAN FRANCE, Fuveau, France) working with a field emission gun (FEG) (TESCAN FRANCE, Fuveau, France). The chemical composition of TiTaZrHfW_{100-x}Y_x films is evaluated using an energy dispersive X-ray spectrometer (EDS) in the SEM (Hirow SH-4000M) (Hirox europe, Limonest, France).

2.4. Transmission Electron Microscopy (TEM)

TEM lamellae were prepared by mechanical polishing in order to remove as much of the Si substrate as possible for the observation of the film in the thinnest areas. The lamellae were ground down to a thickness of 1 μm using progressively finer grit SiC abrasive paper (down to 0.1 μ of roughness). Then, they were thinned down to about 100 nm using a Precision Ion Polishing System (PIPS-Gatan) working with Ar and using progressively reduced energies, from 5 to 2 kV, and incidence angles from 8° to 2°, respectively, to the polished face of the lamella.

High-resolution electron microscopy (HREM) images were carried out with a field emission gun FEI Titan Cs-corrected TEM (FEI, Eindhoven, Nederland) operating at 200 kV, and allowing a point-to-point resolution of 1 $\text{\AA}$. Selected area ED patterns were acquired using a LaB6 FEI Tecnai TEM (FEI, Eindhoven, The Netherlands) at 200 kV.

2.5. Nano-Indentation

Hardness and Young's modulus of all TiTaZrHfW_{100-x}Y_x films are measured using the Nano Indenter, Hysitron TI 980 TriboIndenter (Bruker Nano Surfaces and Metrology, Tucson, AZ, USA), MTS Systems equipped with a three-sided pyramidal diamond tip Berkovitch indenter (Bruker Nano Surfaces and Metrology, Tucson, AZ, USA). The maximum penetration depth is limited to less than 10% of the film thickness in order to avoid the influence of the substrate stiffness. Various indents, around one hundred, were performed for each film to provide an average value of the hardness and Young's modulus.

3. Results and Discussion

3.1. Sputtering Yield, Deposition Rate, and Chemical Composition

The sputtering yield of six elements (Ti, Ta, Zr, Hf, W, Y) was calculated using Stopping and Range of Ions in Matter (SRIM) at different energies of Ar^+ ions (Figure 1a). Zr and W have almost similar values of the sputtering yield considering Ar^+ ions with energies less than 1000 eV, while the values for Ti and Ta are lower. The sputtering yield of Hf is larger than that of the other elements Ti, Ta, Zr, and W. Some studies have been conducted using sectioned target sectors of equal or different sizes to deposit multielement films [42,43]. In this study, a single TiTaZrHfW target was designed to reproduce an equimolar film, while Y was added from another target.

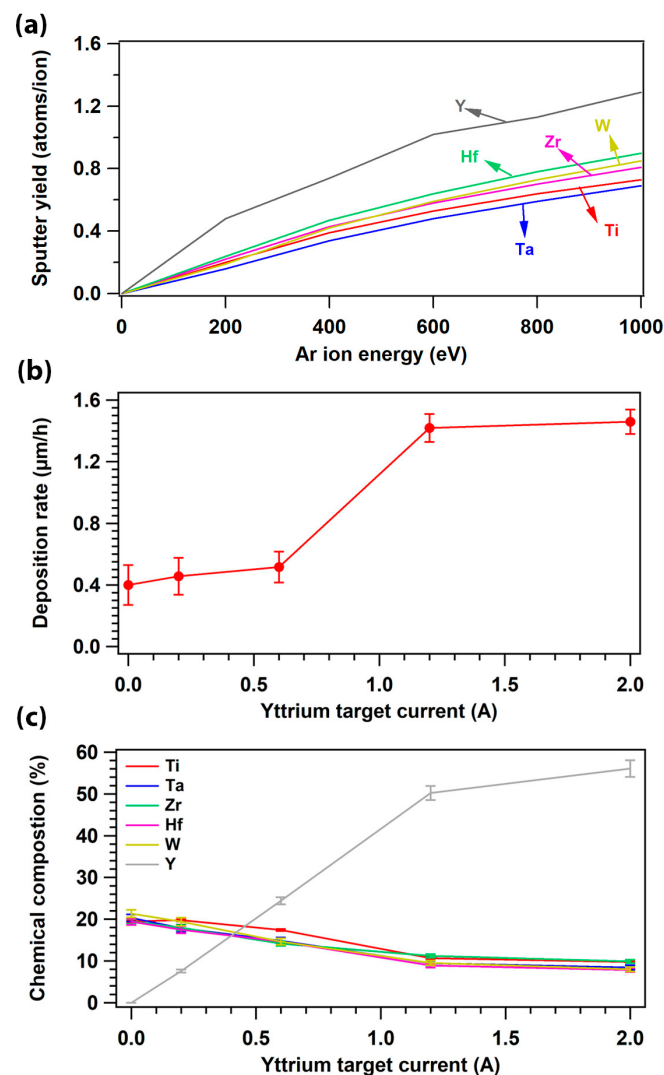


Figure 1. Sputter yield of (Ti, Ta, Zr, Hf, W, Y) elements at different Ar^+ ions calculated from SRIM (a), deposition rate (b), and chemical composition (c) of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ HEFs.

The deposition rate of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ HEF is presented in Figure 1b. It is obvious that the deposition rate increases as a supplementary element is added. A slight increase can be observed when the current of the Y target varies between 0 and 0.6 A. However, the deposition rate increases with the current (from 0.6 to 1.2 A) and reaches a maximum of $\sim 1.5 \mu\text{m}/\text{h}$, which remains almost constant up to 2 A. This rise is due to the high sputtering yield of Y compared to other elements (cf. Figure 1a).

The chemical composition was estimated by Energy Dispersive Spectroscopy (EDS) in a SEM. The results are presented in Figure 1c as a function of the Y target current, which is

related to Y content. At 0 A, an equimolar quinary TiTaZrHfW film is formed. By increasing the current, the element content of the HEA target starts to decrease at the same time as the Y content increases. When the current is ranging from 0 to 1.2 A, Y content increases quickly to reach 50 at.%, then more slowly up to 56 at.% at 2 A. The content of other elements is about 9 at.%.

3.2. Structure of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$

The microstructural characterization of the $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ films by XRD is presented in Figure 2. One halo-shaped peak is present at around 38.5° for Y-free TiTaZrHfW, $(\text{TiTaZrHfW})_{0.93}\text{Y}_{0.07}$, and $(\text{TiTaZrHfW})_{0.75}\text{Y}_{0.25}$ films. We suppose that these three films are amorphous or nanocrystalline. Crystalline nano-domains may be presents, but the X-ray diffraction technique is not relevant to characterize them. By increasing the Y content, two peaks appear on the diffractograms (Figure 2). The first peak is always located at 38.5° , representing the first phase (amorphous or nanocrystalline). A new broad peak appears at 31° , revealing the formation of a new phase. Li et al. [38] studied the $\text{FeCoNi}_{1.5}\text{CuBY}_x$ powder and sintered alloy where two phases have been reported as functions of the Y amount. The sintered alloy has a FCC structure. However, the addition of Y with a content of $x = 0.1$ leads to the formation of a small amount of precipitates defined in the primitive compact hexagonal (hcp). In our case, XRD analysis shows no significant change in the structure when the film is doped with a small amount of Y. However, adding a large amount of Y can lead to its precipitation, and a new phase is formed. Moreover, Y in a hexagonal structure shows that its main peaks are located between 28° and 30° [44,45]. Thus, we suspect that the new phase formed after adding Y with a high content could correspond to the precipitation of Y in TiTaZrHfW.

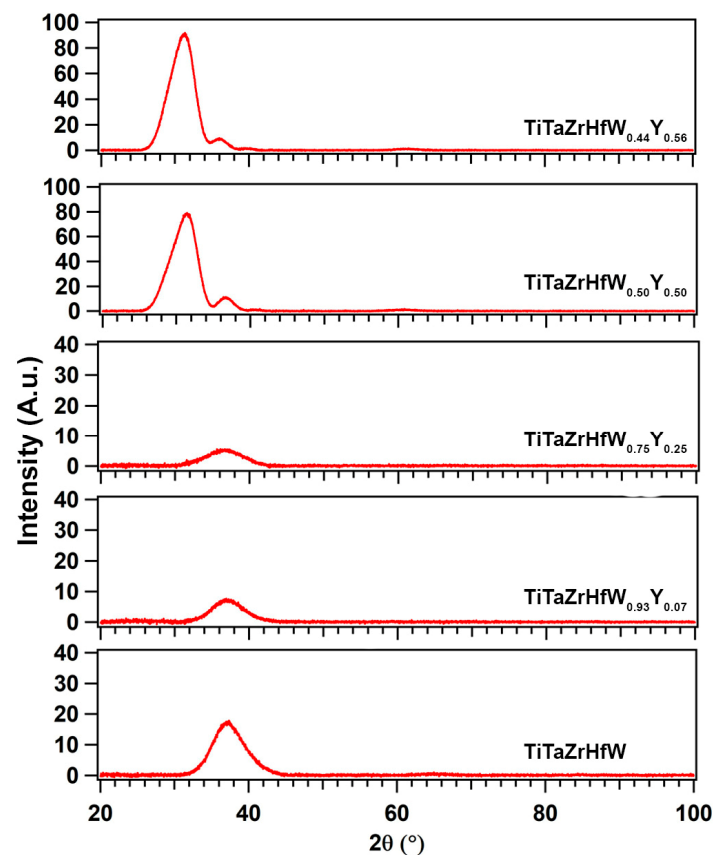


Figure 2. Normalized X-ray diffractograms of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ HEF.

3.3. Microstructure of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$

In order to correlate the XRD analyses obtained on different compositions and identify the two phases formed after the addition of Y, a TEM characterization was carried out on three films, namely TiTaZrHfW , $\text{TiTaZrHfW}_{0.75}\text{Y}_{0.25}$, and $\text{TiTaZrHfW}_{0.44}\text{Y}_{0.56}$. A low magnification bright-field image obtained in scan mode (BF-STEM) shows the Si substrate as well as the Y-free TiTaZrHfW deposited film (Figure 3a). The latter is observed on the edge of the thinned lamella where the substrate was removed by polishing. A high-magnification image reveals that the Y-free film is amorphous; no crystalline order can be observed. This is confirmed by a selected area electron diffraction (SAED) pattern recorded on the film. The presence of only one bright diffuse ring with a radius of 3.84 nm^{-1} ($2.6 \text{ \AA}$) is characteristic of an amorphous film.

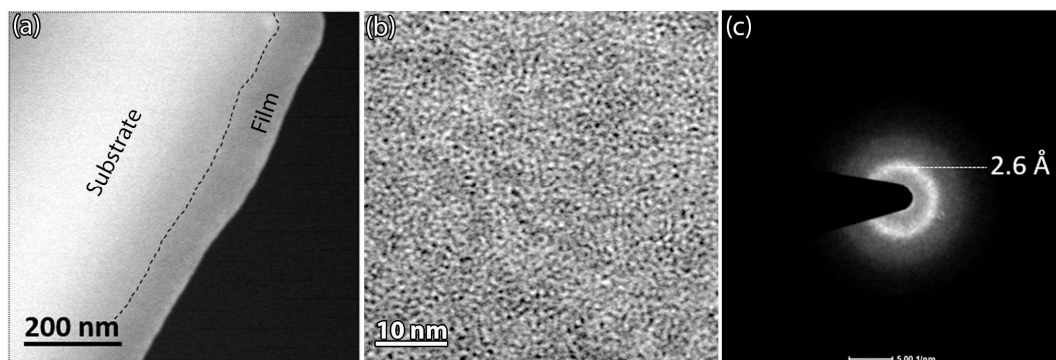


Figure 3. (a) BF-STEM image showing the Si substrate (left) and the film (right) on either side of the hatched line. (b) HRTEM image of the Y-free film. (c) SAED pattern of the corresponding film showing an amorphous structure.

At 25 at.% Y, TEM observations clearly show the homogeneous nanometric crystalline grains ($\sim 10 \text{ nm}$) embedded in a likely amorphous matrix (Figure 4a), as well as the growth of a nanocomposite film. The corresponding SAED pattern exhibits bright spots distributed on several circular rings corresponding to a polycrystalline microstructure (Figure 4b). As discussed above in Section 3.3, XRD analysis showed the presence of one large peak, revealing the formation of an amorphous or nanocrystalline phase for three Y-free TiTaZrHfW , $\text{TiTaZrHfW}_{0.93}\text{Y}_{0.07}$, and $\text{TiTaZrHfW}_{0.75}\text{Y}_{0.25}$ films. However, according to TEM characterization, these films are bi-phased after adding Y in a low amount (the image of $\text{TiTaZrHfW}_{0.93}\text{Y}_{0.07}$ is not shown as its XRD diffractogram is similar to the first composition). The first phase can be attributed to the amorphous when Y is added in a very low amount (7 at.% in this case). By increasing the Y content to 25 at.%, small grains ($\sim 10 \text{ nm}$) are formed. Their phase is difficult to identify by XRD, but the corresponding SAED pattern (Figure 5c) reveals a FCC structure ($L1_2$) attributed to TiTaZrHfWY .

At 56 at.% of Y content, the size of the grains has increased to about $\sim 200 \text{ nm}$ (Figure 4c). Moreover, it can be clearly seen that the grains are also bi-phased (grains contain other small ones that are around 10 nm in size). The corresponding SAED pattern (Figure 4d) exhibits one much more intense additional ring of 3.2 nm^{-1} radius ($3.12 \text{ \AA}$), confirming the presence of a second crystal phase. As mentioned above, the Y atoms crystallize in a hexagonal structure, and precipitation can be obtained by adding them in high content. A first family of nanoparticles constituting large grains around 200 nm can therefore be attributed to the $L1_2$ phase. The small grains (those inside of the big ones) present the $L1_2$ phase. A second family of nanoparticles located outside the large grains is defined in the Y hexagonal structure. The addition of Y in large amounts first leads to the dissolution of a small part to form the $L1_2$ phase, while the rest is precipitated into the Y hexagonal structure. By comparing XRD and TEM analyses, TiTaZrHfW is amorphous, while the addition of Y with a large content leads to the formation of two nanocrystalline phases ($L1_2$ and Hexagonal). Besides, the grain size is proportional to the Y content.

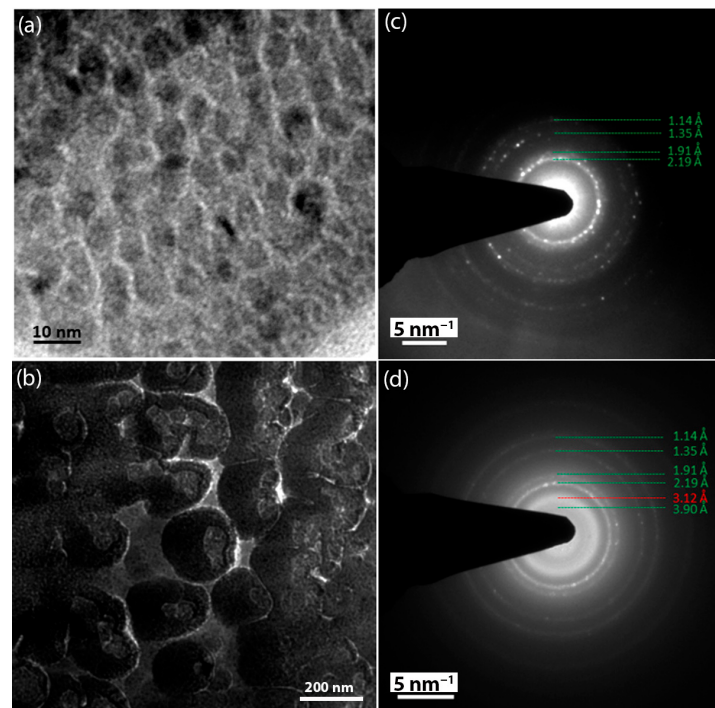


Figure 4. Bright-field images and corresponding SAED patterns of $(\text{TiTaZrHfW})_{0.75}\text{Y}_{0.25}$ (a,b) and $(\text{TiTaZrHfW})_{0.44}\text{Y}_{0.56}$ (c,d) films. The green and red indices correspond to the L_{12} and hexagonal yttrium structures, respectively.

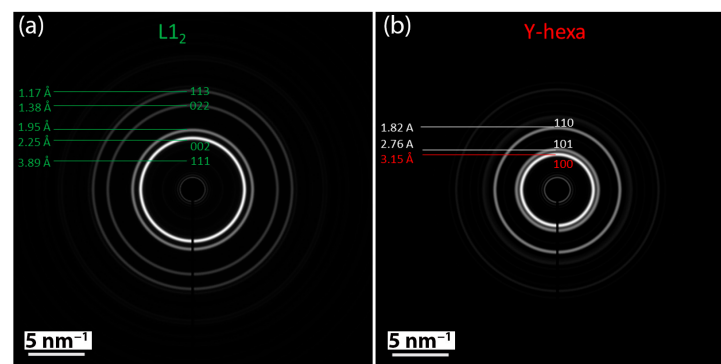


Figure 5. Simulated SAED polycrystalline patterns showing the L_{12} (a) and Y-P6/mmm (b) microstructures.

The calculation of the polycrystalline electron diffraction (ED) pattern [46] of both phase L_{12} (Figure 5a) and Y-hexagonal (Figure 5b) structures indicates their presence in the film at a high Y concentration (56 at.%). Indeed, diffraction rings located at 4.44 nm^{-1} (2.25 Å) and 5.13 nm^{-1} (1.95 Å) corresponding to the L_{12} structure as well as those at (3.17 nm^{-1}) 3.15 Å and (3.62 nm^{-1}) 2.76 Å attributed to the Y-hexagonal structure, are present in the experimental pattern.

An HREM image was recorded on an individual nanoparticle about 4 nm wide located outside the large grains (Figure 6a). From the corresponding fast fourier transformation, the pattern is indexed in the $[421]$ zone axis of the Y-hexagonal structure (Figure 6b). Indeed, the corresponding ED calculations are in agreement with the experiment. The bright dots, like those indexed (104) and (120), belong to a zero-order Laue Zone (red dots in Figure 6c) while the weaker dots belong to a first-order Laue Zone (green dots in Figure 6d).

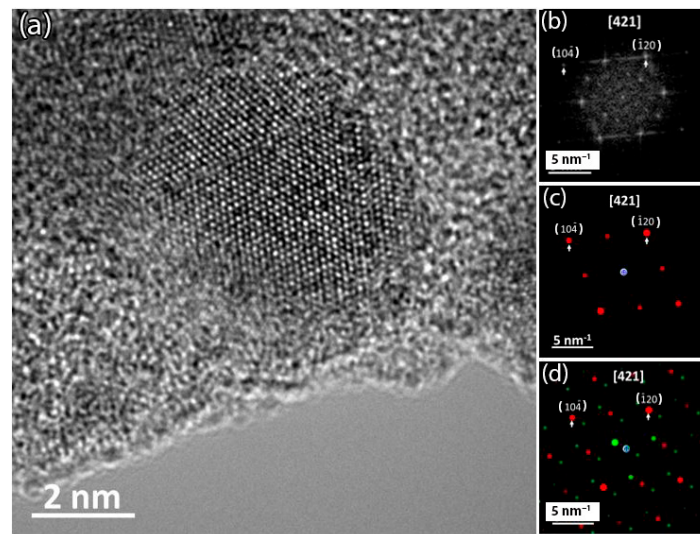


Figure 6. (a) HREM image of an yttrium nanoparticle present in the $(\text{TiTaZrHfW})_{0.44}\text{Y}_{0.56}$ film. (b) Experimental FFT. (c) Calculated FFT with ZOLZ (red) reflections. (d) ZOLZ and FOLZ (green) reflections.

Concerning the second-phase L_{12} , an HREM image was recorded on an individual nanoparticle of about 12 nm wide located in a large grain (Figure 7a). The corresponding FFT is indexed in the $[010]$ zone axis of the FCC structure (Figure 7b), which is in agreement with the calculation (Figure 7c).

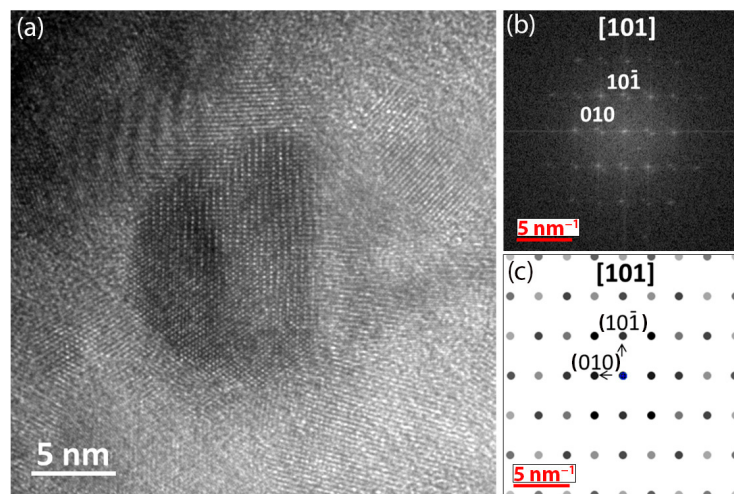


Figure 7. (a) HREM image of a nanoparticle present in the $(\text{TiTaZrHfW})_{0.44}\text{Y}_{0.56}$ film showing the L_{12} phase. (b) Experimental FFT. (c) Calculated ED pattern.

3.4. Thermodynamic Criteria

The formulas of different phase selection criteria are presented by the following equations:

$$\Delta S_{mix} = -R \sum_{i=1}^n c_i \ln c_i$$

$$\Delta H_{mix} = \sum_{i=1, j \neq 1}^n 4\Delta H_{AB}^{mix} c_i c_j$$

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|}$$

$$T_m = \sum_{i=1}^n c_i (T_m)_i$$

$$\delta = \sqrt{\sum_{i=1}^n c_i \left(1 - r_i / \sum_{j=1}^n c_j r_j\right)^2}$$

where n and c_i present the number of the element and the concentration, respectively. ΔH_{AB}^{mix} is the enthalpy of binary systems. Ω is the thermodynamic parameter showing the influence of the enthalpy and the entropy of elements as well as their melting temperatures T_m .

Basing on the equations above, the variations of mixed enthalpy and mixed entropy are presented in Figure 8a, as well as the evolutions of calculated Ω and δ . The results reveal a strong dependence of the films on Y content. ΔH_{mix} is calculated from the mixed enthalpy of each binary system as presented in the Table 1. It displays an increasing trend as Y content increases up to 11 kJ/mol at 56% at. Y. However, ΔS_{mix} increases to 14.8 J/K.mol with Y content up to 25 at.%, then decreases to 11.6 J/K.mol at 56 at.% (Figure 8a). In the case of HEAs, the increase in ΔS_{mix} can promote the formation of solid solutions. However, a drop of ΔS_{mix} can favor the formation of intermetallic compounds. In this study, when ΔS_{mix} increases by adding Y in a small amount, a single-phase solid solution is obtained, which is in good agreement with TEM analysis showing the presence of the L1₂ phase. At high content (>25 at.%), the ΔS_{mix} drop reveals the formation of another compound identified as nanoparticles (Y-hexagonal) formed besides nano-composites ((TiTaZrHf)_{100-x}Y_x—L1₂).

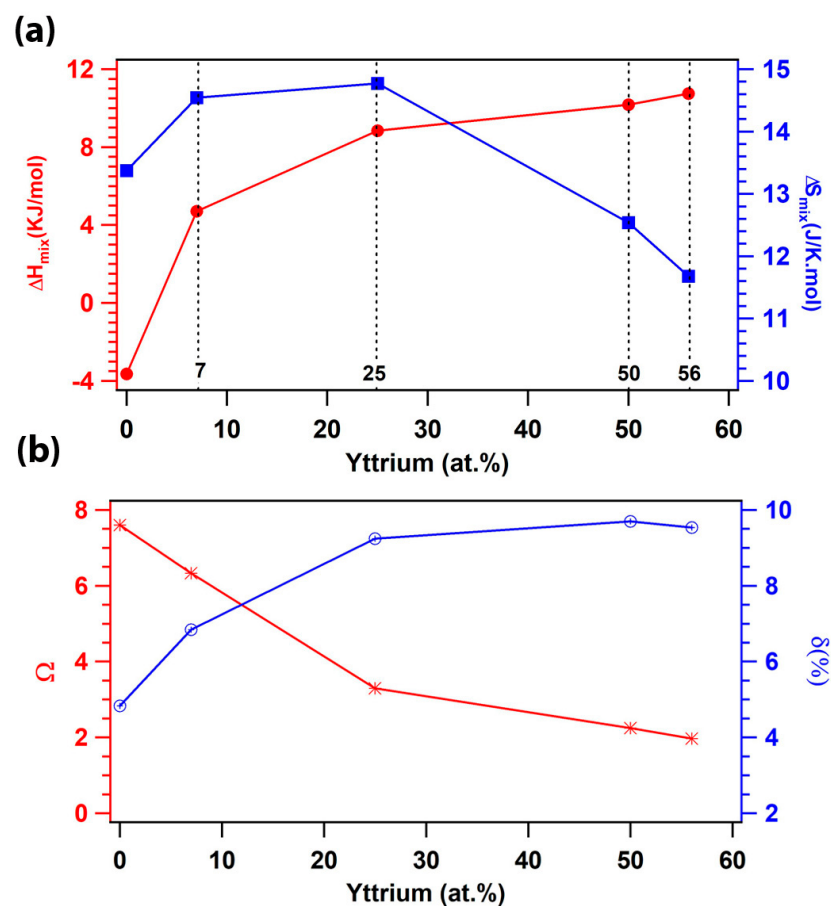


Figure 8. (a) Calculated ΔH_{mix} and ΔS_{mix} of (TiTaZrHfW)_{100-x}Y_x HEF. (b) Calculated Ω and δ of (TiTaZrHfW)_{100-x}Y_x HEF.

Table 1. Mixed enthalpy KJ/mol between different elements constituting the film (Ti, Ta, Zr, Hf, W, Y).

Element (Melting Point, Atomic Size)	Ti	Ta	Zr	Hf	W	Y
Ti (1660 °C, 176 pm)	-	1	0	0	−6	15
Ta (2850 °C, 200 pm)	-	-	3	3	−7	27
Zr (1852 °C, 206 pm)	-	-	-	0	−9	9
Hf (2200 °C, 208 pm)	-	-	-	-	−6	11
W (3410 °C, 193 pm)	-	-	-	-	-	24
Y (1500 °C, 212 pm)	-	-	-	-	-	-

On the other hand, it has been reported that the solid solution of HEAs can be obtained in cases where $\Omega > 1.1$ and $\delta < 6.6\%$ [47]. From our results, δ shows values less than 6.6% for the films having a low Y concentration, indicating the formation of a solid solution (Figure 8b). However, δ is higher at Y contents >25 at.%, which can be attributed to the formation of intermetallic compounds or nanocomposites. Ω presents values higher than 1.1 but decreasing as a function of Y content. This confirms the trend for the formation of metal compounds. As mentioned above, XRD and TEM showed the formation of a $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ solid solution at low Y content, while nanocomposites were formed at high Y content.

3.5. Morphology of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$

From the cross-section SEM images, the morphology of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ films without Y exhibits viscous-like features with shear striations and partial vein patterns corresponding to the characteristics of metallic glass films (Figure 9a) [48,49]. Stratification can be clearly observed on the zoomed SEM. We assume that the film is metallic glass and the that stratifications result from the breaking away of the substrate during SEM analysis. When the Y content increases to 7 at.%, 25 at.%, and 50 at.%, the morphology of the films becomes dense, smooth, and featureless (Figure 9b–d). At 56 at.% Y, it appears columnar, especially near the substrate (Figure 9e). Additionally, the thickness of the film increases from 0.6 to 2 μm as a function of Y content.

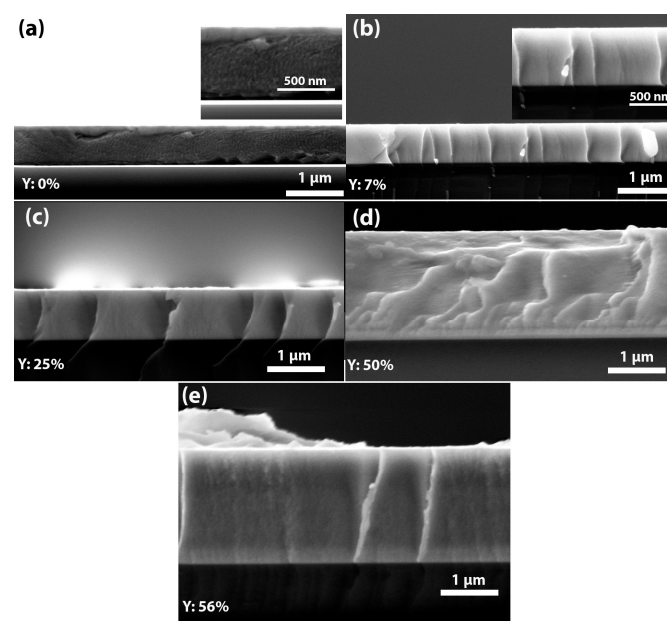


Figure 9. Cross-sectional SEM image of Y-free TiTaZrHfW (a), $(\text{TiTaZrHfW})_{0.93}\text{Y}_{0.07}$ (b), $(\text{TiTaZrHfW})_{0.75}\text{Y}_{0.25}$ (c), $(\text{TiTaZrHfW})_{0.50}\text{Y}_{0.50}$ (d) and $(\text{TiTaZrHfW})_{0.44}\text{Y}_{0.56}$ (e).

3.6. Mechanical Properties of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$

The mechanical properties of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ HEFs were characterized by nano-indentation measurements (Figure 10a). When the Y content increases, the hardness and Young's modulus (YM) of films decrease from 9.69 GPa to 5.04 GPa and 111.63 GPa to 82 GPa, respectively. The maximum values are obtained for the film without the Y element. Hardness and YM quickly decrease when Y varies from 0 at.% to 25 at.% and then stabilizes at a higher content (Figure 10a). Zhang et al. reported the influence of Y content on the mechanical properties of the CoCrFeNiY_x alloy ($x = 0, 0.05, 0.1, 0.2$, and 0.3) [40]. The addition of Y to the CoCrFeNi alloy leads to the formation of two phases: face-centered cubic (FCC) and hexagonal structure. The latter one was composed of two crystalline phases: HS1: $\text{P6}/\text{mmm}$ (CaCu5 type) and HS2: $\text{P63}/\text{mmc}$ (Ni_3Y type). The results report an increase in the nano-hardness and Young's modulus of the FCC phase from 2.9 GPa (without Y) to 3.3 GPa ($\text{CoCrFeNiY}_{0.3}$). HS1 and HS2 showed a stable evolution (around 10.5 GPa). In our case, the results reveal the opposite tendency, i.e., the hardness decreases as the Y content increases (Figure 10a). The main reasons for this behavior could be explained by the increase in the mean grain size, as shown in Section 3.3. Small grains were formed when Y was added in low amounts to the TiTaZrHfW film. Their size, according to TEM analysis, was estimated at ~ 10 nm. However, the grain size increases with the Y content, up to about 200 nm. The precipitation of Y and the formation of large grains lead to the diminution of the film's hardness.

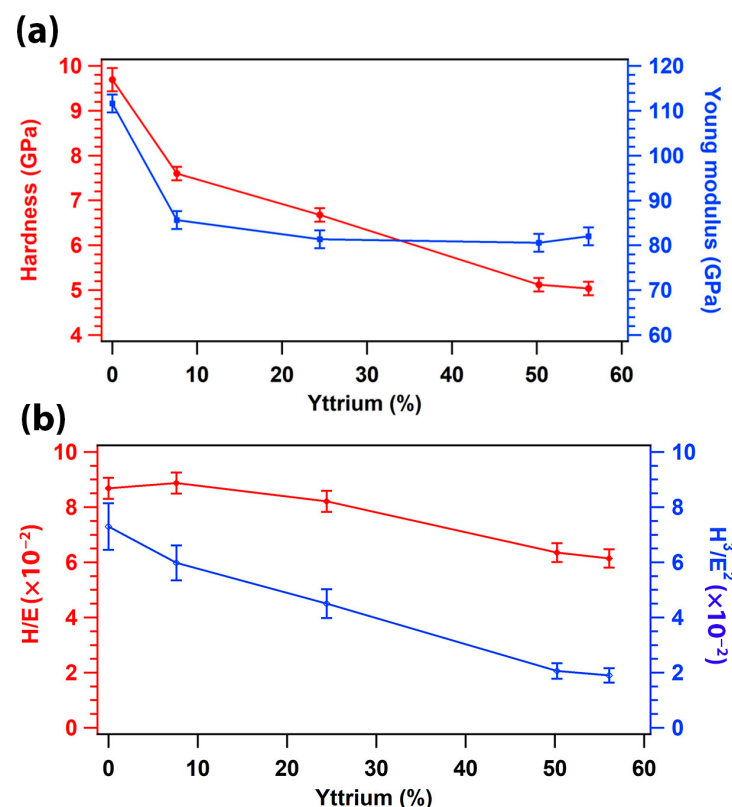


Figure 10. (a) Hardness (red) and Young's modulus (blue) of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ HEFs. (b) H/E and H^3/E^2 ratios of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ HEF.

In general, the tribological performance of films can be estimated from their mechanical properties. They can be predicted by two indices: elasticity (H/E) and plasticity (H^3/E^2), respectively. H/E and H^3/E^2 ratios characterize the resistance of the material and its ability to dissipate energy during the plastic deformation. High values of H/E and H^3/E^2 ratios may indicate good tribological properties. In Figure 10b, it can be observed that the variation of both ratios is consistent with the hardness and Young's modulus evolution

of $(\text{TiTaZrHfW})_{100-x}\text{Y}_x$ HEF. The maximum values of H/E (8.87×10^{-2}) and the H^3/E^2 (7.3×10^{-2}) obtained at 0 at.% Y indicate that the (TiTaZrHfW) film has good toughness and resistance to elastic deformation. However, as the Y content increases, the H/E and H^3/E^2 ratios decrease. This is mainly due to the drop in hardness and Young's modulus with the increasing Y content.

4. Conclusions

In this work, the microstructure and mechanical properties of TiTaZrHfW RHEFs were examined as a function of Y content. When Y is added in a small amount, the films exhibit an amorphous structure. TEM analysis revealed the formation of a nanocrystalline structure with grain sizes of tens of nanometers. However, when Y was added in high amounts, a bi-phased system was formed with two distinct identified structures ($(\text{TiTaZrHf})_{100-x}\text{Y}_x$ — L1_2 and Y-hexagonal). The grains that are about 200 nm wide are composed of nanograins defined in the L1_2 structure. The other family of nanograins, located in an amorphous matrix apart from the large grains, is defined in the Y-hexagonal structure (space group $\text{P6}_3/\text{mmc}$). The grain coarsening after the addition of Y caused a degradation of hardness from 9.69 GPa for Y-free TiTaZrHfW RHEFs to 5.04 GPa for $(\text{TiTaZrHfW})_{0.44}\text{Y}_{0.56}$. Calculations of thermodynamic phase selection criteria (ΔH_{mix} , ΔS_{mix} , Ω and δ) predict the formation of metallic compounds when Y is added in high amounts to the RHEFs. However, with a low Y amount, the films exhibit a single phase that can be attributed to L1_2 according to TEM analyses.

The formation of nanoparticles in RHEFs, especially when doped with rare earth elements, could have great potential for developing coatings to improve resistance to high temperature oxidation. The addition of Y in an appropriate amount could help reach this objective. Such an approach will be the subject of future experiments.

Author Contributions: Conceptualization, M.E.G.; methodology, M.E.G. and L.P.; validation, M.E.G., A.C. and F.S.; formal analysis, M.E.G. and L.P.; investigation, M.E.G., L.P. and A.B.; writing—original draft preparation, M.E.G.; writing—review and editing, M.E.G., L.P., A.B., A.C. and F.S.; visualization, M.E.G.; supervision, M.E.G.; project administration, M.E.G., A.C. and F.S.; funding acquisition, M.E.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by University of Technology of Troyes (UTT), Conseil Départemental de l'Aube (CD10), and the University of Aix Marseille.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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