Nonstoichiometric Multicomponent Nitride Thin Films

Rui Shu

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Rui Shu

Thin Film Physics Division
Department of Physics, Chemistry, and Biology (IFM)
Linköping University
Linköping, Sweden

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Abstract

High entropy ceramics have rapidly developed as a class of materials based on high entropy alloys; the latter being materials that contain five or more elements in near-equal proportions. Their unconventional compositions and chemical structures hold promise for achieving unprecedented combinations of mechanical, electrical and chemical properties. In this thesis, high entropy ceramic films, $(\text{TiNbZrTa})\text{N}_x$ were deposited using reactive magnetron sputtering with segmented targets. The stoichiometry x was tuned with two deposition parameters, i.e., substrate temperature and nitrogen flow ratio f_N , their effect on microstructure and mechanical, electric, and electrochemical properties were investigated.

Understoichiometric MeN_x ($\text{Me} = \text{TiNbZrTa}$, $0.25 \leq x \leq 0.59$) films were synthesized at a constant f_N when substrate temperature was varied from room temperature (RT) to 700 °C. For low-temperature deposition, the coatings exhibited *fcc* solid-solution polycrystalline structures. A NaCl-type structure with (001) preferred orientation was observed in $\text{MeN}_{0.46}$ coating deposited at 400 °C, while an *hcp* structure was found for the coatings deposited above 500 °C. The maximum hardness value of 26 GPa as well as the highest H/E_r and H^3/E_r^2 values (0.12 and 0.34 GPa) were obtained for the $\text{MeN}_{0.46}$ coating. These films exhibited low RT electrical resistivities. In 0.1 M H_2SO_4 aqueous solution, the most corrosion resistant film was $\text{MeN}_{0.46}$ featured dense structure and low roughness.

The MeN_x films ($x=0$, $0.57 < x \leq 0.83$) were deposited with different f_N . The maximum hardness was achieved at 22.1 GPa for $\text{MeN}_{0.83}$ film. Their resistivities increased from 95 to 424 $\mu\Omega\text{cm}$ with increasing nitrogen content. The corrosion resistance is related to the amount of nitrogen in the films. The corrosion current density was around 10^{-8} A/cm^2 , while the films with lower nitrogen contents ($x < 0.60$) exhibited a nearly stable current plateau up to 4.0 V, similar to the metallic films, while the films with a higher nitrogen content only featured a plateau up to 2.0 V, above which a higher nitrogen content resulted in higher currents. The reason was that the oxidation of these films at potentials above about 2.0 V vs. Ag/AgCl resulted in the formation of porous oxide layers as significant fraction of the generated N_2 was lost to the electrolyte.

Hence, these observed effects of deposition temperature and nitrogen content on the overall properties of nonstoichiometric MeN_x films provide insights regarding protective multicomponent nitride films, e.g. as corrosion resistant coatings on metallic bipolar plates in fuel cells or batteries.

Preface

The work presented in this licentiate thesis is part of my doctoral studies in Materials Science, started in June 2018 in the Thin Film Physics Division of the Department of Physics, Chemistry, and Biology (IFM) at Linköping University. This work is supported by the VINNOVA Competence Center FunMat-II, in close collaboration with the Department of Materials Chemistry at Uppsala University, Impact Coatings AB, Sandvik Materials Technology, and Plansee. During the course of the research, I was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University supported by the Swedish Government Strategic Research Area on Materials Science.

Rui Shu

Linköping, 2020

Included papers

Paper I

Microstructure and mechanical, electrical, and electrochemical properties of sputter-deposited multicomponent (TiNbZrTa) N_x coatings

Rui Shu, Eirini-Maria Paschalidou, Smita G. Rao, Jun Lu, Grzegorz Greczynski, Erik Lewin, Leif Nyholm, Arnaud le Febvrier, and Per Eklund

Surface & Coatings Technology 389(2020) 125651

Contribution:

I selected the materials system, was involved in the planning of the work, performed the film deposition and a large part of the characterization and analysis, except for part of corrosion measurement and XPS, and wrote most of the paper.

Paper II

Effect of nitrogen content on microstructure and properties of sputter-deposited multicomponent (TiNbZrTa) N_x coatings

Rui Shu, Eirini-Maria Paschalidou, Smita G. Rao, Babak Bakhit, Robert Boyd, Marcos Vinicius Moro, Daniel Primetzhofer, Grzegorz Greczynski, Leif Nyholm, Arnaud le Febvrier, Per Eklund

Surface & Coatings Technology, 2020, accepted.

Contribution:

I was responsible for the planning of the work, performed the thin-film deposition and most of the characterization and analysis, and wrote most of the paper.

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Table of Contents

1. Introduction.....	1
1.1. High Entropy Alloys and beyond.....	1
1.1.1. <i>High entropy alloys</i>	1
1.1.2. <i>Multicomponent nitride</i>	3
1.1.3. <i>Stoichiometry of nitride film</i>	4
1.2. Coatings in Fuel Cells	6
1.2.1. <i>Bipolar plates</i>	6
1.2.2. <i>Main challenges for metallic bipolar plates</i>	8
1.3. Objective	8
2. Thin Film Deposition and Growth	11
2.1. Magnetron Sputtering	11
2.1.1. <i>Sputtering</i>	11
2.1.2. <i>Plasma</i>	12
2.1.3. <i>Reactive sputtering</i>	13
2.1.4. <i>Material targets</i>	14
2.2. Thin Film Growth	14
2.2.1. <i>Nucleation and growth</i>	15
2.2.2. <i>Crystallographic texture</i>	15
3. Characterization of Thin Films	17
3.1. Structural Analysis.....	17
3.1.1. <i>X-ray diffraction</i>	17
3.1.2. <i>Electron microscopes</i>	19
3.1.3. <i>Atomic force microscopy</i>	20
3.2. Chemical Composition Analysis.....	21
3.2.1. <i>Energy-dispersive X-ray spectroscopy</i>	21
3.2.2. <i>X-ray photoelectron spectroscopy</i>	21
3.2.3. <i>Ion beam analysis</i>	22
4. Characterization of Properties	25
4.1. Mechanical Properties (Nanoindentation)	25
4.2. Electrical Properties	26
4.2.1. <i>Four-point probe</i>	26
4.2.2. <i>Contact resistance</i>	27
4.3. Corrosion Resistance Properties	27
4.3.1. <i>Open circuit potential</i>	28
4.3.2. <i>Potentiodynamic polarization measurement</i>	29

Chapter 1

4.3.3. Electrochemical impedance spectroscopy	29
5. Main Results and Contribution to the Field.....	31
5.1. Growth of Nonstoichiometric (TiNbZrTa) N_x Film ($x < 1$).....	31
5.2. Effect of Deposition Temperature.....	32
5.3. What is the Role of Nitrogen Content?	33
6. Future Work.....	35

Chapter 1

1. Introduction

1.1. High Entropy Alloys and beyond

1.1.1. High entropy alloys

High-entropy alloys (HEA), a concept introduced by Yeh *et al.* in 2004, are single-phase alloys made of five or more elements in equal or near-equal proportion (5~35 at.% for each) ^[1]. The high entropy stabilizes a solid-solution phase as average body-centered cubic (*bcc*), face-centered cubic phase (*fcc*) or hexagonal close-packed phase (*hcp*) through suppressing the formation of inter-metallic compounds such as L12, B2, Laves, or sigma ^[2,3]. In the early stage of the development of HEAs, researchers sought single-phase solid-solution alloys because they considered that intermetallics are brittle and may degenerate the properties of HEAs^[3]. However, the fact that in most engineering alloys, secondary phases contribute significantly to the alloy properties is also verified in HEAs^[4,5].

Another entropy-based definition of HEAs was introduced in 2007 ^[6,7], where HEAs are defined as alloys having configurational entropies (ΔS_{conf} , $\Delta S_{conf} = R \ln(n)$) for equiatomic, where n is the number of solute elements, R is the universal gas constant) at a random state larger than $1.61R$, no matter they are single phase or multiphase at room temperature. As this definition somewhat relaxes the equiatomic composition rule and explaining better how entropy works in thermodynamic. The stability of materials, including HEA, is related the Gibbs free energy (ΔG). The relationship between ΔG_{mix} , mixing enthalpy ΔH_{mix} and entropy ΔS_{mix} is the following:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1.1)$$

Since configurational entropy ΔS_{conf} dominates in the entropy part, the other three vibrational, electronic and magnetic contributions are usually neglected. The more randomly distributed components lead to higher ΔS_{mix} , and then lower the ΔG_{mix} of entire material system. It is also termed high-entropy effect. Apart from the high-entropy effect, there are other three so-called core effects: the lattice distortion effect, the sluggish diffusion effect, and the “cocktail” effect. These effects are well explained in several review articles ^[3,7].

Also, it should be pointed out that the definition of “high-entropy” composition is not unambiguous. To quote a recent summary article ^[8]: “HEAs were

Chapter 1

originally defined as a blend of 5 or more elements with concentrations between 5 and 35 atomic percent, but the field now includes materials with as few as 3 principal elements, and where the maximum element concentration may be higher than 35 atomic percent.”

The number of newly reported HEAs and related studies have increased steadily in last sixteen years. Among them, main two groups of notable HEAs can be classified for use at high temperatures: (i) *fcc* HEAs based on the 3d-transition metals Cr, Mn, Co, Fe, Cu and Ni; which also referred to Cantor alloy ^[9]. (ii) *bcc* refractory HEAs ^[2,10] based on refractory elements, Ti, Zr, Hf, V, Nb, Ta, Mo and W. Compared to conventional alloys containing one and two base elements, HEAs have proven to have superior mechanical properties. These advanced properties include excellent strength, exceptional ductility and fracture toughness at cryogenic temperatures, superior mechanical performance at high temperatures, superior irradiation resistance properties ^[11].

The development of HEAs is far more than the improvement of this field itself, such as exploring HEAs possessing excellent properties, but also energized the entire alloy community, as well as promoted technique revolution in materials science. Here several remarkable directions are listed:

New materials: Novel dual-phase HEAs, consisting of *fcc* and *hcp*, enhance the strength by so-called bidirectional transformation-induced plasticity (B-TRIP) effect ^[4,12]. Medium entropy alloys.

Understanding new mechanisms by modern techniques: A scanning transmission electron microscopy (STEM) study ^[13] with mapping atomic-scale element distribution in CrFeCoNiPd HEA alloy, offer an understanding chemical structure and thus providing a basis for tuning composition and atomic configurations to obtain outstanding mechanical properties. The demand on understanding on local lattice distortion also improved the application of synchrotron/neutron-based techniques ^[14].

New opportunities relevant to material design: The design based on “high entropy” extends to some traditional materials, such as perovskite oxides ^[15], layered MAX-phase carbides ^[16], for catalyst ^[17,18], thermoelectric ^[19], thermal barrier, batteries ^[20], protective coatings and other wide-ranging applications.

Navigating the huge compositional space: The ability of calculation of phase diagram (CALPHAD) approach for handling complex system, no matter for predicting phase stability and metastable phase, or phase diagram calculation. Moreover, combining with the concept of the Materials Genome Initiative ^[21],

Chapter 1

the exploration of HEAs has already accelerated in some cases [22]. However, new strategies/approaches are needed to quickly navigate the path between properties that sensitively depend on composition and exquisitely designed microstructures [7,23,24]. For example, applying machine learning algorithms to identify trends in large datasets (from both theoretical simulations [25] and experimental work [26]) and also to make predictions on HEAs has not yet been fully studied [24,27].

1.1.2. Multicomponent nitride

As mentioned in last subsection, the concept of “high-entropy” has significantly energized this niche of materials science research. Plenty of interesting derivatives have developed such as medium-entropy alloys [28,29], non-equiatomic high-entropy alloys [30] and high-entropy ceramics [31]. The latter one is developing high-entropy materials via an approach by adding one (or more) light element, specifically nitrogen, carbon, boron, oxygen and silicon, leading to the new-generation high entropy materials labelled high-entropy nitrides [32], carbides [33,34], borides [35], oxides [36] and silicides [37].

Table 1.1 Periodic table highlighting that the times of element as constituent for refractory HENs films (definition, see main text) in 73 latest articles investigated (adapted from [24]).

atomic number

5

10.81

mass

symbol

B

times as constituent in multicomponent nitride film system

Nitride formation

strong ionic bond

weak ionic bond

non reaction

covalent bond

p-block

13

14

15

5

10.81

6

12.01

7

14.01

B

C

N

d-block

3

4

5

6

7

8

9

10

11

12

13

25.98

14

28.09

15

30.97

Al

Si

P

3d

21

44.96

22

47.87

23

50.94

24

52.00

25

54.94

26

55.84

27

58.93

28

58.69

29

63.55

30

65.39

31

69.72

32

72.63

33

74.92

Sc

Ti

V

Cr

Mn

Fe

Co

Ni

Cu

Zn

Ga

Ge

As

4d

39

88.91

40

91.22

41

92.91

42

95.94

43

(98)

44

101.07

45

102.91

46

106.42

47

107.87

48

112.41

49

114.62

50

118.71

51

121.76

Y

Zr

Nb

Mo

Tc

Ru

Rh

Pd

Ag

Cd

In

Sn

Sb

5d

57-71

72

176.43

73

180.95

74

183.84

75

186.21

76

190.23

77

192.22

78

195.08

79

196.97

80

200.59

81

204.38

82

207.2

83

208.98

Lanthanides

Hf

Ta

W

Re

Os

Ir

Pt

Au

Hg

Tl

Pb

Bi

High-entropy nitrides (HENs) constitute the majority of multicomponent nitrides [31] (no restriction on equal composition). The classification of HENs is similar with that of HEAs, but HEN materials are more general studied in thin films. HENs films are also based on *d*-block transition metals (TM), and three classes can be identified according to the origin of their metallic component: (i) the early TMs [2] among groups 4-6, such as, Ti, Zr, Hf, Nb, Ta and W; (ii) the late TM for example, CoCrCuFeNiN [38]; and (iii) metals from the cross-groups,

Chapter 1

i.e., combining metals from one or both of the abovementioned two categories with a main-group element (e.g., Al), such as in TiZrNbAlYN^[39] or AlCrMoNiTiN^[40]. Table 1.1 is a summary of the times of element as constituent for the first class (also referred as refractory HENs) by investigating among 73 latest relevant articles. Group 4, 5 and Cr in group 6, and Al, Si are the most highly utilized constituents. The second class is 3d-TM multicomponent nitrides, their constituent elements, i.e., late TMs, have much poor nitride-formation ability compared to refractory metals (also seen in Figure 1.1). Even there are a few studies on 3d-TM multicomponent nitride films, for example, (FeCoNiCrCuAlMn)N_x^[41], (CoCrCuFeNi)N_x^[38] and (FeMnNiCoCr)N_x^[42], this direction still requires wider both theoretical and experimental studies. In addition, the abilities of forming nitrides vary with transition metals (Table 1.1 and Figure 1.1a), for example, refractory metals in first class have stronger abilities to bond with nitrogen, in particular, when nitrogen is not sufficient.

1.1.3. Stoichiometry of nitride film

Figure 1.1 (a) A schematic Ellingham Richardson diagram for nitride stability [based on and redraw from ref. ^[43]], (b) Formation enthalpies of TM binary nitrides as a function of stoichiometry x in MeN_x [data retrieved from the Materials Project ^[44]].

Thin films and coatings of transition-metal nitrides are well known for their impressive properties and have drawn continuously increasing interest and application in many fields of technology. Apart from the fundamental research on deposition, characterization and properties, most of the investigations for early transition-metal nitrides are related to their use as protective coatings for tools,

Chapter 1

such as wear/corrosion-resistant, hard coatings. Other applications are in the field of decorative and energy-related materials, such as diffusion barriers, contact materials in electrical devices, energy harvesting materials ^[45]. Most intensively utilized nitride materials are stoichiometric (or nearly stoichiometric) nitride films (Me_1N_1 , Me = metals), to some extent, avoiding defects.

Generally, the hardness of quinary and higher-order nitrides of the same groups (Group 4 and 5) is considerably higher than the hardness of the binary constituents ^[46]. For near-stoichiometric nitrides, in Figure 1.2, the Group 4 binary nitrides generally have higher hardness than those of Group 5, which is related to the greater contribution of M-N bonding in group 4, but in substoichiometric range, $\text{TaN}_{0.4}$ ^[47] and NbN_x ^[48] ($0.92 > x > 0.75$) with stronger interstitial effects have higher hardness than TiN_x and ZrN_x , due to different interstitial effects. This suggests that there are more possibilities to increase hardness in substoichiometric ends, which may generate a stoichiometry-hardness trade-off in future multicomponent nitride films.

Figure 1.2 Lattice constant, hardness and room-temperature (RT) resistivity of early TM binary nitride as a function of the stoichiometry x in MeN_x . [redrawn from Group 4, 5 and 6 references ^[48–60]].

Chapter 1

Compared to the active research work on stoichiometric multicomponent nitrides, fewer reports about the non-stoichiometric multicomponent nitrides are available. These under or over-stoichiometric nitride materials can be modified in a larger composition range between stoichiometric nitride and metallic films with a small amount of dissolved nitrogen.

The nitrogen content of the film deposited using physical vapor deposition depends on the metal condensation rate and the N₂ impinging rate as well as the N₂ reaction rate or the nitride formation ability, in some cases, resputtering effects caused by bias also will play a role ^[61]. As displayed in Figure 1.1a and b, even the four metals Ti, Nb, Zr and Ta are relatively strong nitride formation elements, while compared within each other, Nb is with much weaker nitride formation ability than other three elements, which may be related to the hysteresis behavior of elemental targets when reactive sputtering, and thus influence the tuning the equiatomic chemistry in the films.

1.2. Coatings in Fuel Cells

1.2.1. Bipolar plates

Table 1.2 Classification of materials for bipolar plates used in PEMFCs ^[62].

Classification	Non-coated	Coated		
		Bases	Coatings	
non metal	non-porous graphite			
metals	stainless steel austenitic ferritic	aluminium titanium nickel stainless steel	carbon-based	graphite diamond-like
			metal-based	noble metals carbides nitrides
composites	metal-based	graphite, stainless steel		
	carbon-based	resin, fiber, filler		

A fuel cell is an electrochemical cell that converts energy from a fuel into electricity through an electrochemical reaction (e.g., hydrogen fuel reacting with oxygen). The applications as stationary power station, power source for transportation (fuel cell electric vehicles), long-term portable power for digital products has been widely studied in academic and industrial communities. Bipolar plates are one of the main constituents and vital components in fuel cell stacks, with the main functions of separating the individual cells in the stack, distributing the fuel and oxidant, collecting the current, and facilitating the management of the heat and water. The bipolar plates can be classified as non-metallic,

Chapter 1

metallic, and composite plates. Graphite and carbon-based composite plates generally offer lower material costs, excellent corrosion resistance, potential for lower weight, and higher design formability. However, plate strength is low and processing times is long, leading to high processing costs. The electrical conductivity of carbon composite plates is also lower compare to the metallic bipolar plates. Different stainless steels or metals are promising industrial candidates for bipolar plate materials, since they have good mechanical stability, electrical and thermal conductivity and are easy to process into the desired shape compared to graphite and related composites. However, a major challenge is corrosion in the acidic environment in polymer electrolyte membrane fuel cells (PEMFCs), the operating pH should be below three while the operating temperature is around 100 °C. Therefore, a corrosion-protective coating is usually necessary for the bipolar plates made of metals. The main characteristics of these coatings ^[62–64] should include: a low interfacial contact resistance ($<10 \text{ m}\Omega\text{cm}^{-2}$); a sufficient corrosion resistance in a cell environment (current density $<1 \text{ }\mu\text{A}/\text{cm}^2$ in H_2SO_4 solution, pH3); good gas-tight properties, and thermal stability up to 100 °C.

Table 1.3 Metallic bipolar plates developed in companies and their performance compared to US Department of Energy (DoE) 2020 target ^[65].

Characteristic	units	DoE	ANL, LANL, ORNL, NREL	UTRC	Ford	Ford, Treadstone	Treadstone	SINTEF	Impact Coatings	Sandvik Materials Technology
Plate material			SS-316L	Graphite		SS foil		SS-316L	SS-316L	ALSI-304L/316L
Coating materials					Au-nano-clad	Au-dots	TiO _x	Carbon-based	Ceramic MAX phase	Graphite-like carbon
			Uncoated		Pre-coated					Pre-coated
Plate cost	\$/kW	3							3	10 €/m ²
Plate weight	kg/kW	0.4								
Flexural strength	MPa	>25								
Forming elongation	%	40				53-64				
coating process									PVD	PVD
Corrosion current, anode	$\mu\text{A}/\text{cm}^2$	<1	0.3		No active peak					<1
Corrosion current, cathode	$\mu\text{A}/\text{cm}^2$	<1	0.4		~1.0	~0.1	<0.02		<1	
Electrical conductivity	S/cm	>100								
Areal specific resistance	$\text{m}\Omega/\text{cm}^2$	10	420	~15	5~6	8.4~6.4	6~8	10~40	20	3~6

The Table 1.3 summarizes the bipolar technology against US DoE 2020 targets. SS 316L has been studied as baseline bipolar plate materials. Corrosion currents were $<1 \text{ mA}/\text{cm}^2$, but interfacial contact resistance (ICR) was high, 1-2 orders of magnitude higher than the target of $5 \text{ m}\Omega\text{cm}^2$. This suggests these coatings are needed to prevent the formation of passivating but resistive oxide film. Many

Chapter 1

coatings investigated for protecting metallic bipolar plates could be categorized into metallic coatings (Nb, Au), Ceramic coatings (TiN, CrN, TiO_x and carbides). Some of them have been tested in the industrial field, such as Au nanocladd coating by Ford (US); Au-dots, and TiO_x-based coatings by Treadstone (US); Ceramic MAXphase coatings by Impact Coatings (Sweden), Graphite-like carbon on 304L steel studied by SINTEF in Norway and Sandvik Materials Technology in Sweden.

1.2.2. Main challenges for metallic bipolar plates

The bipolar plate is the driver for cost. The issues limiting coating technologies for metallic bipolar plates are mainly cost, and coating quality. The high cost of coating technology comes from two parts, one is coating materials itself, in case of precious metal coating, such as Au. The other part is from the complex forming process. Most current coatings need to be applied post-forming. If the coating can be applied pre-forming, it will much lower costs due to easier processing. The presence of defects and imperfections in the coatings can result in unacceptable corrosion to the substrate metal. The adequacy of the coating for corrosion protection depends on the base material. Current coatings can provide sufficient corrosion protection for Stainless Steel 316L, but the cost of the base material is too high, for example, the use of Au. For materials such as Al, the coating needs to be perfect, and the present technology is not adequate. High priority R&D areas identified for coatings include coatings that can be formed (applied pre-forming), coating-manufacturing interactions, and more detailed corrosion studies, including following corrosion at specific locations such as coating defects and imperfections.

HEN films are among the promising candidates for such an application. Their unconventional compositions and chemical structures hold promise for achieving unprecedented combinations of mechanical, electrical and chemical properties under extreme environment, in particular as thin films for industrial application, a highly competent example is in fuel system, to be as protective coating possess of good mechanical stability.

1.3. Objective

In this thesis, the arrangement of “TiZrNbTa” was chosen in the first stage, because we found these four elements possess relatively strong nitride formation abilities and native good anti-corrosion abilities. Moreover, this quinary nitride system had not been studied when investigating lower (to binary) and higher-order nitride systems.

Chapter 1

The aim of this thesis project, i.e., exploring multicomponent coatings aiming for corrosion resistant layers in fuel cells/batteries, is a part work of FunMat-II, which is a VINNOVA competence center on materials for cutting tools, fuel cells and batteries. The present results are directly related to WP1 in FunMat-II, a close collaboration with Sandvik Materials Technology, Impact Coatings, and SAFT, which are providing business related to bipolar plates.

The purpose of this licentiate thesis is to provide a material-level evaluation of the multicomponent (TiNbZrTa)N system as potential application of protective coating on BPs. Generally speaking, the effects of the deposition temperature (**Paper I**) and nitrogen content (**Paper II**) on the structural, mechanical, electrical properties and corrosion resistance of the (TiNbZrTa)N system were investigated respectively.

2. Thin Film Deposition and Growth

There is a large variety of thin film deposition techniques for transferring materials in atoms from sources (by target sputtering, evaporating or gas-reaction) to the growth surface on a substrate. One common class of methods is physical vapour deposition, such as thermal or electron beam evaporation, cathodic arc deposition, ion-plating, ion beam sputtering, pulsed laser deposition and various types of sputtering processes. Among these, the physical vapor deposition techniques including magnetron sputtering ^[66–69], and cathodic arc deposition ^[39,70] are utilized for the fabrication of multicomponent nitride films. Chemical vapor deposition (CVD) is another versatile technique to deposit high-quality films by gas chemical reaction with each other. However, there are few reports about preparation TM multicomponent films by CVD, which due to its limitation by the availability of viscous, diffusive, and convective mass transport flux source from transition metals. This chapter therefore focuses on sputtering techniques in the discussion of process parameters governing structure formation of multicomponent nitride films.

2.1. Magnetron Sputtering

2.1.1. Sputtering

Sputtering is the ejection of atoms by the bombardment of a solid or liquid target (cathode) by energetic particles, mostly ions in a glow discharge. A working gas, typically argon, is introduced after evacuating the chamber and serves as the medium where an electrical discharge is initiated and sustained by the target power supply. The glow discharge is maintained between the electrodes at pressures typically in the range of a few to a hundred millitorr ^[71]. Gas ions are gaining kinetic energies and hence accelerated by the cathode voltage towards the target surface, thereby bombarding the target. Depending on the type of the discharge [e.g. direct current, pulsed direct current, radio-frequency, high-power impulse magnetron sputtering (HiPIMS)], some fractions of the sputtered material are also ionized, in particular, for the latter one, HiPIMS, the ionization of sputtering-ejected atoms can up to 90% by applying short, low frequency, high-voltage pulses.

Magnetron sputtering works with a magnetic field applied in superposition with a parallel or perpendicularly oriented electric field between the substrate and the target source. The magnetron field lines go out from the centre of the cathode and go back into the cathode at the annular. The idea geometry would be to have the magnetron field parallel to the cathode surface; however, in practice, an

Chapter 3

inhomogeneous erosion (also referred to “race-track”) region is formed along with sputtering time increasing, which usually leads to low target material utilization of only 20~40%.

The sputtering system configuration employed in current work is shown in Figure 2.1. The distance between the targets and the substrate is approximately 140 mm. The pumping speed of the turbo pump of 550 l/s resulted in a base pressure lower than 4×10^{-7} Pa (3×10^{-9} Torr) after baking.

Figure 2.1 The configuration of the present ultra-high vacuum sputtering system for thin-film deposition.

2.1.2. Plasma

Characterizing plasma by electrostatic probes is of great interests during deposition. The information about plasma parameters including electron density and temperature, ion density and temperature, as well as plasma potential, are helpful to understand and control the process growth later, since the ionic species may significantly affect structure formation by momentum transfer or implantation of ions into the film structure upon bombardment.

Chapter 2

2.1.3. Reactive sputtering

A wide variety of ceramics compound films, such as oxides, nitrides and carbides, are deposited by sputtering with introducing reactive gas, which is able to react with the sputtered materials. This is called reactive sputtering.

The effect of the so-called hysteresis behavior is displayed schematically in Figure 2.2 a-e. Figure 2.2 a-c shows the relationship between flow of reactive gas and deposition rate, chamber pressure, and discharge voltage. The origin of the hysteresis behavior in reactive sputtering is related to the consumption of the reactive gas. It can be consumed by the reaction with sputtered metals, the target surface, and the pump. According to the flow of reactive gas, the process can be referred to two modes of operation^[72], metal mode (green region) and compound mode (red region). The poisoned mode occurs when gas flow reaches to the first critical point, where chamber has more reactive gas for reacting with sputtered metals compared to that in metallic mode. A lower deposition rate and more target reaction (poisoning) will be observed in higher gas flow. The main following parameters influencing the hysteresis effect are reactive gas type, working pressure, target materials, pumping speed, and distance from target to substrate.

Figure 2.2 (a-c) Schematic illustration of hysteresis curves for reactive magnetron sputtering as a function of reactive gas flow; (d) and (e) is the first and second critical point.

Typically, stoichiometric or over-stoichiometric films are formed above first critical point, and under-stoichiometric film can be prepared in metallic mode.

Chapter 3

To maximize the sputtering rate and reducing the target poisoning, the flow of gas in reactive sputtering deposition is usually suggested to be near first critical point, which can be defined by experimentally obtaining rapid response by mass spectrometer of the reactive gas, or optical emission spectrometer of the sputtered metal, or measuring the cathode voltage. In theoretical simulation, there are two models, Berg's model ^[73,74] based on balance equations and extended RSD model ^[72,75] based on Monte Carlo modeling, which can be utilized to simulate the hysteresis behavior and predict the processing behavior.

In **Paper I**, the reactive gas N_2 were controlled in metallic mode to achieve sub-stoichiometric multicomponent nitride film. The effects of nitrogen flow on film growth and properties were independently studied in **Paper II**.

2.1.4. Material targets

In general, a majority of multicomponent nitride films were deposited using compound targets, and segmented or mosaic targets. To achieve a specific near-equal composition, the related compound targets are more popular to be utilized to simplify the deposition process by reducing quantity of magnetron spots and power supplies. The disadvantage of this strategy is the limited possibility of tuning relative metal ratios within one compound target. Co-depositing using individual elemental targets can easily handle the control of composition, but it requires multi-magnetrons in the deposition system. The target configuration utilized in **Paper I** and **II** are two opposite-placed segmented targets of Nb/Zr and Ti/Ta with an area ratio of 50/50 (Figure 2.3). The reason of these configurations is aiming to achieve an equimolar composition. Nb and Zr have near equal sputtering yields, and Ti and Ta can be the only arrangement rest.

Figure 2.3 A schematic of the segmented targets used for sputtering.

2.2. Thin Film Growth

When the sputtered atoms with kinetic energies reach to the substrate after being sputtered and transported, they condense on the substrate forming a film. The final structure can range from crystalline film (single crystal or polycrystalline film with columnar or equiaxed grains), to amorphous film, depending on

Chapter 2

materials system, and deposition parameters. It is crucial to connect processing and structure, in following determining the properties and performance of films.

2.2.1. Nucleation and growth

Thin film growth encompasses a series of events in which the condensation of adatom and the gather-forming clusters by atomic surface diffusion. Re-evaporation can also happen. A schematic illustration of the atomic processes occurring during nucleation in PVD are shown in Figure 2.4. There are three typical growth modes to describe the nucleation and following film growth. (i) *Frank-van der Merwe* (FM) is a layer-by-layer growth, where the adatoms form a complete monolayer before growth is initiated on a second layer. This growth requires high adatom surface mobility. (ii) *Volmer-Weber* (VW), island growth, where small clusters of the adatoms nucleate on the substrate surface and continue to grow into islands. This growth occurs when the kinetic mobility of adatom is not enough. (iii) *Stranski-Krastanov* (SK), island on layer growth, which is initially a layer-by-layer growth followed by island growth. These growth modes can be used to discuss and understand the resulting thin film microstructure, which can show large variations depending on the parameters during deposition, in particular deposition rate and substrate temperature.

Figure 2.4 Schematic illustration of the atomic process leading to film formation on substrates

2.2.2. Crystallographic texture

The films exhibit a crystallographic texture, also called preferred orientation, which in turn may strongly affect their properties, such as elastic modulus, hardness, yield strength, fracture toughness, stress corrosion cracking, and electric and magnetic properties. Typical texture observed in the film produced by PVD technique are fiber texture and biaxial texture. Fiber texture is the crystallites have a specific orientation along the growth direction, but random in plane orientation^[76]. Biaxial texture has not only a preferential crystallographic out-of-

Chapter 3

plane orientation, but also have an alignment along certain directions parallel to the substrate plane ^[77]. There are well-explained in above two review articles. The formation of texture is related to how they reach to (the angular spread of the incoming materials flux, deposition rate, energetic bombardment), and the mobility of the adatoms at the growing surface, which typically determined by the thermodynamic energy, coming from the power supply when ejecting atoms from target, and accelerated by bias supply, as well as the substrate heating. Generally, (111) plane for *fcc* phase and c-plane for *hcp* phase are easily formed. Which plane dominates the texture is a complex question, since it is determined not only by the elementary process of diffusion and also influenced the structure formation, i.e, nucleation, crystal growth (competitive), and recrystallization during grain growth. In the **Paper I**, the *fcc* phase showing a (001) fiber texture was observed in the multicomponent TiZrNbTa nitride coating deposited at 400 °C. The study shows that temperature is a crucial parameter on the control of crystallographic texture of the film.

3. Characterization of Thin Films

The synthesis of transition-metal nitride films with well-defined properties requires a basic understanding of the mechanisms which govern their formation and growth process, as well as microstructural evolution. It can only be achieved by a detailed characterization in different aspects. In this chapter, a brief introduction about the characterization methods will be given in three main parts: structure analysis (X-ray methods, and high-resolution electron microscopes), chemical composition analysis, mainly including X-ray photoelectron spectroscopy and Rutherford backscattering, as well as characterization of related properties.

3.1. Structural Analysis

3.1.1. X-ray diffraction

X-ray diffraction (XRD) is an extremely important technique in the field of materials characterization to obtain information on the atomic scale from both crystalline and nanocrystalline materials. It is widely applied to determine crystal structures of materials, such as metals, alloys, inorganic compounds, and polymers. It is also applied to derive information such as lattice constants, lattice strain, preferred orientation, grain size, chemical composition, state of ordering, etc.

Using different geometries, as displayed in Figure 3.1, it is possible to obtain information of different crystal planes in the materials, especially out of plane and in-plane for thin films. A Bragg-Brentano ($\theta/2\theta$) scan (Figure 3.1a), where the angle of the incident X-ray beam is equal to the angle of the diffracted X-ray, can only give information of planes parallel to the sample surface. In grazing incidence X-ray diffraction (GIXRD) configuration (Figure 3.1b), reflections with distinct Bragg angles are caused by lattice planes that are neither parallel nor perpendicular with sample surface, but in between. While for a pole figure geometry (Figure 3.1c), the diffracted beam is fixed at certain $\theta/2\theta$ location, corresponding to an expected peak, and then information is collecting by tilting in ψ direction along with rotating sample in ϕ direction.

Chapter 3

Figure 3.1 The geometry of Bragg-Brentano (a), grazing incidence diffraction (b), and pole-figure goniometer (c).

In **Papers I** and **II**, $\theta/2\theta$ scan measurements were performed with a PANalytical X'Pert PRO diffractometer with a Cu $K\alpha$ radiation and a nickel filter with a Bragg-Brentano geometry. For **Paper I**, pole figures were acquired using Philips X'Pert-MRD operating with Cu $K\alpha$ radiation with a configuration of crossed slits ($2 \times 2 \text{ mm}^2$) as primary optics and a parallel plate collimator (0.27°) as secondary optics. The angle ranges for pole figure were $0\sim 85^\circ$ for ψ , and $0\sim 360^\circ$ for φ . An example from **Paper I** is shown in Figure 3.2. The $\{111\}$ pole figures of the $(\text{TiNbZrTa})\text{N}_x$ coating deposited at RT exhibit a broad spot at the centre, while a broad ring is observed in $\{001\}$ pole figure, which indicates a $\{111\}$ preferred orientation for the RT sample. For the sample deposited at 400°C , one sharp peak at the centre is observed in the $\{001\}$ pole figure, while a distinct ring is seen at $\psi \approx 54.0^\circ$ in the $\{111\}$ pole figure, showing that this film exhibit a fibre-texture with $\{001\}$ out-of-plane orientation.

Figure 3.2 The evolution of 111 and 002 pole figures of the fcc MeN_x ($\text{Me}=\text{TiNbZrTa}$) coatings deposited on Si (100).

Chapter 3

3.1.2. Electron microscopes

Figure 3.3 Signals generated by the electron-mater interaction [modified from ref^[78]]

Electron microscopes are scientific instruments that use a beam of energetic electrons to examine information in materials on a very fine scale (micro, nano). As shown in Figure 3.3, both scanning electron microscopy (SEM), and transmission electron microscopy (TEM) use high energy electron interaction with specimen to generate different signals.

Scanning Electron Microscopy (SEM) is one of the most versatile techniques available for examination and analysis of the surface/near-surface microstructure of materials. For thin film material, SEM could be used to check cross-section growth structure as well as top-view surface morphologies.

Transmission electron microscopy (TEM) is a technique of atomic-scale compositional and structural analysis for materials. TEM generates a tremendous range of signals giving information as images, diffraction patterns, and several different spectra.

The axiom for preparation of TEM specimen is “*the thinner, the better*”, since the electrons are strongly scattered or even absorbed, rather than being transmitted in the thick specimen. Typical thickness (< 50 nm) could be achieved by focused ion beam (FIB) or mechanical polishing, including main thinning procedures of polishing, and ion-milling.

In this work, TEM is utilized to obtain deeper understanding about the structure, check the growth structure in atomic scale , and verify the homogeneous

Chapter 3

composition with EDS-mapping for multicomponent metals, and determine the passive layer for the corroded samples providing valuable information to understand the corrosion behaviour of TiZrTaNb nitride samples. Besides imaging, TEM can also be used for electron diffraction (selected area electron diffraction, SAED) to provide crystal information about the phases in the film.

A drawback of TEM images is that they provide no depth sensitivity. X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS) are necessary complementary if a full characterization of sample needed.

3.1.3. Atomic force microscopy

Atomic force microscopy (AFM, schematic shown in Figure 3.4) ^[79], one type of scanning probe microscopies (SPM), is a powerful imaging technique by using deflection signal between a tip mounted on the force-sensing cantilever and sample, translating to the surface topography and roughness. Both conductors and insulating materials can be measured without sample preparation. Note that it is necessary to be aware of tip shape convolution, tip contamination and breaking to spot artifacts, for example, pyramidal tips get broader as depth increases. Moreover, contrast in phase image can show difference in mechanical properties in different region in the sample.

Figure 3.4 Schematic of tapping mode used for AFM measurement.

Chapter 3

3.2. Chemical Composition Analysis

3.2.1. Energy-dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDS) is a type of chemical analysis combined in an electron microscope, making use of the characteristic X-ray generated by interaction between high energy electron beams and atoms in samples. Quantitative analysis entails measuring line intensities for each element in the sample and for the same elements in calibration standards of known composition. The great advantage of EDS is a fast-qualitative determination of the elements present in a sample. Moreover, it is possible to obtain information on the distribution of elements along scanned line or over the detected area (mapping), which is remarkably useful to check the local homogeneous distribution for multicomponent materials. However, EDS is ordinarily incapable of detecting with elements lighter than carbon accurately. It is because the light elements have low fluorescent yield and produce low energy X-rays, which are easily absorbed by heavier elements, yielding a high uncertainty for quantification. Therefore, EDS were utilized for fast semi-quantitative analysis during film growth, in particular to achieve equal metal atomic ratio. Other techniques in following subsections were applied to determine actual nitrogen content in films.

3.2.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a widely used technique to investigate the chemical composition of surfaces. XPS was developed based on the photoelectric effect in the 1960s by Kai Siegbahn^[80] and his group at Uppsala University. XPS can be utilized to identify elements near the surface and surface composition, study local chemical environments, oxidation states of elements (in particular, transition metals), valence band electronic structure, and depth-profile investigation of chemical composition

The general formula for XPS peak area is:

$$I = n \times f \times \sigma \times \theta \times y \times \lambda \times A \times T \quad (3.1)$$

where n is the atomic concentration. To perform quantitative chemical analysis for a homogenous sample with XPS, it gives: $\frac{n_1}{n_2} = \frac{I_1/S_1}{I_2/S_2}$, where n_i ($i=1, 2$) is number of I atoms, I_i is area of I photoemission peak, S_i is sensitivity factor for I . The concentration C_x of element x could be calculated by the formula 3.2.

Chapter 3

$$C_x = \frac{n_x}{\sum_i n_i} = \frac{I_1/s_1}{\sum_i I_i/s_i} \quad (3.2)$$

To analyse multicomponent nitrides, X-rays (XPS) is less prone to damage surface than electrons (EDS) and ions (RBS). However, there are two big drawbacks in obtaining accurate composition, i.e., the overlapping in spectra, such as Ta 4p_{3/2} overlapping with N 1s. The other one is XPS information coming from surface area.

It is worth to point out that the binding energy (BE) scale of the spectrometer was calibrated using the ISO-certified procedure to avoid problems related to the use of the C 1s peak of adventitious carbon ^[81,82].

3.2.3. Ion beam analysis

Ion beam analysis methods are generally non-destructive and thus are suitable for delicate materials. As shown in Figure 3.5, the series of high energy ion interaction techniques mainly includes secondary-ion mass spectrometry (SIMS), Rutherford Backscattering Spectrometry (RBS), Proton induced X-ray Emission (PIXE), and Elastic Recoil detection analysis (ERDA). In this study, RBS and ERDA are introduced to measure the accurate nitrogen composition in multicomponent films.

Figure 3.5 Ion-solid interactions

ERDA is an excellent technique for determination of the chemical composition of thin films. Bombarding the sample with heavy mass ions of high energy usually generates an elastic recoil of their nucleus. Coincident measurement of

Chapter 3

energy and time-of-flight with fixed path for the out-scattered atoms (recoils) from the sample (Figure 3.5). The equation $E=M/2V^2$, makes it possible to identify and separate the various masses in the two-dimensional scatterplot time vs. energy (an example given in Figure 3.7a). It is specially with high capability of quantifying light elements in sample, such as B, N, O and C. In this case, time-of-flight elastic recoil detection analysis (ToF-ERDA) measurements were performed at Uppsala University using a 40 MeV $^{127}\text{I}^{9+}$ beam at 67.5° incidence relative to the surface normal and a 45° recoil angle. In **paper II**, ToF-ERDA were applied to determine the composition of TiNbZrTa nitride films. Some drawbacks appeared that the overlapping in the recoils of neighbor elements Nb and Zr. Ta has heavier mass than iodine, yielding a slight overestimate, which also effects the relative content of other elements.

Figure 3.6 Schematic of RBS measurement setup

The non-destructive RBS technique consists of irradiating the specimen to be analyzed with a beam of monoenergetic MeV ions (typical $^4\text{He}^+$, Figure 3.6). The energy loss of the backscattered ions is measured, providing depth-profile composition information.

$$k = \frac{E_1}{E_2} = \left[\frac{\sqrt{M_2^2 - M_1^2 \sin^2(\theta)} + M_1 \cos(\theta)}{M_1 + M_2} \right]^2 \quad (3.3)$$

Where k is the kinematic factor, θ is the scattering angle, M_1 and E_1 , M_2 and E_2 are corresponding mass and energy of the recoil ions and scattered ions. The kinematic factor is usually a key parameter to deduce the calibration offset and

Chapter 3

energy per channel. Energy calibration for the surface edge of atoms with various masses could be conducted, and the recoils spectrum can be simulated by separate elements (an example given in Figure 3.7b). The thickness of sample for RBS measurement is supposed to be less than 200 nm.

Figure 3.7 (a) Detected element separation with ToF-ERDA plot, inset is the geometry of TiNbZrTa nitride film on Si substrate with native oxide layer; The data was analysed using the Potku code ^[83]. (b) RBS spectra from TiNbZrTa nitride film, and the color lines show the simulated data from elements. The analysis of the RBS spectrum was done using the SIMNRA software ^[84]

4. Characterization of Properties

4.1. Mechanical Properties (Nanoindentation)

Nanoindentation is commonly used to measure two properties of bulk or thin film materials: the hardness and the elastic modulus. The principal components in nanoindentation measurement are the indenter tip, the sensors and actuators used to apply and measure the mechanical load and indenter displacement, and the test sample. The indenter is conventionally made of diamond in the form of a three-sided or four-sided pyramid, commonly referred to as the Berkovich or Vickers tip, respectively. When the indenter penetrates a sample surface at a specified load or displacement rate, the corresponding displacement during loading and unloading periods is continuously recorded. The hardness and reduced elastic modulus are calculated from the load and displacement curve of the indenter using the Oliver and Pharr method^[85]. The reduced elastic modulus (E_r) is defined by the equation 4.1:

$$E_r = \left(\frac{(1-\nu_s^2)}{E_s} + \frac{(1-\nu_{in}^2)}{E_{in}} \right)^{-1} \quad (4.1)$$

where E_s and ν_s , and E_{in} and ν_{in} , are the elastic modulus and Poisson ratio of the sample and the diamond indenter, respectively. Typically, $E_{in} = 1140$ GPa and $\nu_{in}=0.07$.

Figure 4.1 Typical load-displacement curve recorded with a TiNbZrTa nitride coating.

Nanoindentation measurements in this thesis were performed using a Berkovich diamond tip with an apex radius of 100 nm with Triboindenter TI 950. The tip

Chapter 4

area function was calibrated using a fused-silica reference sample. Figure 4.1 shows an example of indentation load F versus displacement curve for the TiNbZrTa nitride coating deposited at 400 °C. As the indenter is released from a maximum load $F_{\max}$, only the elastic portion of the displacement is recovered from a maximum value of $h_{\max}$. The residual depth h_r is the permanent displacement left by the plastic impression upon complete removal of the indenter from the surface.

To avoid any substrate effect, the indent should normally not be deeper than 10% of the thickness of film to obtain accurate data [86]. All measured films had thickness at least 500 nm and a series of indentations (> 25) have been made for each load to obtain as reliable results as possible.

4.2. Electrical Properties

4.2.1. Four-point probe

Figure 4.2 Principle sketch of four-point probe measurement setup

Four-point-probe method was used to determine the resistivity of the films (see Figure 4.2 for a sketch of the set-up). Current passes through the outer probes through the film and the inner probes measure the voltage. The measured value is voltage, the sheet resistance (R_s) in unit of Ω/square can be deduced with the correction factor, depending on the substrate size and probe spacing (S). The resistivity (ρ) was obtained by multiplying the sheet resistance R_s with the sample thickness (d), which can be measured by X-ray reflectivity or electron microscopes (SEM/TEM).

Chapter 4

4.2.2. Contact resistance

Compared to resistance, a physical property of material itself, contact resistance is a performance of device system, in closer evaluation to industrial application. The typical technique applied is interfacial contact resistance (ICR), which refers to the out-of-plane electrical resistance across two different materials and is related to the performance of interface between them. In this work, they are multicomponent nitride coating on stainless steel substrate. The ICR may be affected by the oxide layer, interfacial microstructure. As mentioned in the Section 1.2, The interfacial contact resistance of multicomponent nitride aiming for protecting metallic bipolar plate requires to be lower than $10 \text{ m}\Omega\text{cm}^{-2}$. The ICR has not been determined in this thesis, but it will be in the continuing studies.

4.3. Corrosion Resistance Properties

Corrosion can be defined as the deterioration of a material due to its interaction with its environment. In PEMFCs, the operating pH should be below three, while the temperature is around 100°C . Aiming for a long-term power utilization system composed of fuel cells with metallic bipolar plates, corrosion related issues may represent a very compelling engineering challenge. Therefore, a corrosion resistant-protective film is usually necessary for producing metallic bipolar plates.

Figure 4.3 Schematic illustration of three-electrode electrochemical measurement setup. Drawn based on an original by Aishwarya Srinath.

Chapter 4

In order to estimate the corrosion resistance of films (**Paper I** and **II**), electrochemical methods such as potentiodynamic polarization curves (i.e. linear sweep voltammetry, Figure 4.3) and electrochemical impedance spectroscopy (EIS) were performed in the electrochemistry lab of Uppsala University. A PGSTAT302N potentiostat/galvanostat (Metrohm Instruments) was used in conjunction with a typical three-electrode electrochemical cell, containing a 0.1 M H_2SO_4 aqueous solution to simulate the acid environment in PEMFCs ^[87]. The film sample was used as the working electrode, while an Ag/AgCl (3.0 M NaCl) electrode and a Pt wire served as reference electrode and counter electrode, respectively. Potentiodynamic polarization measurements were performed to evaluate the corrosion resistances of multicomponent TiNbZrTa nitride coatings deposited on a Si(001) substrate and a reference sample, hyperduplex stainless steel sample (SAF 3207HD, Sandvik AB), was used for comparison ^[88]. Prior to the polarization curve experiments, the samples were kept in the electrolyte solution for 60 minutes under open circuit potential (OCP) conditions. All polarization curves were recorded with a scan rate of 1 mV/s. The polarization curves were recorded between -0.7 V and 1.5 V vs. Ag/AgCl in **Paper I**, as well as 2 V and 4 V vs Ag/AgCl in **Paper II**. The corrosion potential (E_{corr}), and corrosion current (i_{corr}) were determined from the polarization curves.

It is worth pointing out that the corrosion tests conducted in both **Paper I** and **II**, are for multicomponent nitride films deposited on a Si substrate. This is because it is on the level of coating materials, and not considering at this stage how it will protect the stainless-steel substrate in industry. The current results should be viewed as a first checkpoint on the material itself (and a “no-go” decision point, should the coating fail), rather than an application-oriented study. The next step will be to study the corrosion closer to an applied situation, including deposition on technologically relevant steels. This, however, is not included in this licentiate thesis.

4.3.1. Open circuit potential

Open circuit potential (OCP) measurement provides information about the changes in corrosion behaviour of an electrode surface immersed in an electrolyte solution, with increasing exposure time. OCP is a mixed potential of a working electrode surface with respect to the reference electrode, when no external potential or current flows from or to it. Mixed potential arises when more than one electrode reaction occurs on the electrode surface and can be generated when the cathodic and anodic currents are equal. All samples were monitored for about 1 h OCP to study their corrosion potential with respect to the reference electrode.

Chapter 4

4.3.2. Potentiodynamic polarization measurement

A potentiodynamic polarization curve is the most commonly used electrochemical method to evaluate the corrosion behaviour of materials in certain electrolyte. They are important since they provide information about the active, passive and transpassive potential regions and the magnitude of the currents.

Figure 4.4 A schematic diagram of potentiodynamic polarization. Drawn based on an original by Sara Munktel^[89].

A schematic curve of the typical polarization curve is illustrated in Figure 4.4. The film starts to be corroded and I_{corr} corresponds to the corrosion potential E_{corr} . At this potential, the sum of the anodic and cathodic reaction rates on the electrode surface are equal. Point C is known as the passivation potential, and as the applied potential increases, the current density is seen to decrease until reaching its minimum value, named passive current density. Once the potential reached a sufficiently positive value, that is located as point E, sometimes referred to “breakdown” potential, the applied current rapidly increases until termination at point F. In general, a film with lower I_{corr} , higher E_{corr} values and an extended passive region corresponds to a better corrosion performance.

4.3.3. Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy^[90] (EIS) is a relatively complex technique, but a powerful approach to establish a hypothesis using equivalent circuit models with measuring the AC current at a DC potential in electrochemical system. A data-fitted equivalent circuit model will suggest valuable chemical

Chapter 4

processes or mechanisms for the electrochemical system being studied. In this thesis, EIS measurements were then carried out at the OCP before and after a polarization curve within an applied frequency range from 100 kHz (initial frequency) to 100 mHz (final frequency), using an ac amplitude of 10 mV. The recorded spectra were plotted as Nyquist plots ($-\text{Im}Z$ vs $\text{Re}Z$).

5. Main Results and Contribution to the Field

5.1. Growth of Nonstoichiometric (TiNbZrTa) N_x Film ($x < 1$)

To explore the microstructure and properties of nonstoichiometric (TiNbZrTa) N_x , we mainly focused on to achieve a composition of nitrogen ($0 < x < 1$) by playing with deposition parameters. One of the strategies was tuning deposition temperature, yielding to $0 < x < 0.59$ in **Paper I**. The other approach was to control nitrogen content by adjusting nitrogen flow ratio [$f_N = N_2 / (Ar + N_2)$] during deposition, achieving $0.59 < x < 1$ in **Paper II**.

Figure 5.1. Element composition determined by EDS and XPS of TiNbZrTa nitride coatings as a function of the substrate temperature. (**Paper I**)

Figure 5.1 presents the elemental compositions of the TiNbZrTa nitride coatings in atomic percent. A standard deviation of ± 0.5 at. % is estimated for metals, while the uncertainty in the nitrogen content is about 3~7 at. %, according to EDS and XPS measurements. The atomic percentages of the metals are estimated from the EDS, while nitrogen percentage is calculated using the $N/(Nb+Zr)$ ratio based on the XPS results. The inset shows that the Zr/Nb ratios determined by EDS and XPS both are around 1.0, indicating that the two techniques are consistent with respect to the determination of these metal concentrations. The compositions regarding Ti, Nb, Zr and Ta are kept close to the equimolar ratios. The N content was 37 at. %, i.e., $MeN_{0.59}$, for the film deposited

Chapter 6

at room temperature and decreased with temperature to 20 at.%, i.e., $\text{MeN}_{0.25}$ for the film deposited at 700 °C. These results indicate that all the $(\text{TiNbZrTa})\text{N}_x$ samples are more metallic and much less stoichiometric in nitrogen (with $x = 0.25 \sim 0.59$). The decrease in the N content at elevated deposition temperatures might be due to the higher nitrogen desorption rates at higher substrate temperatures.

In **Paper II**, the percentage of reactive gas allowed to control the content of nitrogen x . A series of $(\text{TiNbZrTa})\text{N}_x$ films were deposited at room temperature. The nitrogen flow ratio f_N was varied between 0 and 30.8%. Table 5.1 shows the chemical composition of the $(\text{TiNbZrTa})\text{N}_x$ films was estimating by a combination of EDS and ToF-ERDA, given in Table 5.1 in atomic percent (at.%). In general, the nitrogen content x increases from 0 to 0.91 as a function of f_N . The compositions of four metals were determined by EDS while the nitrogen and oxygen content were determined using ToF-ERDA. The oxygen contents were less than 0.5 at.% for all the samples, whereas the carbon contaminations were close to the detection limit from ERDA, indicating that the samples were clean.

f_N (%)	Thickness (μm)	EDS (± 0.5 at.%)				ERDA (± 0.4 at.%)			Formula
		Ti	Zr	Nb	Ta	Me	N	O	
0.0	1.24	25.6	21.8	23.8	28.9	99.7	0.0	0.30	Me
3.1	1.23	26.9	22.3	22.6	28.2	63.6	36.3	0.13	$\text{MeN}_{0.57}$
6.2	1.16	24.2	22.5	24.0	29.3	62.6	37.4	0.04	$\text{MeN}_{0.60}$
12.3	0.79	21.0	21.0	26.2	31.9	59.5	40.5	0.03	$\text{MeN}_{0.68}$
24.6	0.45	18.5	19.6	28.4	33.5	56.9	43.0	0.06	$\text{MeN}_{0.76}$
30.8	0.23	14.5	24.5	27.3	33.7	54.7	45.2	0.05	$\text{MeN}_{0.83}$

Table 5.1 The chemical compositions of the TiNbZrTa nitride films on Si substrates, metals percentages determined by EDS, and the light elements (N and O) measured by ERDA. (Paper II)

5.2. Effect of Deposition Temperature

XPS data indicates a gradual change in the chemical state of the transition metals with increasing growth temperature T_s , from nitridic with $T_s = \text{RT}$ to metallic with $T_s = 700$ °C. For low-temperature deposition, the coatings exhibited *fcc* solid-solution polycrystalline structures, with a rough surface (i.e. 6.2 to 7.0 nm). Upon increasing the temperature in the range of 400 – 600 °C, the coatings

Chapter 5

developed a (001)-texture, a roughness of 0.9 to 1.2 nm and dense structures without visible grain features. An *hcp* structure was observed together with the *fcc* phase in the coating deposited at 700 °C which had a roughness of 10.1 nm due to a grain coarsening effect caused by the elevated temperature. The maximum hardness value of 26 GPa as well as the highest H/E_r and H^3/E_r^2 values (0.12 and 0.34 GPa) were obtained for the coating deposited at 400°C. The RT electrical resistivities of the TiNbZrTa nitride coatings were found to be around 200 $\mu\Omega\text{cm}$. The corrosion behavior of the RT and 400°C coatings seen in 0.1 M H_2SO_4 aqueous solutions demonstrate that these coatings were more corrosion resistant than the hyper-duplex stainless-steel reference sample. This makes the present type of TiNbZrTa nitride coatings potentially well-suited for use as corrosion resistant coatings on metallic bipolar plates in PEMFCs.

5.3. What is the Role of Nitrogen Content?

The effect of nitrogen content on the microstructure, mechanical and electrical properties, and in particular corrosion behaviour has been studied in multicomponent TiNbZrTa nitride films, covering the entire composition range from metal to near-stoichiometric nitride $\text{MeN}_{0.83}$. The crystal structure transferred from *bcc* phase of metallic film to *fcc* phase of nitrogen-containing films, and the corresponding lattice constants increased from 3.38 to 4.61 Å. The maximum hardness is achieved at 22.1 ± 0.3 GPa when N = 45.2 at.%. The room-temperature resistivities are between 95 and 424 $\mu\Omega\text{cm}$.

The effect of nitrogen content on the corrosion behavior of these series of $(\text{TiNbZrTa})\text{N}_x$ films was investigated, combined with a comparison analysis of chemical information microstructure evolution. As shown in Figure 5.2, the amount of nitrogen has an effect on the polarization curves in 0.1 M H_2SO_4 depending on the potential region. The corrosion current density is about 1.3×10^{-8} A / cm^2 for the nitrogen free film and around 8.7×10^{-7} and 4.7×10^{-7} A / cm^2 for nitrogen-containing films; lower nitrogen films up to 37.4 at.% have an almost stable current plateau up to 4.0 V, similar to the metallic films, while for the films with a higher nitrogen content, the plateau is limited up to 2.0 V, where higher nitrogen content in the films results in higher current values. Hence, this corrosion behaviour is related to the amount of nitrogen in the coatings. The XPS results indicated the presence of molecular nitrogen in the oxide films, for values up to 37.4 at.%, while for values above this threshold it is not detected. TEM results gave the evidence that the oxide layer formed after LSV measurement in $(\text{TiNbZrTa})\text{N}_x$ films, became thicker and porous for $x = 0.76$, allowing further the oxygen diffusion and hence further corrosion of the material.

Chapter 6

Figure 5.2 Polarization curves for the $(\text{TiNbZrTa})\text{N}_x$ films deposited on Si substrates with different x . The top is schematic of the corrosion process for TiNbZrTa metallic and nitride-contained films.

The main contribution of this study on the effect of nitrogen on corrosion behavior could provide material-level information to design nitrogen-containing multicomponent films, knowledge important for potential applications such as corrosion resistant coatings on metallic bipolar plates in fuel cells or batteries.

6. Future Work

To further study the nonstoichiometric multicomponent nitride films, the following extended directions can be explored.

1. *Investigation of chemical bonding information and lattice distortion in non-stoichiometric multicomponent (TiZrTaMe) $N_{0.5\pm\delta}$ film, where Me= Hf, Nb, Mo or Cr.*

The chemical complexity of HENs can induce local structural distortion, local chemical ordering or clustering, which could affect their performance in different temperature. Theoretical works and experimental studies on bulk materials^[7] have confirmed the effect of short-range order in atomic scale by scanning transmission electron microscopy^[13], neutron powder diffraction^[14] and synchrotron X-ray diffraction^[91]. The diffraction techniques provide structural information but only for long-range order. In contrast, multicomponent nitride films have not been studied for in-depth understanding of their local structure, emphasizing the need for synchrotron-based X-ray spectroscopy, which provides a unique manner of probing short-range order in materials. It is therefore difficult to obtain bonding quantification and local distortion in TiNbZrTa nitride materials using normal lab characterization methods such as X-ray techniques (Bragg-Brentano/grazing incidence), X-ray photoelectron spectroscopy and analytical TEM with electron-energy-loss spectroscopy (EELS). The chemical complexity of TiZrTa-based alloy/nitride films also makes it difficult to quantify nitrogen bonding using XPS, since there are many overlapping contributions in the core-level regions, not even in high temperature. X-ray absorption spectroscopy (XAS) makes it possible to study in-situ, to obtain evidence of N preferred bonding and in-depth information about the local distortion information (1st shell bond length). Initial X-ray Absorption Spectroscopy measurements were performed at MAX IV, beamline BALDER (XANES and EXAFS) in September 2020.

2. *Plasma characterization for multicomponent nitride films deposited in HiP-IMS discharges.*

Many challenges^[24] are still outstanding for the study on multicomponent nitride coating, in particular it is complicated process to achieve near-equal composition and microstructure providing superior performance. High-power impulse magnetron sputtering (HiPIMS), as a sputtering technique that achieves a degree of ionization of source materials leading to smooth and dense films (at least binary transition metal nitrides). Moreover, a large fraction of

Chapter 6

ionized deposition flux is controllable with electric and magnetic fields, which can offer a more effective way to tailor the composition by steering incident metal ions and microstructure of coatings during deposition process. It may give a new way to tune stoichiometry for multicomponent nitrides. For HiPIMS, producing multicomponent nitride may offer a better fundamental understanding beyond to material itself, and also giving insights about how to apply it to handle more complicate process. However, only one multicomponent nitride system, i.e., (AlCrNbSiTiV)N^[92,93] has been studied by HiPIMS deposition using a compound targets.

3. Effect of Nb content on electrochemical properties of (TiNbZrTa)N_{0.5} films

Based on the work on the electrochemical properties of TiNbZrTa nitride coatings (**Paper II**), the component Nb was able to enhance the corrosion resistance behavior of (TiNbZrTaN)_x system. Therefore, a series of specimens aiming to explore the role of Nb will be investigated to optimize this coating system as protective coating for PEM fuel cells.

4. The evaluation of multicomponent nitride films for fuel cell application in industrial scale.

The optimized coating system with respect to composition, local structure and properties should be prepared in industrial deposition systems. It will be also connected to a Master's project on multicomponent TiNbZrTa coatings conducted by Jakob Steneteg within the FunMat-II Center. The outcome will provide an industrial scale understanding of structure and properties of the multicomponent coating, promoting support for further studies for industrial application.

Bibliography

- [1] J.-W. Yeh, S.-K. Chen, S.-J. Lin, J.-Y. Gan, T.-S. Chin, T.-T. Shun, C.-H. Tsau, S.-Y. Chang, *Adv. Eng. Mater.* **2004**, 6, 299.
- [2] O. N. Senkov, D. B. Miracle, K. J. Chaput, J.-P. Couzinie, *J. Mater. Res.* **2018**, 33, 1.
- [3] D. B. Miracle, O. N. Senkov, *Acta Mater.* **2017**, 122, 448.
- [4] Z. Li, K. G. Pradeep, Y. Deng, D. Raabe, C. C. Tasan, *Nature* **2016**, 534, 227.
- [5] Y.-J. Liang, L. Wang, Y. Wen, B. Cheng, Q. Wu, T. Cao, Q. Xiao, Y. Xue, G. Sha, Y. Wang, Y. Ren, X. Li, L. Wang, F. Wang, H. Cai, *Nat. Commun.* **2018**, 9, 1.
- [6] J. W. Yeh, Y. L. Chen, S. J. Lin, S. K. Chen, Trans Tech Publ, 2007; Vol. 560, pp. 1–9.
- [7] E. P. George, D. Raabe, R. O. Ritchie, *Nat. Rev. Mater.* **2019**, 4, 515.
- [8] D. B. Miracle, *Nat. Commun.* **2019**, 10, 1805.
- [9] B. Cantor, I. T. H. Chang, P. Knight, A. J. B. Vincent, *Mater. Sci. Eng. A* **2004**, 375–377, 213.
- [10] O. N. Senkov, G. B. Wilks, D. B. Miracle, C. P. Chuang, P. K. Liaw, *Intermetallics* **2010**, 18, 1758.
- [11] T. Egami, W. Guo, P. D. Rack, T. Nagase, *Metall. Mater. Trans. A* **2014**, 45, 180.
- [12] W. Lu, C. H. Liebscher, G. Dehm, D. Raabe, Z. Li, *Adv. Mater.* **2018**, 30, 1804727.
- [13] Q. Ding, Y. Zhang, X. Chen, X. Fu, D. Chen, S. Chen, L. Gu, F. Wei, H. Bei, Y. Gao, M. Wen, J. Li, Z. Zhang, T. Zhu, R. O. Ritchie, Q. Yu, *Nature* **2019**, 574, 223.
- [14] S. Maiti, W. Steurer, *Acta Mater.* **2016**, 106, 87.
- [15] S. Jiang, T. Hu, J. Gild, N. Zhou, J. Nie, M. Qin, T. Harrington, K. Vecchio, J. Luo, *Scr. Mater.* **2018**, 142, 116.
- [16] Y. Li, J. Lu, M. Li, K. Chang, X. Zha, Y. Zhang, K. Chen, P. O. Å. Persson, L. Hultman, P. Eklund, S. Du, J. S. Francisco, Z. Chai, Z. Huang, Q. Huang, *Proc. Natl. Acad. Sci.* **2020**, 117, 820.
- [17] T. Löffler, A. Savan, A. Garzón-Manjón, M. Meischein, C. Scheu, A. Ludwig, W. Schuhmann, *ACS Energy Lett.* **2019**, 4, 1206.
- [18] P. Xie, Y. Yao, Z. Huang, Z. Liu, J. Zhang, T. Li, G. Wang, R. Shahbazian-Yassar, L. Hu, C. Wang, *Nat. Commun.* **2019**, 10, 4011.
- [19] S. Shafeie, S. Guo, Q. Hu, H. Fahlquist, P. Erhart, A. Palmqvist, *J. Appl. Phys.* **2015**, 118, 184905.
- [20] D. Bérardan, S. Franger, A. K. Meena, N. Dragoe, *J. Mater. Chem. A* **2016**, 4, 9536.
- [21] National Science and Technology Council (US), *Materials genome initiative for global competitiveness*; Executive Office of the President, National Science and Technology Council, 2011.
- [22] Z. Li, A. Ludwig, A. Savan, H. Springer, D. Raabe, *J. Mater. Res.* **2018**, 33, 3156.
- [23] D. Miracle, B. Majumdar, K. Wertz, S. Gorsse, *Scr. Mater.* **2017**, 127, 195.

- [24] E. Lewin, *J. Appl. Phys.* **2020**, 127, 160901.
- [25] J. M. Rickman, H. M. Chan, M. P. Harmer, J. A. Smeltzer, C. J. Marvel, A. Roy, G. Balasubramanian, *Nat. Commun.* **2019**, 10, 2618.
- [26] L. Zhang, K. Qian, B. W. Schuller, C. Lu, Y. Shibuta, X. Huang, *ArXiv Prepr. ArXiv* **2020**, 2004, 04439.
- [27] Z. Pei, J. Yin, J. A. Hawk, D. E. Alman, M. C. Gao, *Npj Comput. Mater.* **2020**, 6, 50.
- [28] R. Zhang, S. Zhao, J. Ding, Y. Chong, T. Jia, C. Ophus, M. Asta, R. O. Ritchie, A. M. Minor, *Nature* **2020**, 581, 283.
- [29] B. Gludovatz, A. Hohenwarter, K. V. S. Thurston, H. Bei, Z. Wu, E. P. George, R. O. Ritchie, *Nat. Commun.* **2016**, 7, 10602.
- [30] Z. Li, D. Raabe, *JOM* **2017**, 69, 2099.
- [31] C. Oses, C. Toher, S. Curtarolo, *Nat. Rev. Mater.* **2020**, 295.
- [32] C.-H. Lai, S.-J. Lin, J.-W. Yeh, A. Davison, *J. Phys. Appl. Phys.* **2006**, 39, 4628.
- [33] M. Braic, V. Braic, M. Balaceanu, C. N. Zoita, A. Vladescu, E. Grigore, *Surf. Coat. Technol.* **2010**, 204, 2010.
- [34] U. Jansson, E. Lewin, *Thin Solid Films* **2019**, 688, 137411.
- [35] P. H. Mayrhofer, A. Kirnbauer, Ph. Ertelthaler, C. M. Koller, *Scr. Mater.* **2018**, 149, 93.
- [36] M.-I. Lin, M.-H. Tsai, W.-J. Shen, J.-W. Yeh, *Thin Solid Films* **2010**, 518, 2732.
- [37] J. Gild, J. Braun, K. Kaufmann, E. Marin, T. Harrington, P. Hopkins, K. Vecchio, J. Luo, *J. Materiomics* **2019**, 5, 337.
- [38] R. Dedoncker, Ph. Djemia, G. Radnóczy, F. Tétard, L. Belliard, G. Abadias, N. Martin, D. Depla, *J. Alloys Compd.* **2018**, 769, 881.
- [39] A. D. Pogrebnjak, V. M. Beresnev, K. V. Smyrnova, Ya. O. Kravchenko, P. V. Zukowski, G. G. Bondarenko, *Mater. Lett.* **2018**, 211, 316.
- [40] B. Ren, S. Q. Yan, R. F. Zhao, Z. X. Liu, *Surf. Coat. Technol.* **2013**, 235, 764.
- [41] T. K. Chen, T. T. Shun, J. W. Yeh, M. S. Wong, *Surf. Coat. Technol.* **2004**, 188, 193.
- [42] C. Sha, Z. Zhou, Z. Xie, P. Munroe, *Appl. Surf. Sci.* **2020**, 507, 145101.
- [43] M. P. Brady, B. Yang, H. Wang, J. A. Turner, K. L. More, M. Wilson, F. Garzon, *JOM* **2006**, 58, 50.
- [44] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K. A. Persson, *APL Mater.* **2013**, 1, 011002.
- [45] P. Eklund, S. Kerdsonpanya, B. Alling, *J. Mater. Chem. C* **2016**, 4, 3905.
- [46] H. Holleck, *J. Vac. Sci. Technol. Vac. Surf. Films* **1986**, 4, 2661.
- [47] K. Valdez, D. G. Espinosa-Arbeláez, J. E. García-Herrera, J. Muñoz-Saldaña, M. H. Farias, W. D. la Cruz, *Surf. Interface Anal.* **2015**, 47, 1015.
- [48] H. O. Pierson, *Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps.*; William Andrew, 1996.
- [49] R. D. Arnell, J. S. Colligon, K. F. Minnebaevb, V. E. Yurasova, *Vacuum* **1996**, 47, 425.
- [50] E. O. Ristolainen, J. M. Molarius, A. S. Korhonen, V. K. Lindroos, *J. Vac. Sci. Technol. A* **1987**, 5, 2184.
- [51] N. J. Ashley, D. Parfitt, A. Chroneos, R. W. Grimes, *J. Appl. Phys.* **2009**, 106, 083502.

- [52] H.-S. Seo, T.-Y. Lee, I. Petrov, J. E. Greene, D. Gall, *J. Appl. Phys.* **2005**, 97, 083521.
- [53] T. Suszko, W. Gulbiński, A. Urbanowicz, W. Gulbiński, *Mater. Lett.* **2011**, 65, 2146.
- [54] M. Torche, G. Schmerber, M. Guemmaz, A. Mosser, J. C. Parlebas, *Thin Solid Films* **2003**, 436, 208.
- [55] C.-S. Shin, D. Gall, Y.-W. Kim, P. Desjardins, I. Petrov, J. E. Greene, M. Odén, L. Hultman, *J. Appl. Phys.* **2001**, 90, 2879.
- [56] Y. Tsuchiya, K. Kosuge, Y. Ikeda, T. Shigematsu, S. Yamaguchi, N. Nakayama, *Mater. Trans. JIM* **1996**, 37, 121.
- [57] F. F. Klimashin, N. Koutná, H. Euchner, D. Holec, P. H. Mayrhofer, *J. Appl. Phys.* **2016**, 120, 185301.
- [58] F. Vaz, J. Ferreira, E. Ribeiro, L. Rebouta, S. Lanceros-Méndez, J. A. Mendes, E. Alves, Ph. Goudeau, J. P. Rivière, F. Ribeiro, I. Moutinho, K. Pischow, J. de Rijk, *Surf. Coat. Technol.* **2005**, 191, 317.
- [59] P. Hones, N. Martin, M. Regula, F. L. vy, *J. Phys. Appl. Phys.* **2003**, 36, 1023.
- [60] H. M. Benia, M. Guemmaz, G. Schmerber, A. Mosser, J. C. Parlebas, *Appl. Surf. Sci.* **2003**, 211, 146.
- [61] H. A. Jehn, J.-H. Kim, S. Hofmann, *Surf. Coat. Technol.* **1988**, 36, 715.
- [62] A. Hermann, T. Chaudhuri, P. Spagnol, *Int. J. Hydrog. Energy* **2005**, 30, 1297.
- [63] S. Karimi, N. Fraser, B. Roberts, F. R. Foulkes, *Adv. Mater. Sci. Eng.* **2012**, 2012, 1.
- [64] Pre-coated strip steel for bipolar plates for PEM FC. *Sandvik Materials Technology*. <https://www.materials.sandvik/en/products/strip-steel/strip-products/coated-strip-steel/sandvik-sanergy-lt/>.
- [65] J. P. Kopasz, T. G. Benjamin, D. Schenck, *2017 Bipolar Plate Workshop Summary Report*; Argonne National Lab.(ANL), Argonne, IL: United States, 2017.
- [66] K. Johansson, L. Riekehr, S. Fritze, E. Lewin, *Surf. Coat. Technol.* **2018**, 349, 529.
- [67] K. von Fieandt, L. Riekehr, B. Osinger, S. Fritze, E. Lewin, *Surf. Coat. Technol.* **2020**, 125614.
- [68] R. Shu, E.-M. Paschalidou, S. G. Rao, J. Lu, G. Greczynski, E. Lewin, L. Nyholm, A. le Febvrier, P. Eklund, *Surf. Coat. Technol.* **2020**, 389, 125651.
- [69] A. Kirnbauer, A. Kretschmer, C. M. Koller, T. Wojcik, V. Paneta, M. Hans, J. M. Schneider, P. Polcik, P. H. Mayrhofer, *Surf. Coat. Technol.* **2020**, 389, 125674.
- [70] A. D. Pogrebnyak, I. V. Yakushchenko, A. A. Bagdasaryan, O. V. Bondar, R. Krause-Rehberg, G. Abadías, P. Chartier, K. Oyoshi, Y. Takeda, V. M. Beresnev, O. V. Sobol, *Mater. Chem. Phys.* **2014**, 147, 1079.
- [71] M. Ohring, *Materials Science of Thin Films*; Elsevier, 2001.
- [72] K. Strijckmans, R. Schelfhout, D. Depla, *J. Appl. Phys.* **2018**, 124, 241101.
- [73] S. Berg, T. Nyberg, *Thin Solid Films* **2005**, 476, 215.
- [74] S. Berg, H. Blom, T. Larsson, C. Nender, *J. Vac. Sci. Technol. A* **1987**, 5, 202.
- [75] D. Depla, S. Heirwegh, S. Mahieu, R. D. Gryse, *J. Phys. Appl. Phys.* **2007**, 40, 1957.
- [76] G. Abadías, *Surf. Coat. Technol.* **2008**, 202, 2223.

- [77] S. Mahieu, P. Ghekiere, D. Depla, R. De Gryse, *Thin Solid Films* **2006**, 515, 1229.
- [78] D. B. Williams, C. B. Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*; 2nd ed.; Springer US, 2009.
- [79] B. Bhushan, *Springer Handbook of Nanotechnology*; Springer Science & Business Media, 2010.
- [80] K. Siegbahn, C. Nordling, A. Fahlman, *Nova Acta Regiae Soc. Sci. Ups.* **1967**, 20.
- [81] G. Greczynski, L. Hultman, *Prog. Mater. Sci.* **2020**, 107, 100591.
- [82] G. Greczynski, L. Hultman, *Angew. Chem.* **2020**, 132, 5034.
- [83] Potku, analysis software for ToF-ERDA with integrated MCERD. *Mat.-Luonnont. Tiedek.*
- [84] M. Mayer, *SIMNRA User's Guide*; Garching: Max-Planck-Institut für Plasma-physik, 1997.
- [85] W. C. Oliver, G. M. Pharr, *J. Mater. Res.* **1992**, 7, 1564.
- [86] R. Saha, W. D. Nix, *Acta Mater.* **2002**, 50, 23.
- [87] S. Munktel, M. Tydén, J. Högstöm, L. Nyholm, F. Björefors, *Electrochem. Commun.* **2013**, 34, 274.
- [88] P. Malinovskis, S. Fritze, L. Riekehr, L. von Fieandt, J. Cedervall, D. Rehnlund, L. Nyholm, E. Lewin, U. Jansson, *Mater. Des.* **2018**, 149, 51.
- [89] S. Munktel, *Bipolar electrochemistry for high throughput screening applications*, Ph.D. thesis, Uppsala University, **2016**.
- [90] C. M. A. Brett, A. M. O. Brett, *Electrochemistry: principles, methods, and applications*; Oxford science publications; Oxford University Press: Oxford ; New York, 1993.
- [91] S. Y. Chen, Y. Tong, K.-K. Tseng, J.-W. Yeh, J. D. Poplawsky, J. G. Wen, M. C. Gao, G. Kim, W. Chen, Y. Ren, R. Feng, W. D. Li, P. K. Liaw, *Scr. Mater.* **2019**, 158, 50.
- [92] K.-S. Chang, K.-T. Chen, C.-Y. Hsu, P.-D. Hong, *Appl. Surf. Sci.* **2018**, 440, 1.
- [93] Z. Liu, C.-Y. Hsu, M.-C. Wu, C.-C. Tsao, *Int. J. Adv. Manuf. Technol.* **2019**, 104, 4509.

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Department of Physics, Chemistry, and Biology (IFM)

Linköping University
SE-581 83 Linköping, Sweden

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