Research of high entropy alloy coatings for sustainable development goals

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We investigated the effect of nitrogen content and Al content, respectively, on the phase transformation, mechanical properties, and anti-corrosion performance of VNbMoTaWAl and TiZrNbTaFeN high entropy alloy thin films. We can conclude that good performance and unique properties can be obtained through the properly controlled chemical compositions for functional high entropy alloy thin films, which can be further applied as protective or modification thin films in harsh environments in the potential application fields and fulfill the requirement for sustainable development goals.

1. Introduction

After the high entropy alloys (HEAs) and multicomponent alloys (MCA) were investigated by Prof. Yeh and coworkers [1] and Prof. Cantor et al. [2] in 2004, respectively, the research on bulk HEA and MCA materials attracted much attention due to their unique properties, such as high mechanical properties, good ductility, decent wear resistance, good thermal stability, excellent corrosion resistance, and anti-radiation ability. Meanwhile, the HEA thin films deposited by the magnetron sputtering technique have been explored for better corrosion resistance, oxidation resistance, mechanical properties, and wear resistance of the substrates. Some alloy elements, such as CrB_2 [3], Al [4], TiB_2 [5], AlCr [6], Cr [7], or nitrogen [8-13], have been added to HEA coatings to achieve better mechanical properties, corrosion resistance, and high-temperature stabilities. Very promising hardness improvement results can be seen for the nitrogen-added HEA nitride coatings [8-13]. For example, the AlCrTiSiN HEA nitride film exhibited a very high hardness of 39.4 GPa [9], and the $(AlCrNbSiTiV)_{50}N_{50}$ nitride coatings showed extremely high hardness of 42 GPa and an elastic modulus of 360 GPa due to the grain size refinement strengthening, solution hardening, and residual compressive stress [10]. The (AlCrNbSiTiMo)N coatings displayed a high hardness of 34.5 GPa and excellent high temperature tribological performance [12]. The TaNbSiZrCrN coating with a hardness of 35.8 GPa exhibited a three-fold improvement (> 6000 holes) in dry drilling life than the uncoated micro-drills [13]. In this work, the effect of nitrogen content and Al content, respectively, on the phase transformation, mechanical properties, and anti-corrosion performance of TiZrNbTaFeN and VNbMoTaWAl high entropy alloy thin films will be discussed.

2. Materials and methods

2.1 Deposition of HEA coatings

An equimolar VNbMoTaW target and an Al target (99.99 at.% in purity) were used to deposit three VNbMoTaWAl HEA coatings by a pulsed direct current (DC) magnetron sputtering technique under pure Ar atmosphere [4]. On the other hand, an equimolar TiZrNbTaFe target was adopted to grow six TiZrNbTaFeN coatings with different nitrogen contents by a reactive high power impulse magnetron sputtering system [8].

2.2 Properties analysis of HEA coatings

The field emission electron probe microanalyzer (FE-EPMA, JXA- 8500F, JEOL, Japan) was used to analyze the chemical composition of HEA coatings. An X-ray diffractometer (XRD, PANalytical, X'Pert Pro, The Netherlands) was used to evaluate the crystal structure of HEA coatings. A nanoindenter (TI-900, TriboIndenter, Bruker, USA) equipped with a Berkovich 142.3° diamond probe tip (tip radius ≤ 50 nm) was employed to study the nanohardness (H) and reduced elastic modulus (E*) of coatings deposited on Si wafer at an indentation depth of 80 nm. An electrochemical potentiostat (SP-200, Potentiostat, BioLogic, France) was used to conduct the corrosion experiments of HEA coatings deposited on 304 ss substrates in 0.5 M H_2SO_4 aqueous solution.

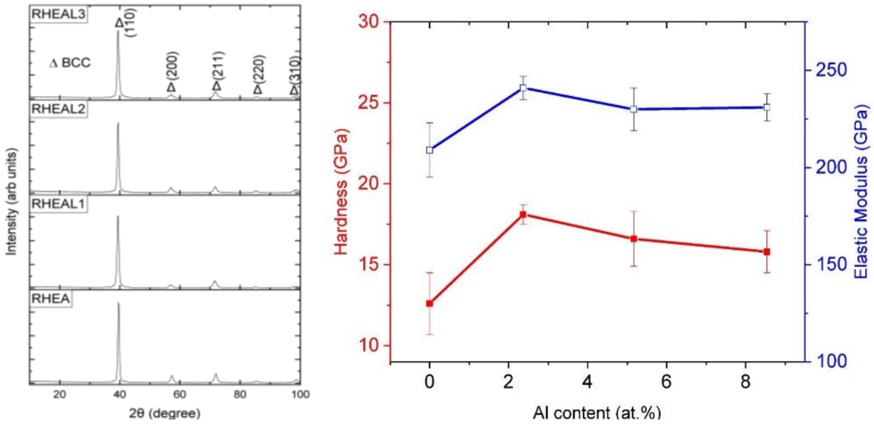
3. Results and discussion

3.1 VNbMoTaWAl coatings

The chemical compositions of VNbMoTaWAl coatings are listed in Table 1. The Al content increased with increasing Al target power. The mixing entropy, ΔS_{mix}, of VNbMoTaW and VNbMoTaWAl coatings increased from 1.55 R to 1.73R as the Al content increased from 0 to 8.54 at.%. The XRD patterns of VNbMoTaW and VNbMoTaWAl coatings are all BCC phases, as depicted in Fig. 1(a). The hardness and elastic modulus of the four coatings are shown in Fig.1 (b). The hardness of VNbMoTaWAl coatings can be enhanced to 18.1 GPa by adding 2.37 at.% Al due to the solid solution hardening effect. The potentiodynamic polarization curves of VNbMoTaWAl coating in 0.5 M H_2SO_4 aqueous solution are revealed in Fig. 2. Table 2 shows the corrosion characteristics of 304 stainless steel substrate and four high entropy alloy coatings tested in 0.5 M H_2SO4 solution.

Table 1. Chemical compositions of VNbMoTaWAl coatings [4]

Chemical composition (at.%)	RHEA	RHEAL1	RHEAL2	RHEAL3
V	16.83	16.54	16.09	15.15
Nb	18.58	18.53	17.97	17.92
Mo	18.57	18.62	18.29	17.88
Ta	18.09	18.17	17.34	17.47
W	19.61	19.56	19.46	19.42
Al	0	2.37	5.17	8.54
O	8.32	5.40	5.68	3.61
ΔS_{mix}	1.55 R	1.64 R	1.69 R	1.73 R



(a) (b)

Figure 1. The (a) XRD patterns, (b) mechanical properties of VNbMoTaWAl coatings [4]

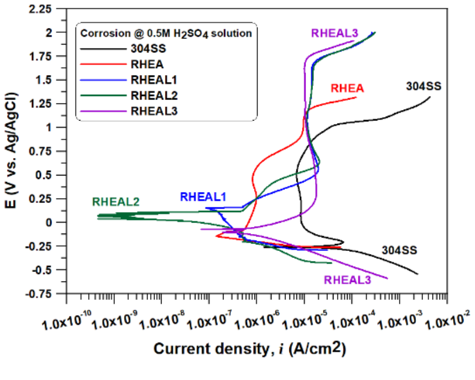


Figure 2. The potentiodynamic polarization curves of VNbMoTaWAl coating in 0.5 M H_2SO_4 aqueous solution [4]

Table 2. Corrosion characteristics of 304 stainless steel substrate and four high entropy alloy coatings tested in 0.5 M H_2SO4 solution [4]

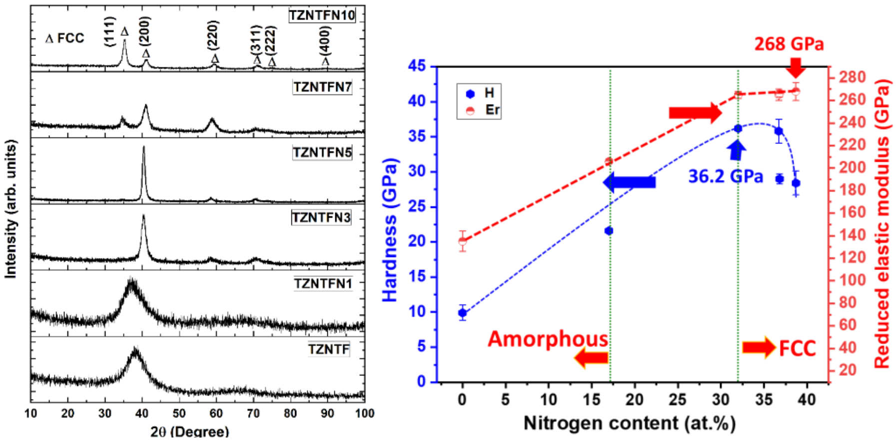
Sample number	E_{corr} (mV)	βa (mV)	βc (mV)	I_{corr} (μA/cm^2)	I_{pass} (mA/cm^2)	E_{pit} (mV)	Passivation range (mV)	R_p (Ω.cm^2)	Rp Ratio
304SS	-243	12.1	62.3	2.624	0.053	1020	1263	1677	1
RHEA	-176	984.5	64.9	0.435	0.011	1168	1344	60777	36
RHEAL1	-77	257.8	104.5	0.042	0.033	1695	1772	768754	459
RHEAL2	-82	438.9	168.7	0.167	0.018	1683	1765	316849	189
RHEAL3	-89	88.8	103.3	0.345	0.001	1700	1789	60100	36

The corrosion resistance of bare 304SS in H_2SO_4 solution was greatly improved by the refractory high entropy alloy coatings in this work. We can find that each HEA coating displays a wider passivation range, around 1344 to 1789 mV than the 304SS substrate, which is 1263 mV. Adding Al to the VNbMoTaW coating can enhance its corrosion resistance. In particular, the corrosion resistance of the RHEAL1 coating in 0.5 M H_2SO_4 solution is 459 times better than the bare 304SS substrate and 12.75 times better than that of the other RHEA coatings.

The fuel cell technology for an electric vehicle is very important because of its ability to solve worldwide pollution threats by conventional internal combustion engine cars and provide future energy demands. The bipolar plate accounts for more than 40% of the total stack cost and about 80% of the total weight of a fuel cell [14]. Through proper surface engineering or coating, bipolar plates can be protected by functional coatings to enhance surface quality and impart good surface properties that will prolong lifespan application in fuel cell vehicles. The possible application of the corrosion resistant VNbMoTaWAl HEA coating as the surface protective layer will be explored in the near future.

3.2 TiZrNbTaFeN coatings

The phase of TiZrNbTaFeN coatings changed from amorphous to FCC as the nitrogen content increased from 0 to 32.0 at.%, as depicted by the XRD patterns in Fig. 3(a). The hardness and elastic modulus versus nitrogen content of TiZrNbTaFeN coatings are shown in Fig.3 (b). The hardness of TiZrNbTaFeN coating can be enhanced to 36.2 GPa by adding 32 at.% N due to the formation of metal-nitride phases and solid solution strengthening by various elements. The possible application of the high hardness TiZrNbTaFeN nitride coating as the protective layer on the cutting tools and forming dies will be studied in the near future.



(a) (b)

Figure 3. The (a) XRD patterns, (b) mechanical properties of TiZrNbTaFeN coatings [8]

4. Conclusion

In this study, the VNbMoTaW and VNbMoTaWAl refractory high entropy alloy coatings were fabricated by a pulsed DC magnetron co-sputtering system. One TiZrNbTaFe and five TiZrNbTaFeN coatings were fabricated by HiPIMS at various nitrogen gas flow ratios. The 2.37 at.% Al contained VNbMoTaWAl coating exhibited the best mechanical properties, including a hardness of 18.1 GPa and an elastic modulus of 241 GPa due to the solution hardening of Al element and its low oxygen content. The corrosion resistance of VNbMoTaW coating was enhanced by the Al addition. The corrosion resistance of 304 stainless steel substrate in 0.5 M H_2SO_4 solution was effectively improved by the VNbMoTaW and VNbMoTaWAl refractory high entropy alloy coatings, which can be applied as the protective coatings on the bipolar plates in the fuel cell of electric cars. The 32.0 at.% nitrogen contained TiZrNbTaFeN coating showed a very dense microstructure with a small grain size and a high hardness of 36.2 GPa, which can be used as a promising protective hard coating in the machinery industry. We can conclude that these high entropy alloy coatings developed in this work can be used to fulfill sustainable development goals, including Goal 7-Affordable and Clean Energy, Goal 9-Industry, Innovation and Infrastructure, and Goal 12-Responsible Consumption and Production, which was launched by the United Nations in 2015.

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