Institute of Metallurgy and Materials Science, PAS

Structure and properties of protective and functional coatings deposited on metal surfaces

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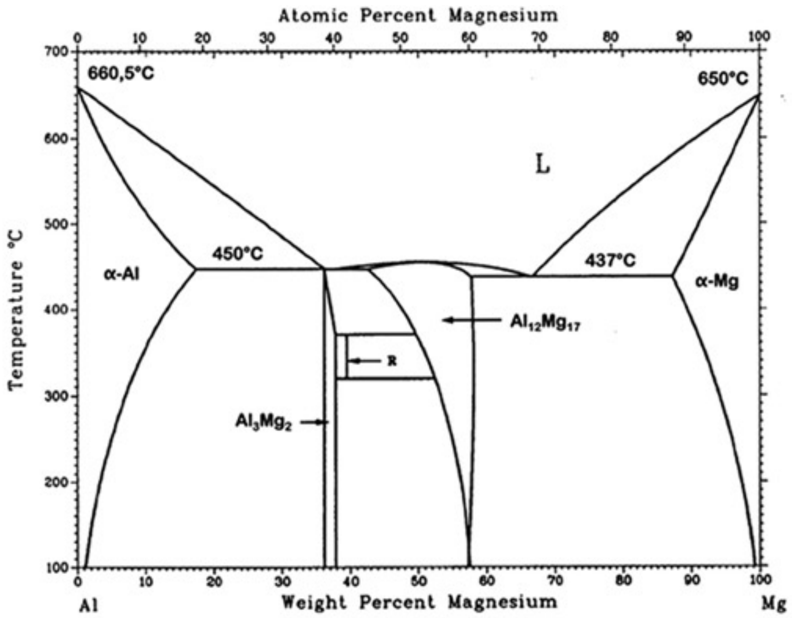
In collaboration with the professor Pavel Korzhavyi
KTH Royal Institute of Technology, Stockholm

Materials

Al alloys:
1XXX - Aluminum min 99.00% - 1000 series
2XXX - Copper (Cu) - 2000 series
3XXX - Manganese (Mn) - 3000 series
4XXX - Silicon (Si) - 4000 series
5XXX - Magnesium (Mg) - 5000 series
6XXX - Magnesium (Mg) Silicon (Si) - 6000 series
7XXX - Zinc (Zn) - 7000 series
8XXX - Other alloying elements - 8000 series

Al:
Application: Light industry, aviation, nuclear reactors, metal-air batteries,
Low atomic mass and the presence of a protective native oxide layer on its surface.

Al-Mg
- Good corrosion resistance (oxidation and seawater)
- For cold and hot work
- Suitable for deep drawing
- Application:
  - Automotive industry
  - Ship structures
  - Chemical industry
- Methods of protecting aluminum alloys against corrosion:
  - Anodization
  - Chemical treatment
  - Organic coatings

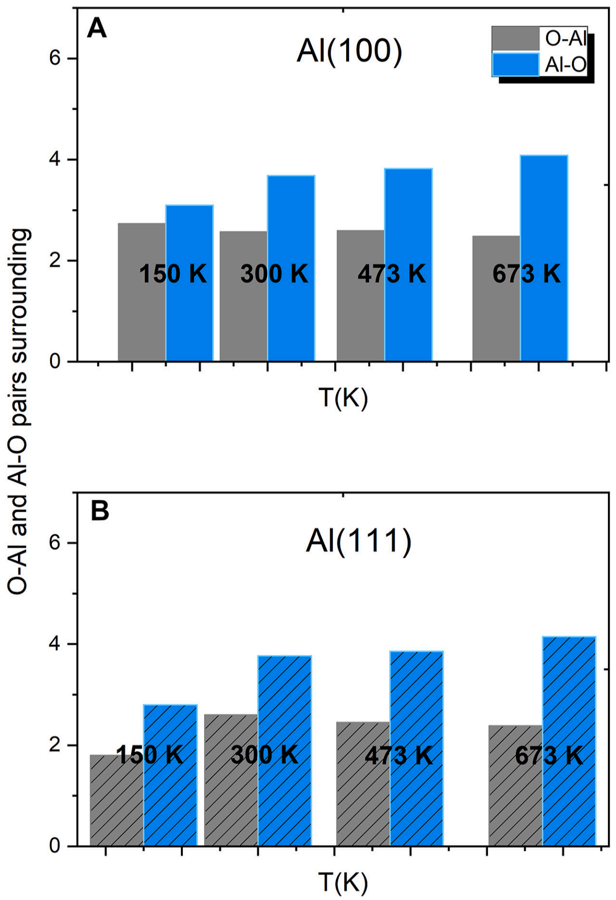


J. L. Murray et al. (1982)

Literature review

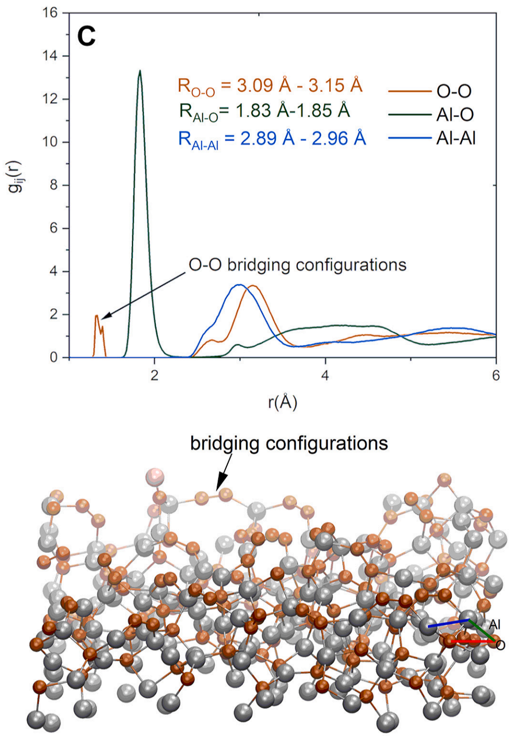
Al oxidation, structure and growth kinetics of the oxide layer

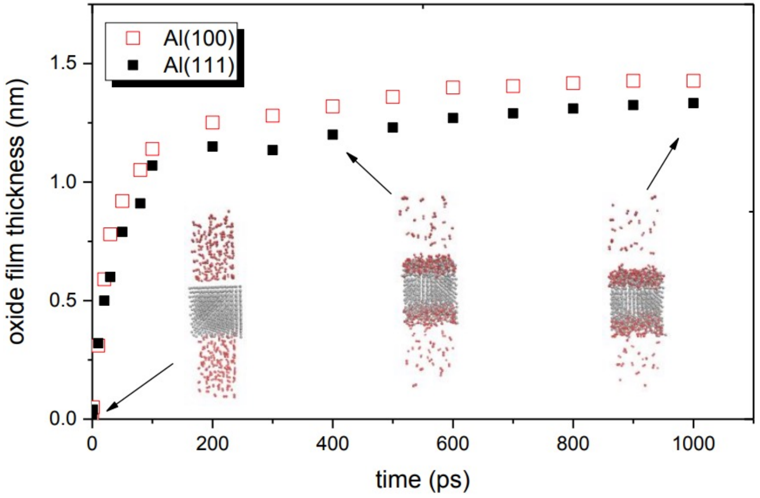
Cooordination number



M. E. Trybula et al., Vacuum V. 190 (2020)

Bond length

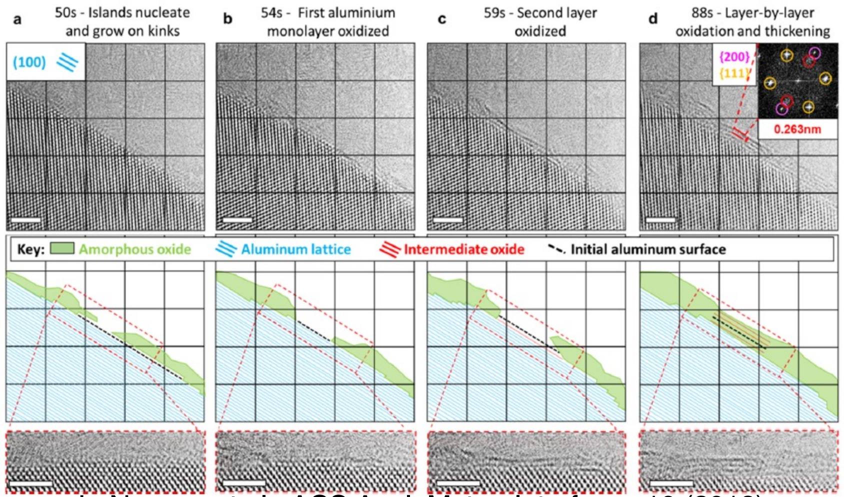




M. E. Trybula et al., JPCC 123 (2018)

Oxidation and growth of the oxide layer on Al - early stages

Experiment



L. Nguyen et al., ACS Appl. Mater. Interfaces 10 (2018)

Literature review

Mechanisms of corrosion in water solution

Corrosion mechanism in an alkaline solution:

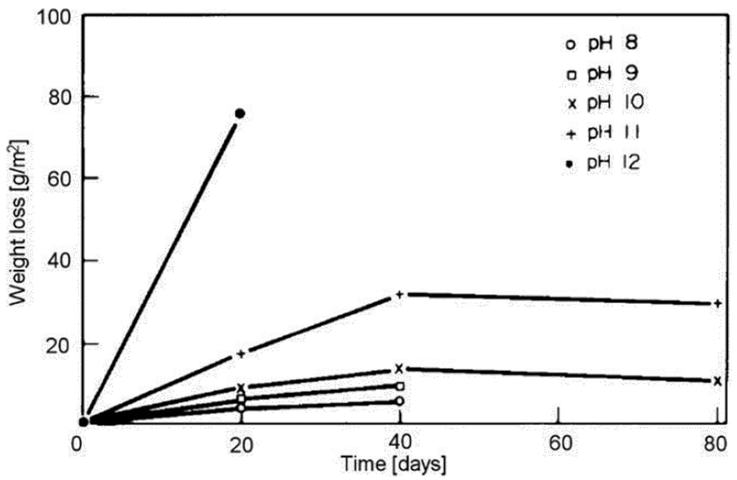
$$Al_{(s)} + OH^-_{(aq)} + H_2O \rightarrow \mathrm{AlO}^-_{2(aq)} + \frac{3}{2}\mathrm{H}_2$$

$$Al_{(s)} + OH^-_{(aq)} + 5H_2O \rightarrow [\mathrm{Al(OH)}_4 * 2\mathrm{H}_2\mathrm{O}]^- + \frac{3}{2}\mathrm{H}_2$$

Corrosion mechanism in an acidicsolution:

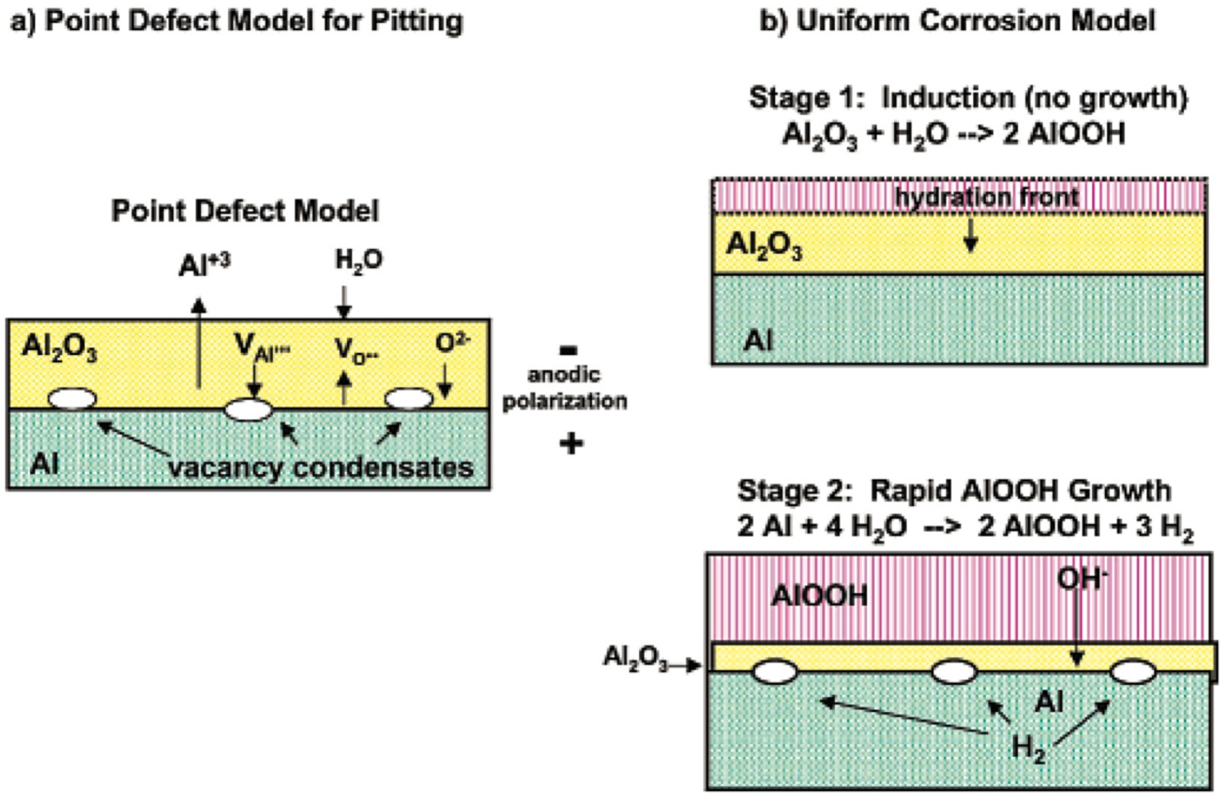
$$Al_{(s)} + H_2O \rightarrow \mathrm{AlOH}_{(ads)} + \mathrm{H}^+ + \mathrm{e}^-$$

Kinetics of aluminum dissolution in an alkaline solution



J. Zhang et al., J. Nucl. Mater. 384 (2009)

Corrosion models



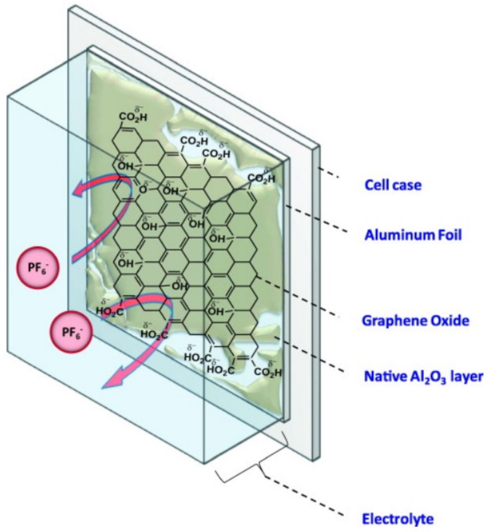
B. C. Bunker et al., J. Phys. Chem. B 106 (2002)

Literature review - protective coatings

Oxide layer

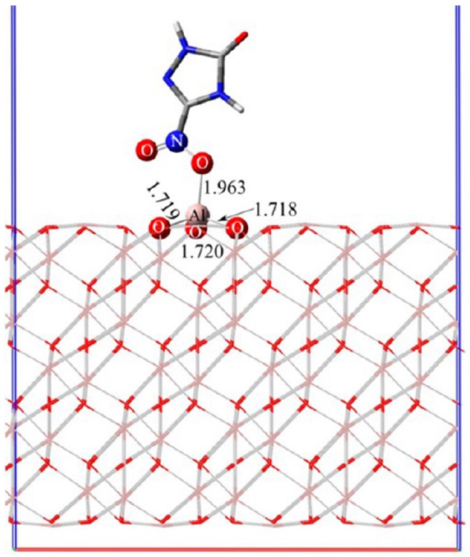
Anode layer

Graphene derivatives

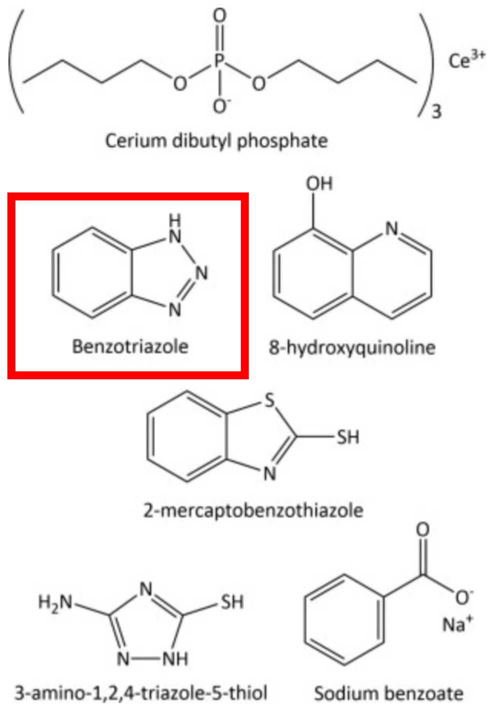


S.J.R. Prabaka et al., Carbon 52 (2013)

Organic compounds: triazole derivatives, polymers



M. K. Shukla et al., JPCC 218 (2014)



Klodian Xhanari et al., Arabian Journal of Chemistry 12 (2019)

Objective of the work

Description at the atomic level of the structure of oxide and organic layers deposited on Al and Al-Mg alloy substrates as well as corrosion properties using modern techniques of computational materials engineering in confrontation with the experiment.

- Determination of the structure and topology of the shell atoms network on the tested substrates
- Study of the adsorption mechanism of the tested organic coatings on substrates
- The need to study corrosion mechanisms of Al and Al-Mg alloys
- Investigation of the influence of oxide and organic layers on the rate of corrosion

Methodology - Molecular Dynamics

Al, Al-Mg

Without coating

Monocrystal
Polycrystal

With coating

Molecular dynamics methods

Voronoi analysis,
Ordering parameter,
Topography and surface roughness,
Concentration profiles,
Chemical analysis,
Corrosion kinetics

Thermal oxidation

300K < T < 663K
O_2
Density = 0.05 g/cm^3
GCMC MD, ReaxFF

Corrosion in water solution

300K < T < 363K
pH: -1, 1, 13, 15
ReaxFF

Methodology - Experiment

Al, Al-Mg

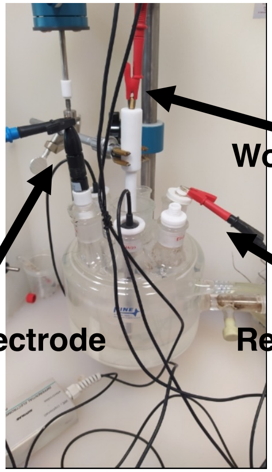
Without coating — Polycrystal — **With coating**

Experimental methods

EOCP plots,
Tafel curves,
AFM, SEM, EDS,
Raman spectroscopy,
Infrared spectroscopy,
Corrosion kinetics

Corrosion in water solution

300K < T <393K
Oxalic acid
pH: 1.5
Time: 5400s



Methodology - Reactive Force Field (ReaxFF)

$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{tors} + E_{vdWaals} + E_{Coulomb}$$

- Modeling of chemical reactions, formation and breakdown of chemical bonds.
- Hydrocarbon, transition metal catalyzed nanotubes, material applications such as lithium-ion batteries, TiO2, polymers and high-energy materials.

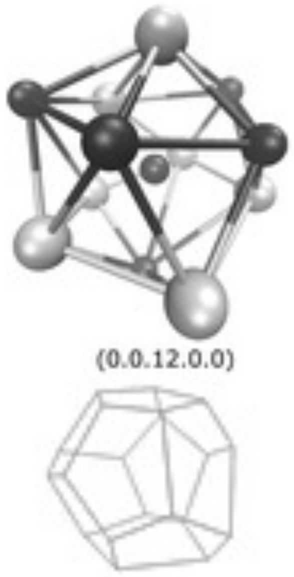
- **Simulation of the formation and breaks of bonds during the oxidation of the metal surface**
- **Interactions of water solution molecules with metal surface**

Adri C. T. van Duin et al.,J. Phys. Chem. A (2001)

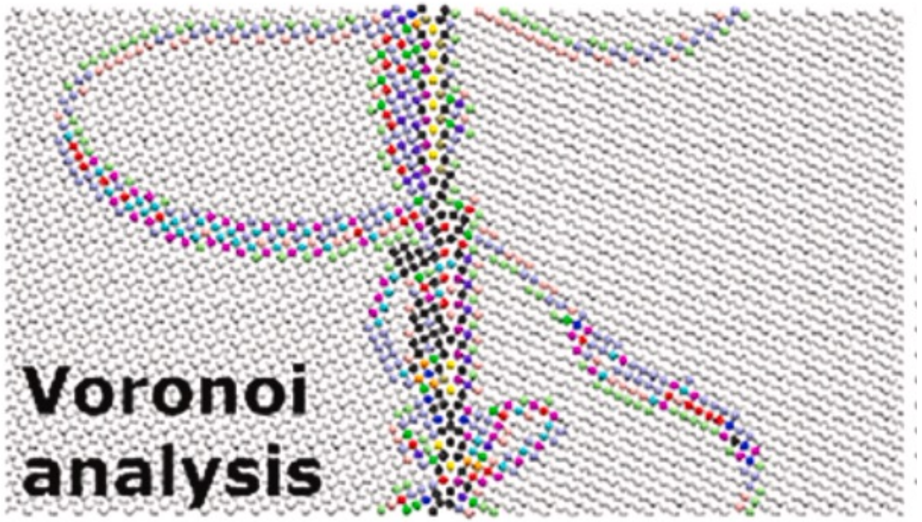
Methodology - Voronoi analysis

- Topological analysis of networks of atoms and their connections
- Voronoi cells - polyhedra whose centers are atoms, while the lines passing through the central atom and the nearest neighboring atoms also pass through the center of the walls of a given polyhedron
- Voronoi indices - (n3.n4.n5.n6.n7), each subsequent digit determines the number of faces of a given type in the polyhedron. For ideal RSC and RPC structures, the Voronoi Indices are (0.12.0.0.0) and (0.6.0.8.0) respectively
- Observation of minimal perturbations of the crystal lattice

Voronoi Cell (VC)

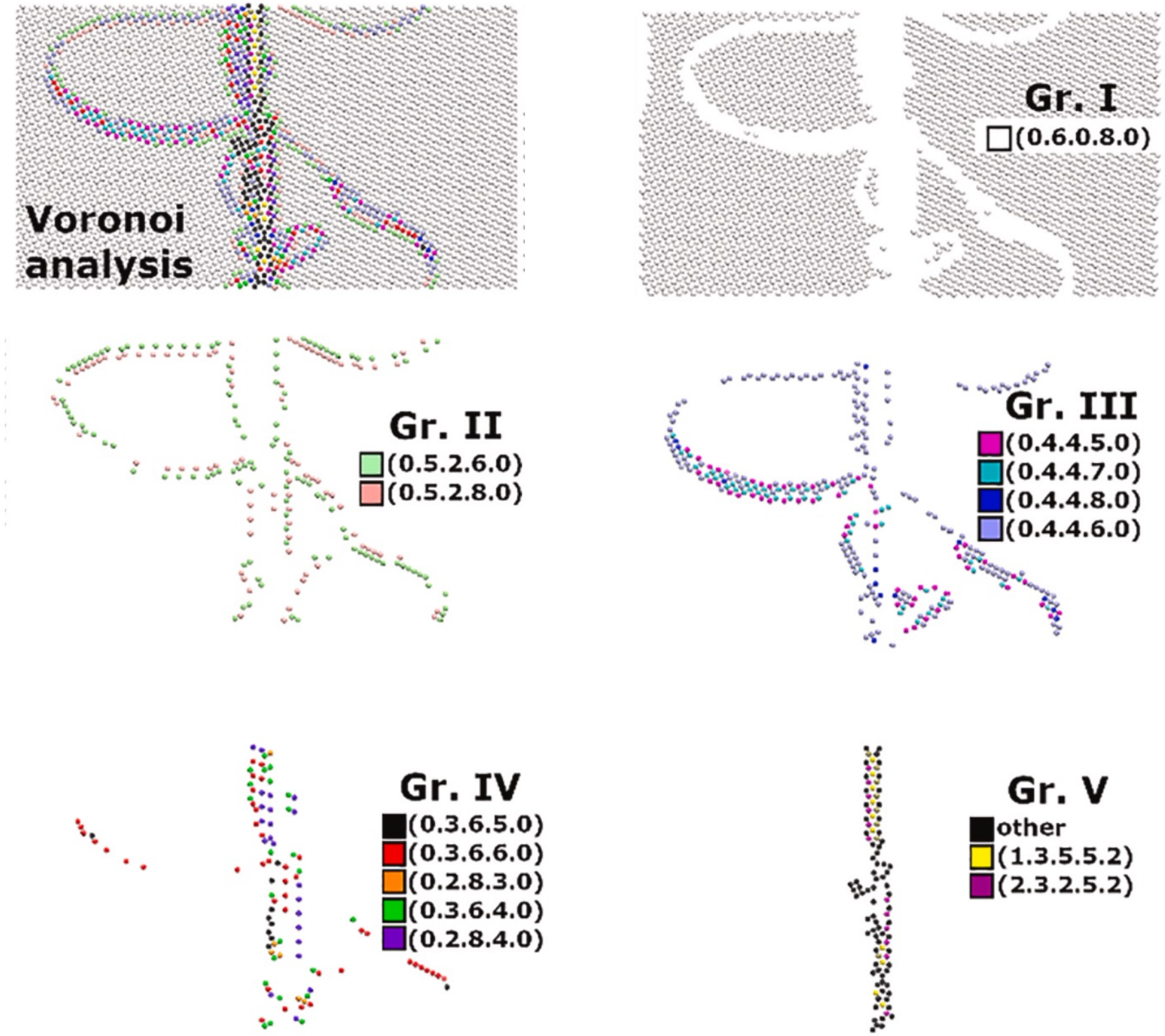


M. E. Trybula et al., J. Mater. Sci. 53 (2018)



A. Żydek, M. Wermiński, M. E. Trybula Com. Mat. Sci. 197 (2021)

Methodology - Voronoi analysis – VC indices



Group	Class	VC indices	Description
I	Perfect lattice	(0.6.0.8.0)	Only tetragonal and hexagonal faces.
II	Small lattice distortions	(0.5.2.6.0), (0.5.2.8.0)	2 pentagonal faces appear, number of tetragonal faces reduced to 5, hexagonal faces reduced or not.
III	Moderate lattice distortions	(0.4.4.4.0), (0.4.4.5.0), (0.4.4.6.0), (0.4.4.7.0), (0.4.4.8.0)	Number of pentagonal faces increased to 4.
IV	Liquid-like or glass-like behavior	(0.2.8.3.0), (0.2.8.4.0), (0.3.6.3.0), (0.3.6.4.0), (0.3.6.5.0), (0.3.6.6.0)	Large number (6–8) of pentagonal faces, accompanied by hexagonal (3–5) and less tetragonal (2–3) faces, characteristic for distorted icosahedra in liquid Al [29], [31], [30].
V	Grain boundary core	(1.3.5.4.2), (1.3.5.5.2), (2.3.2.5.2), (2.3.2.6.2), (2.4.2.4.4), (0.3.8.2.2)	At least 2 heptagonal and usually 1 or 2 trigonal faces. Large numbers of hexagonal faces and high face diversity, characteristic for disordered systems.

A. Żydek, M. Wermiński, M. E. Trybula Com. Mat. Sci. 197 (2021)

Methodology - Analiza Parametru Uporządkowania

This method consists in calculating the interatomic distances between the central atom and its neighboring atoms.

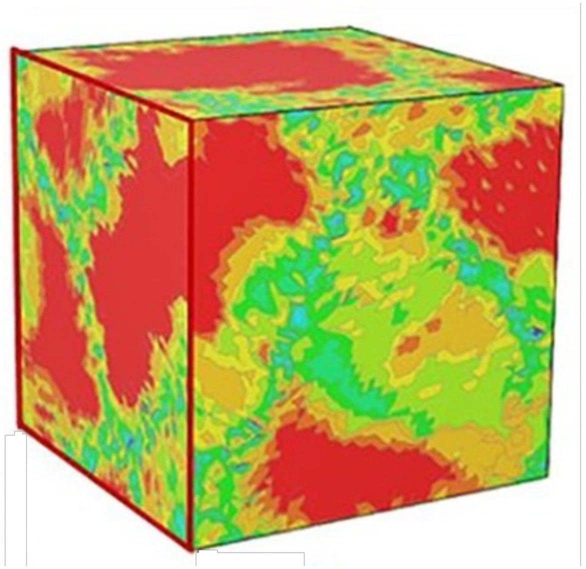
$$\zeta_{ab} = \sum_{i=1}^{CN} |r_a - r_b|$$

CN – coordination number for an ideal crystal lattice

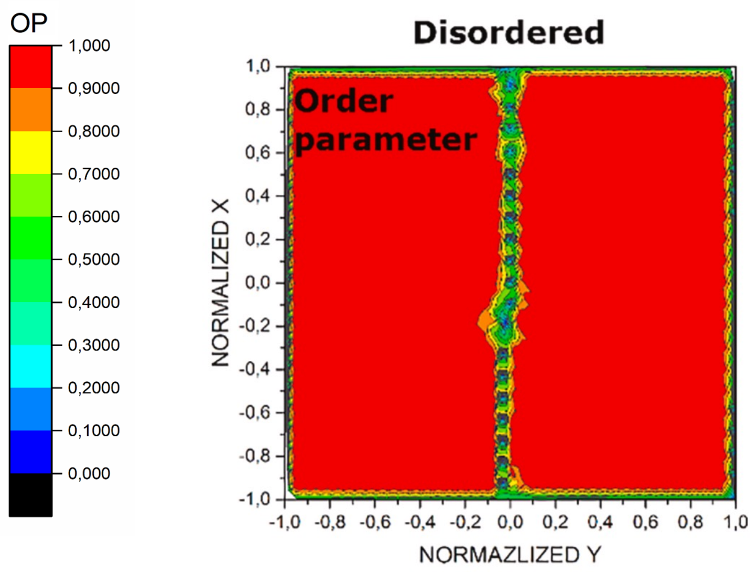
r_a – atom position vector a

r_b – atom position vector b

- Topological analysis
- Observation of crystal lattice disturbances
- Complementary method with Voronoi analysis

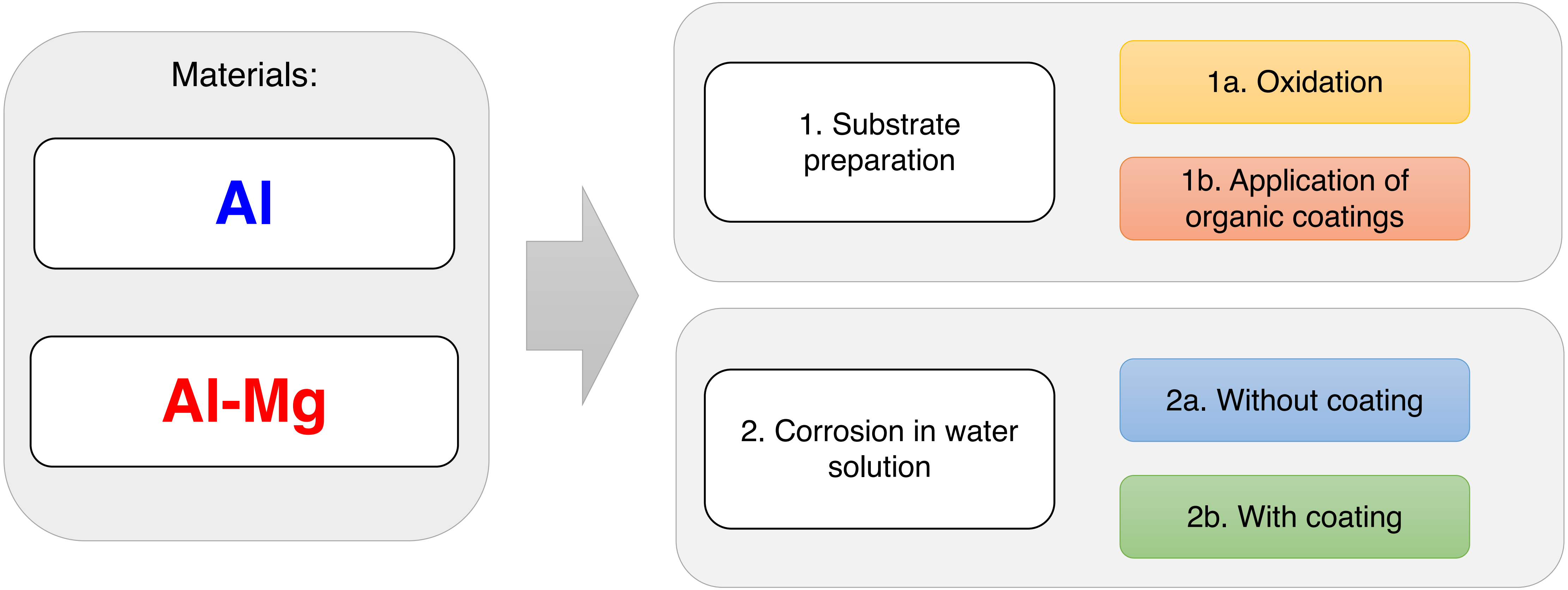


Symmetrical tilt GB(210)[001]



A. Żydek, M. Wermiński, M. E. Trybula Com. Mat. Sci. 197 (2021)

Research scheme MD



Al

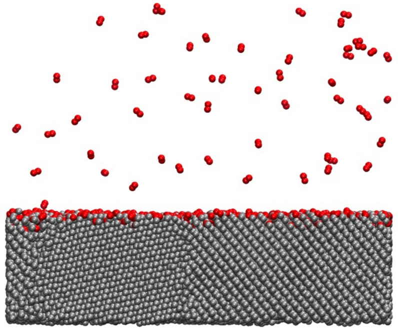
1. Substrate preparation

1a. Oxidation

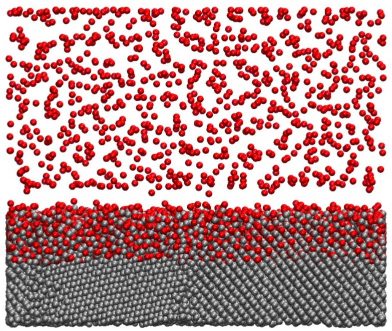
T = 300K
Density O_2 = 0.005, 0.050 g/cm^3

Al 1a Oxidation Al – Structure and growth kinetics of the oxide

- T=300K t=2ns



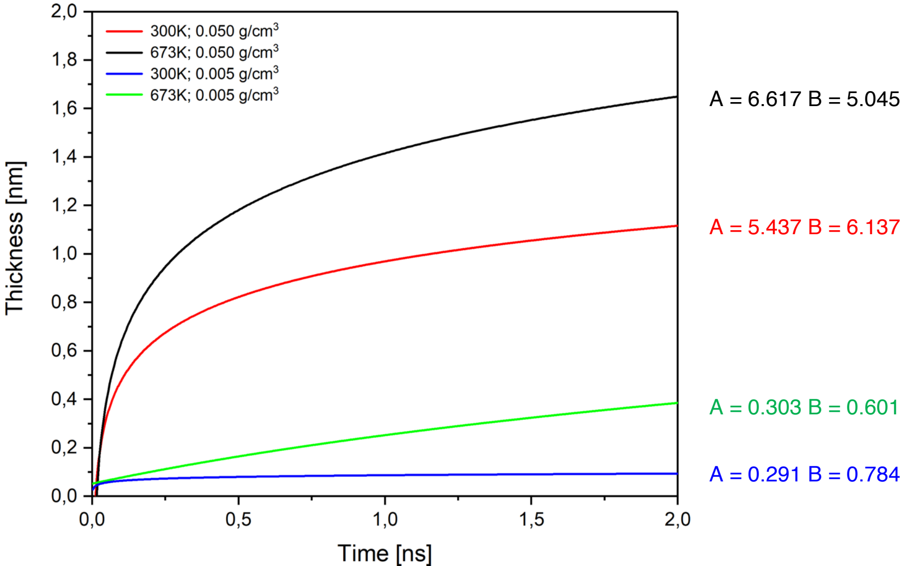
0.005 g/cm³



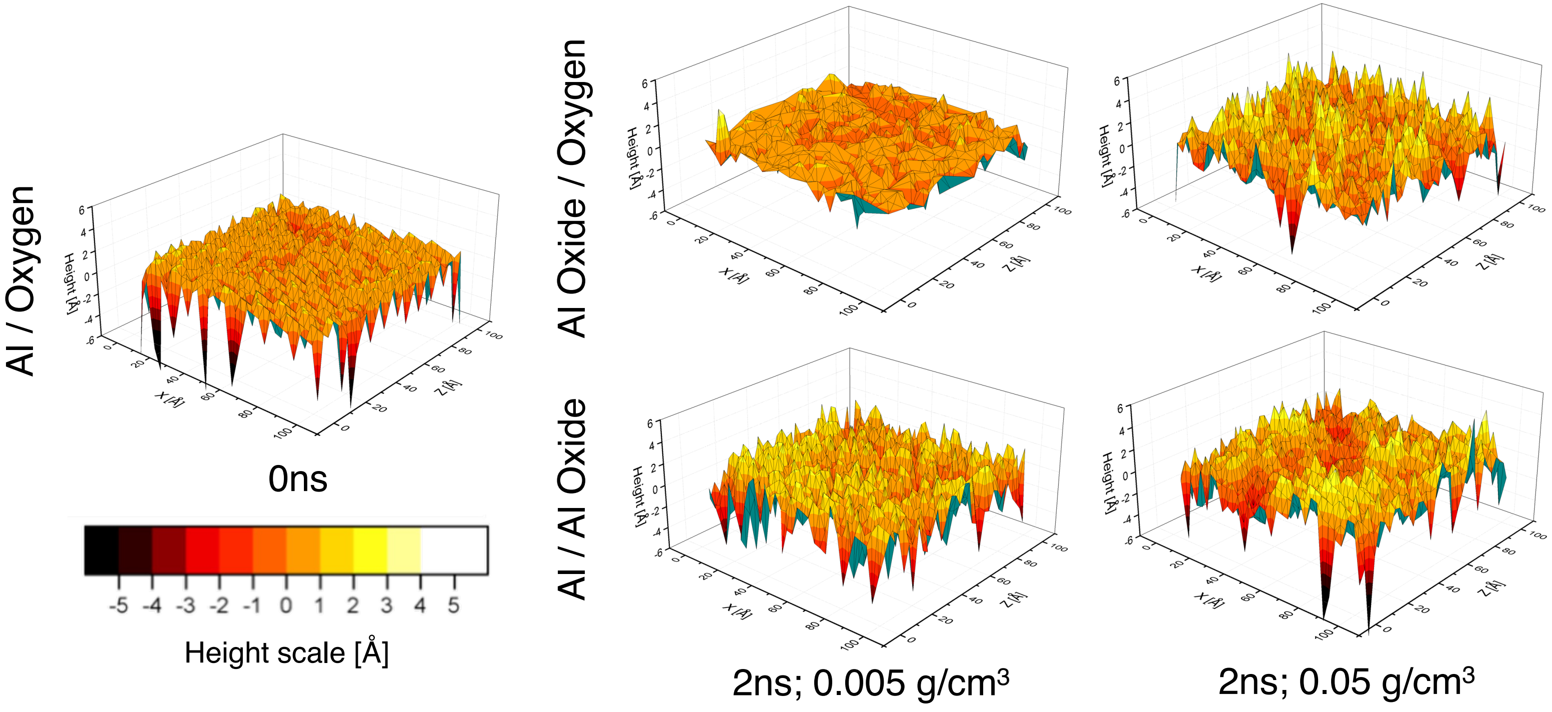
0.050 g/cm³

Kinetics of oxide layer

$$\frac{dx}{dt} = A * \exp(-B * x)$$



Surface topography



Roughness : Al / Al Oxide

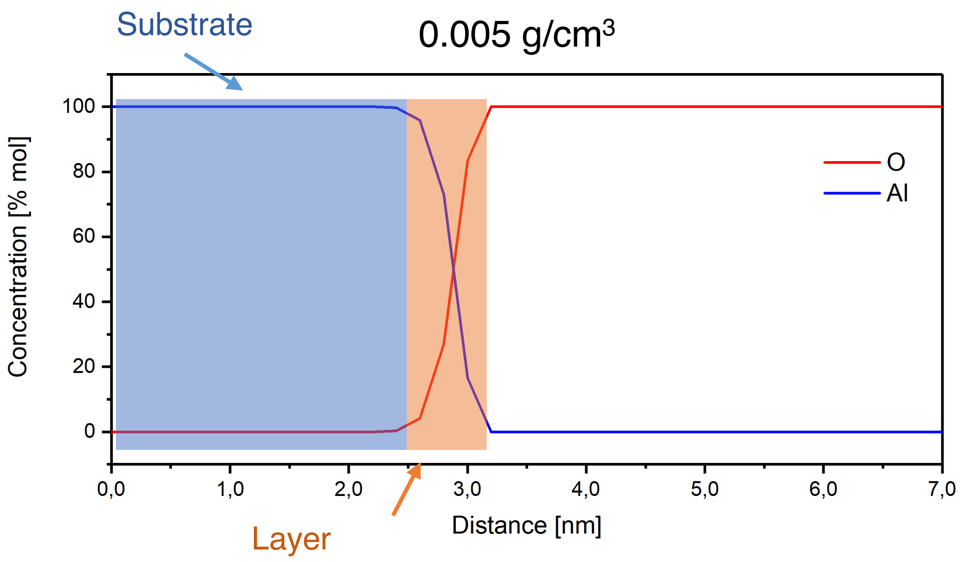
O_2 density [g/cm³]	Temperature [K]	Ra [Å]	Rz [Å]
0.005	300	1.274	7.641
	673	1.761	8.834
0.050	300	1.035	6.773
	673	1.498	9.169

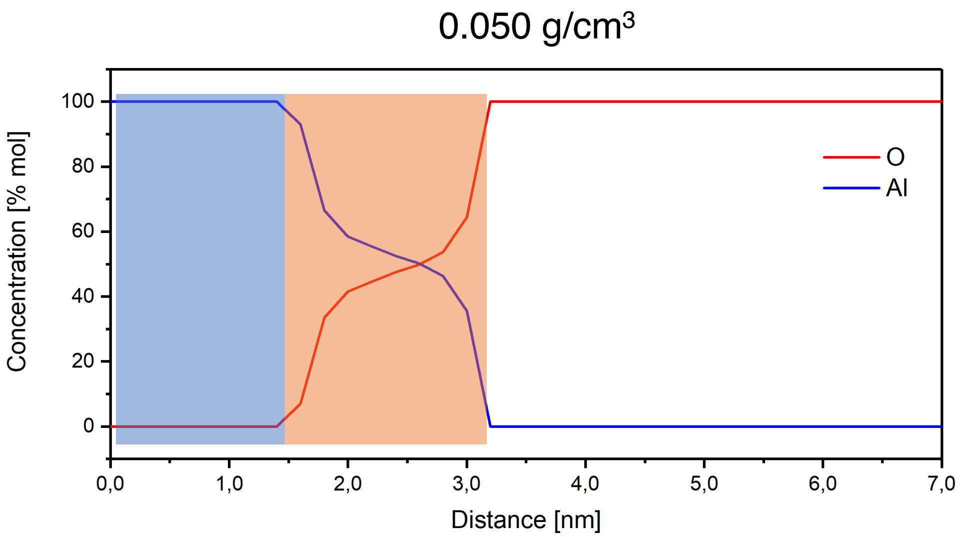
Roughness : Al Oxide / Oxygen

O_2 density [g/cm³]	Temperature [K]	Ra [Å]	Rz [Å]
0.005	300	0.614	5.707
	673	0.902	6.674
0.050	300	0.920	6.880
	673	1.113	9.056

Al 2b

Oxidation Al – Concentration Profiles





Chemical composition

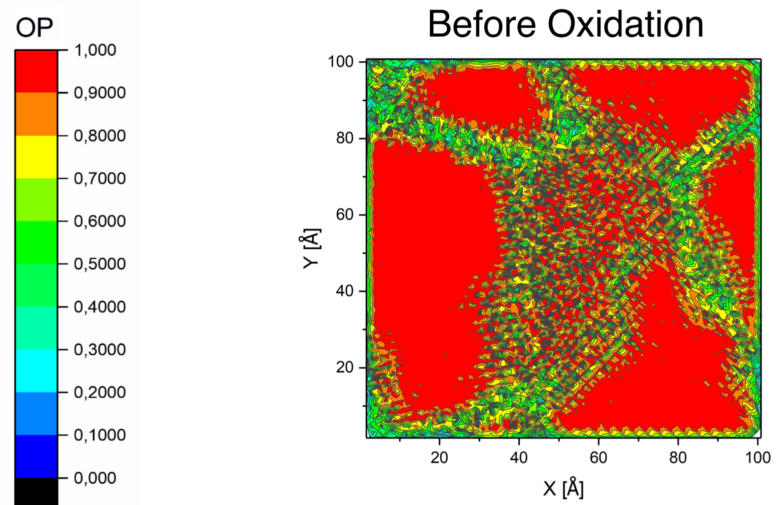
	Al [% mol]	O [% mol]
673K; 0.005 g/cm^3	66.4	33.6
300K; 0.050 g/cm^3	55.2	44.8
673K; 0.050 g/cm^3	54.4	45.6

Al 1a Oxidation Al – topology of Al polycrystal substrate

- T=300K

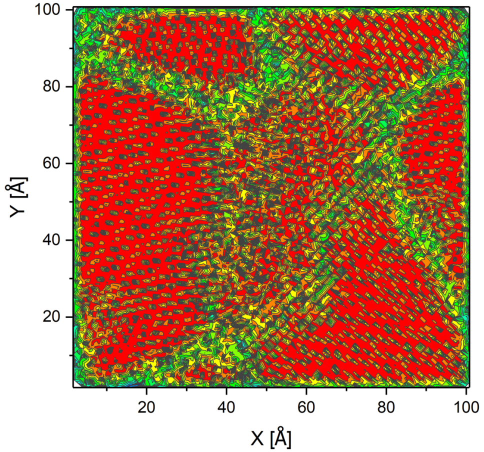
Order Parameter

Before Oxidation

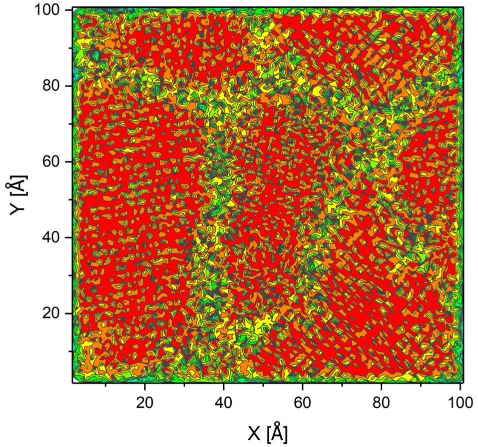


t=0ns

After Oxidation



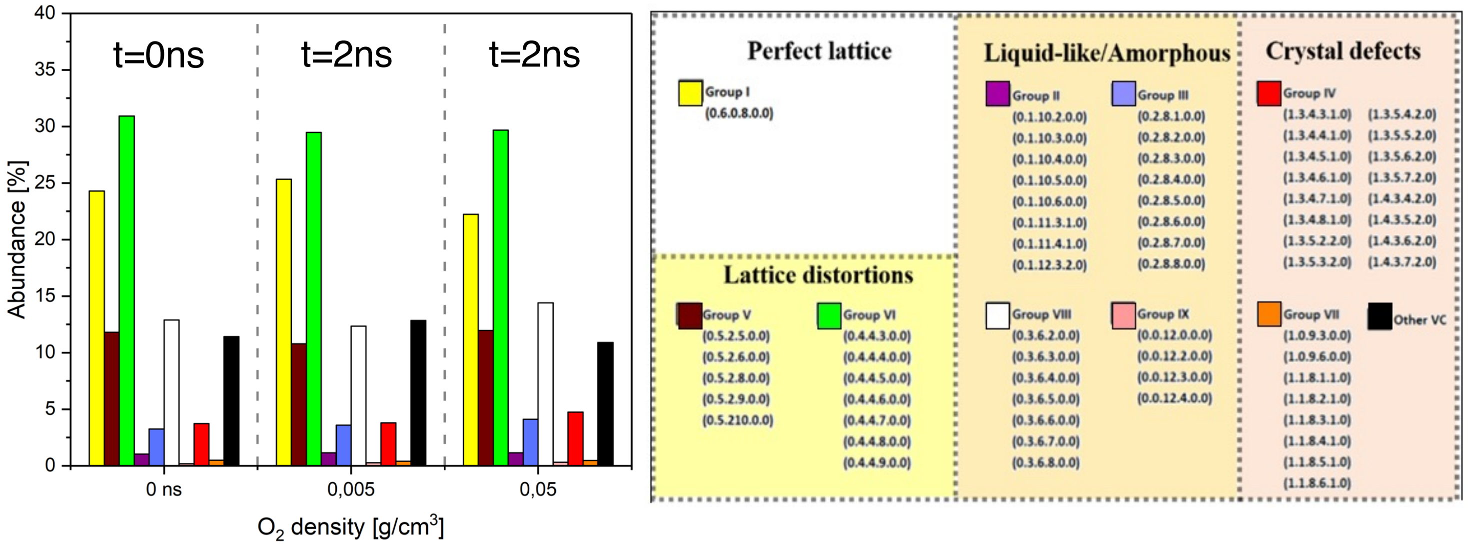
t=2ns; 0.005 g/cm^3



t=2ns; 0.05 g/cm^3

Voronoi analysis

t=0ns | t=2ns; 0.005 g/cm^3 | t=2ns; 0.05 g/cm^3



Al

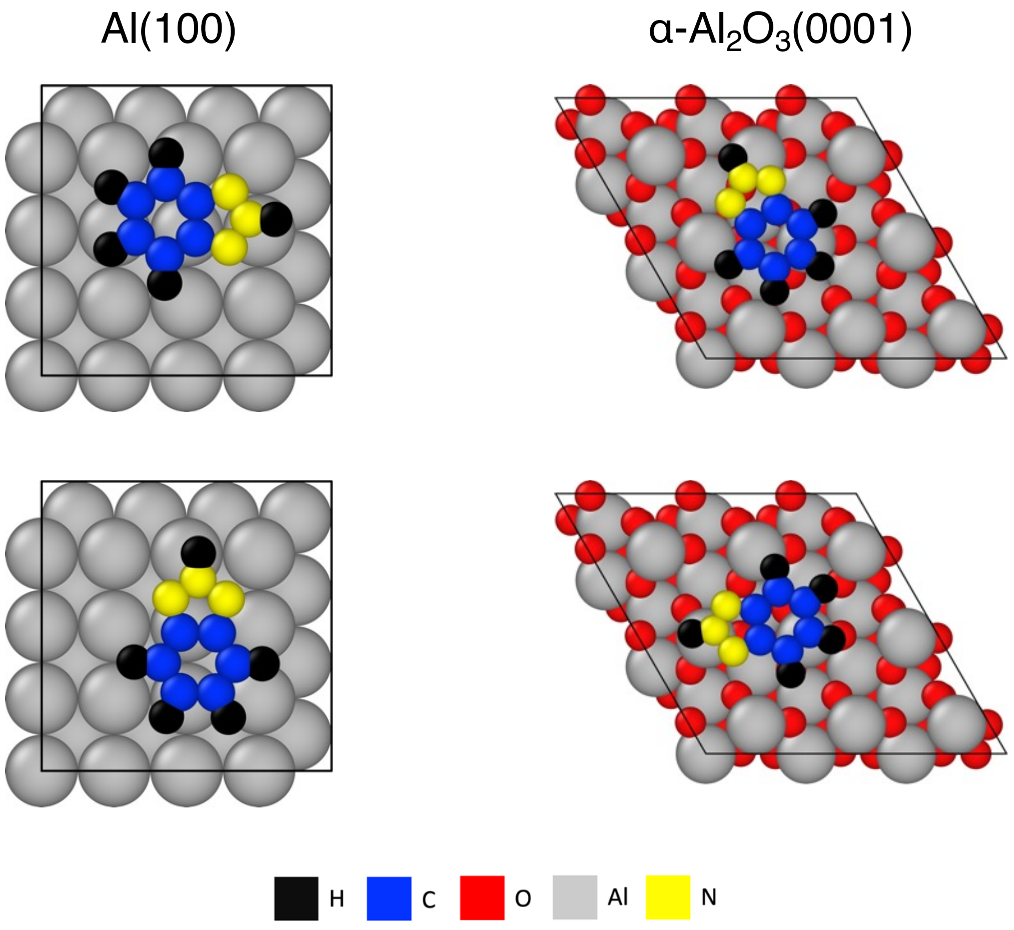
1. Substrate preparation

1b. Application of organic coatings

T = 300K

Al 1b Benzotriazole - adsorption energy

- Comparison of two ReaxFF force field parameterizations with DFT results



adsorption energy

		ΔE [eV]		
Substrate	Position	DFT	ReaxFF 1	ReaxFF 2
Al(100)	a	-0.4715	-0.3861	-4.4140
Al(100)	b	-0.4644	-0.3861	-4.4138
α-Al_2O_3(0001)	a	-2.4432	-2.0283	-6.2162
α-Al_2O_3(0001)	b	-1.2869	-2.0232	-6.2162

ReaxFF 1 - O. V. Mackenzie et al., J. Phys. Chem. C (2015)
ReaxFF 2 – N. Wang et al.," J. Phys. Chem. C (2017)

PROGRAM STER

In collaboration with the professor Pavel Korzhavyi
and dr. Claudio Lousada
KTH Royal Institute of Technology, Stockholm

Al 1b

Deposition of benzotriazole - ReaxFF-MD simulations

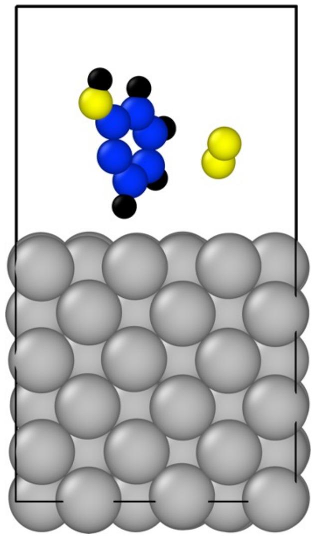
Benzotriazole in a vacuum

1 molecule of benzotriazole

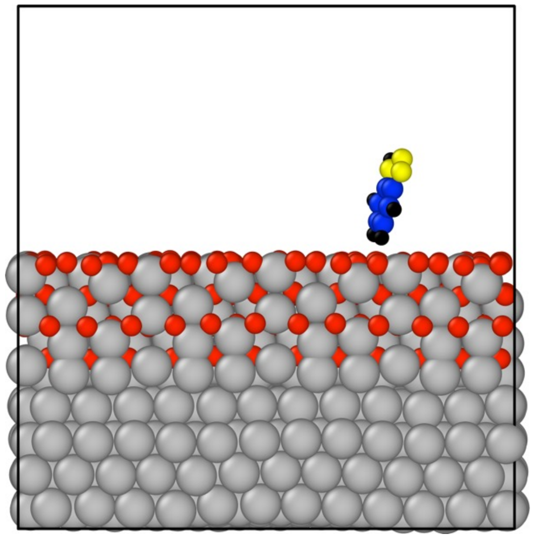
Benzotriazole in methanol

17 molecules of benzotriazole

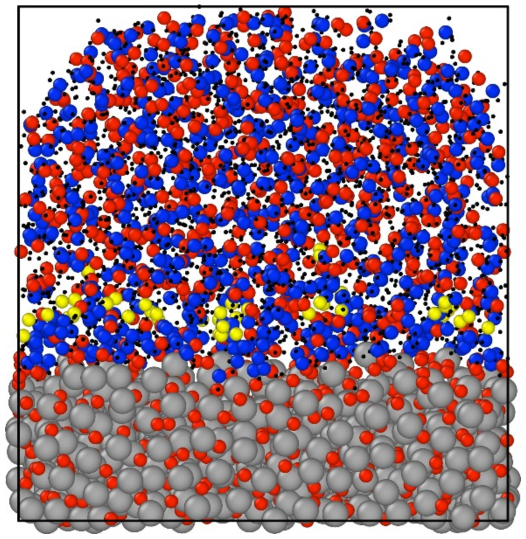
Podłoże Al(100)



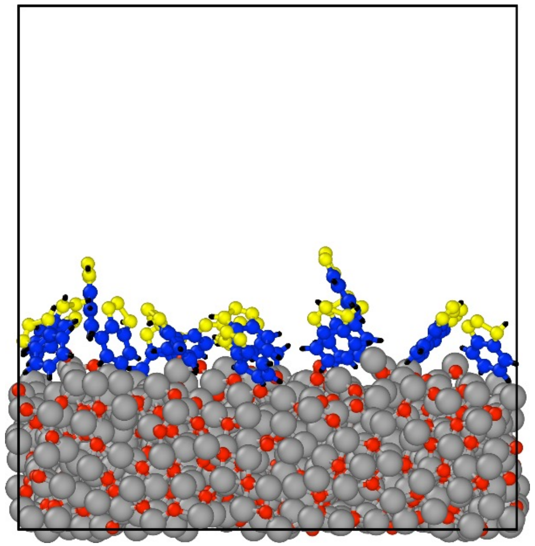
Podłoże α-Al_2O_3(0001)/Al(111)



Podłoże tlenek Al



View with methanol



View without methanol

Al

2. Corrosion in water solution

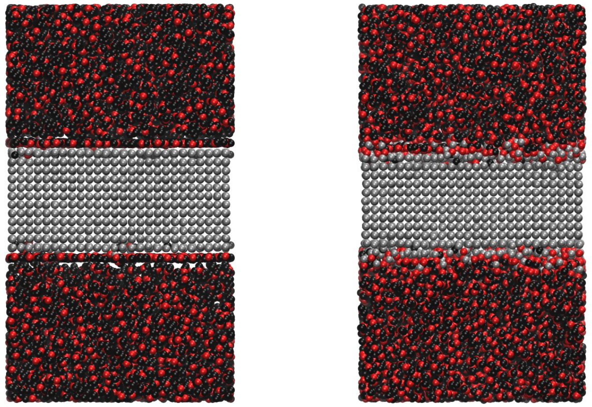
2a. Without coating

T = 363K
pH = 1, 13

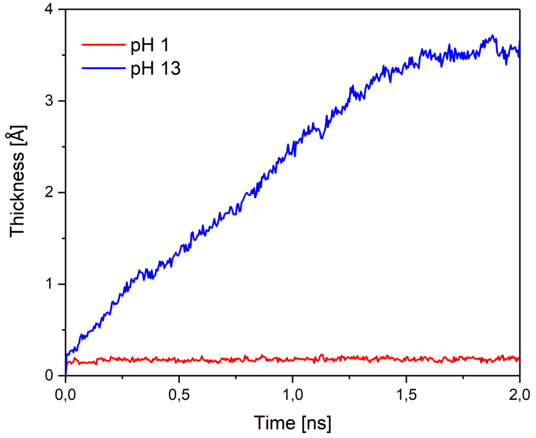
Al 2a Korozja podłoża Al

- Influence of the Al substrate structure on the corrosion mechanism in an water solution with an excess of OH- and H+ ions
- Influence of Al substrate structure on corrosion rate - thickness change over time
- T=363K t=1ns

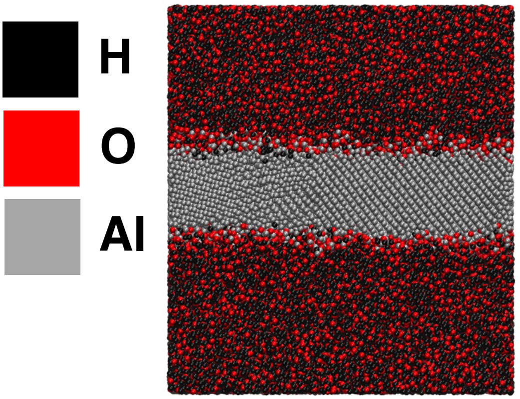
Monocrystal Al



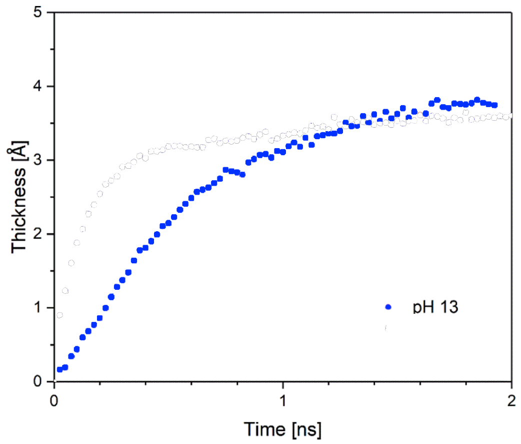
pH 1 ($C_{M(kwasu)}$ = 1 mol/dm^3) pH 13 ($C_{M(zasady)}$ = 1 mol/dm^3)



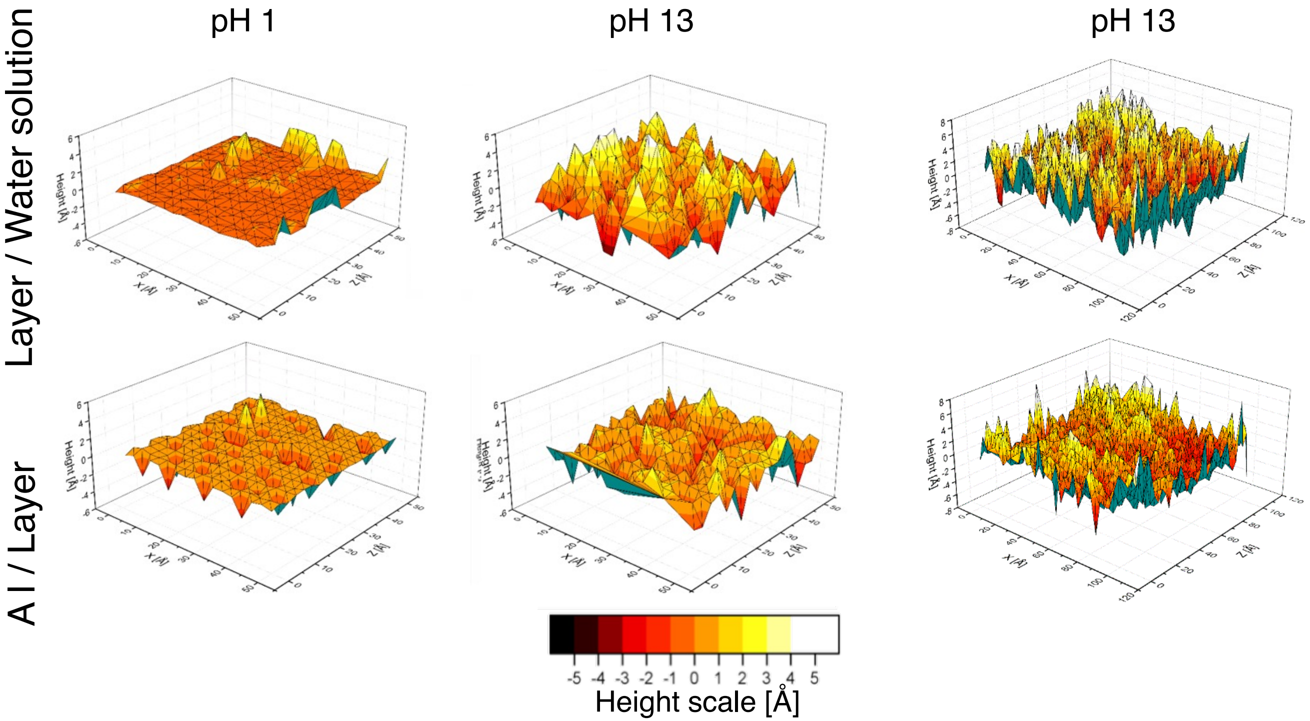
Polycrystal Al



pH 13



Monocrystal Al / Polycrystal Al



Roughness : Al / Layer

Podłoże	pH	Ra [Å]	Rz [Å]
Monocrystal	1	0.8	5.44
	13	1.56	8.81
Polycrystal	13	1.90	12.91

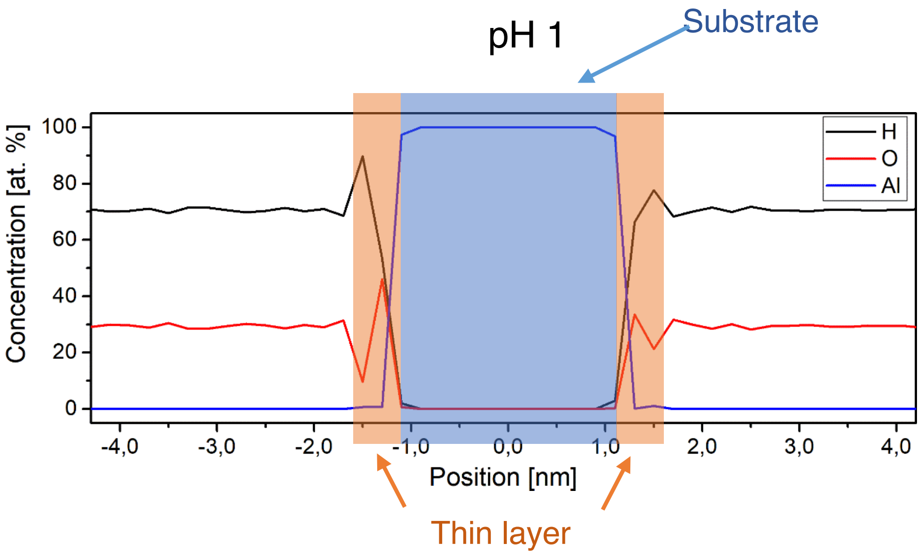
Roughness : Layer / Water solution

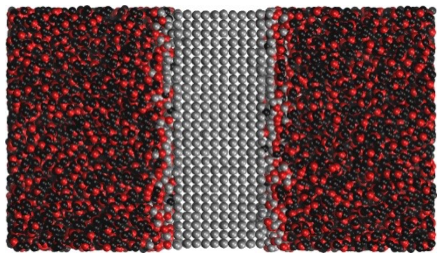
Podłoże	pH	Ra [Å]	Rz [Å]
Monocrystal	1	0.36	4.07
	13	1.17	5.57
Polycrystal	13	1.20	10.17

Al 2a Al substrate corrosion - concentration profiles

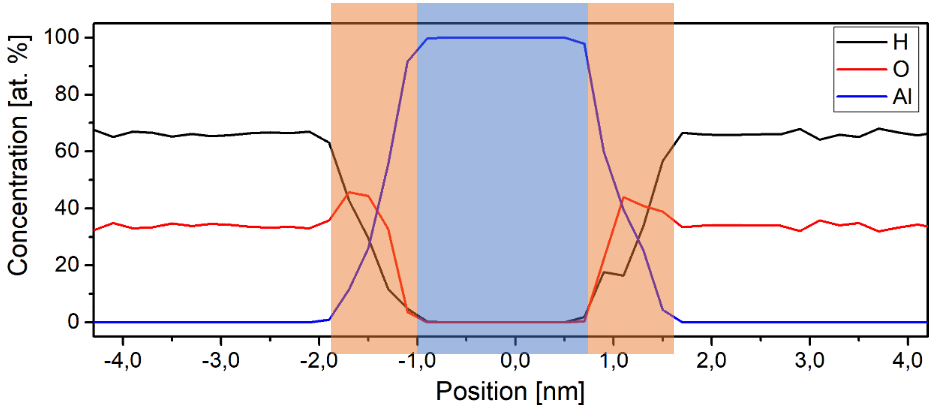
- T=363K t=1ns

Monocrystal Al

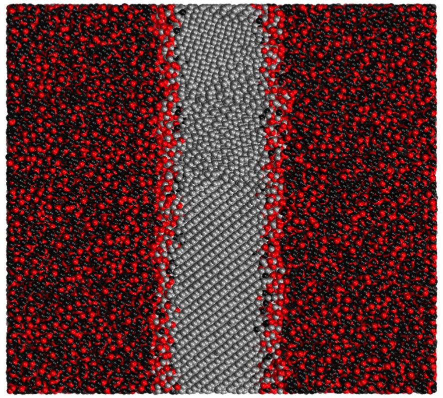




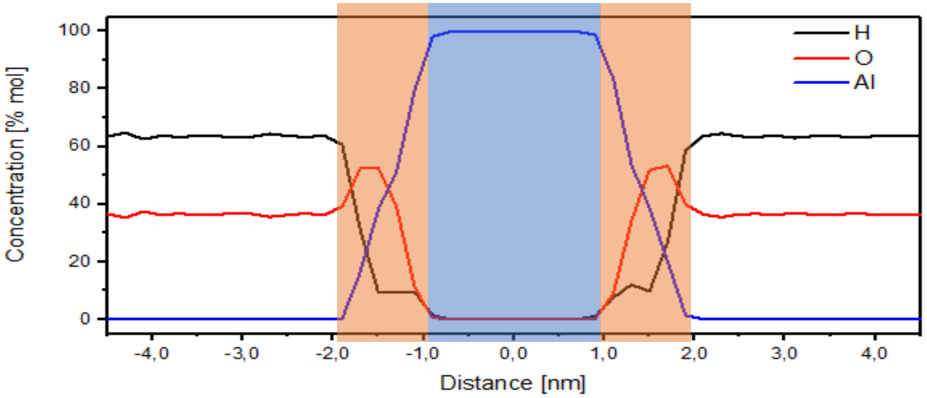
pH 13



Polycrystal Al



pH 13



Chemical composition

Substrate	pH	H [% mol]	O [% mol]	Al [% mol]
Monocrystal	1	17.1	30.2	52.7
	13	25.3	31.0	43.7
Polycrystal	13	23.8	36.9	39.3

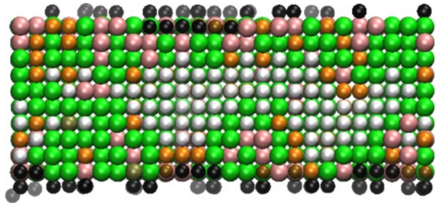
Al 2a

Al Substrate Corrosion - Voronoi Analysis

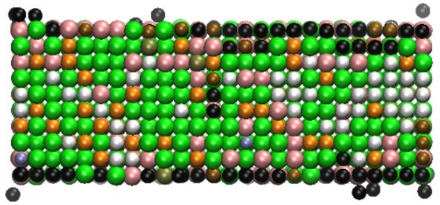
- Characteristics of the type of defects in Al substrates after corrosion - distribution of Voronoi indicies
- T=363K t=1ns

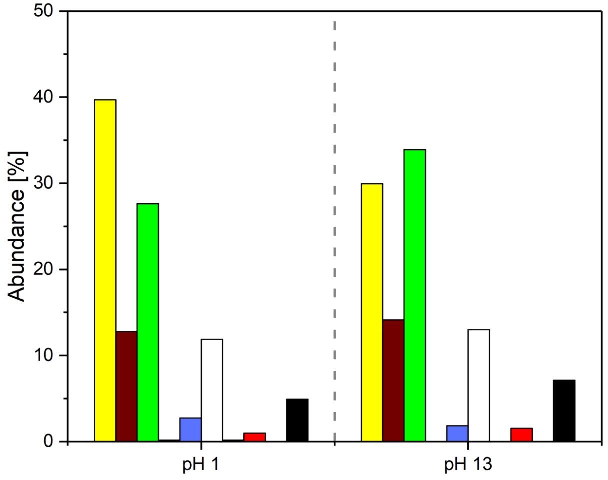
Monocrystal Al

pH 1



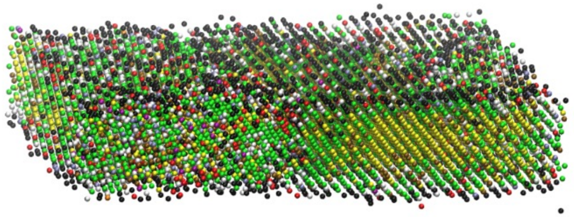
pH 13

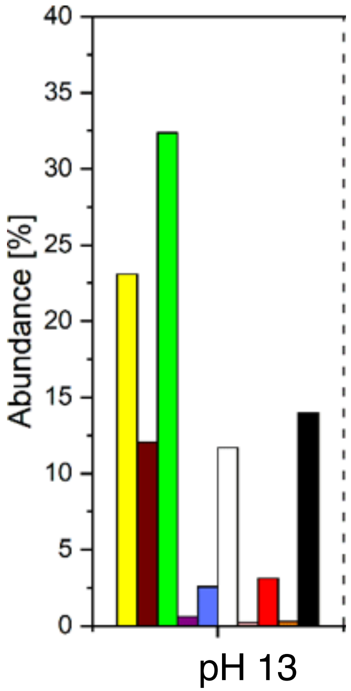


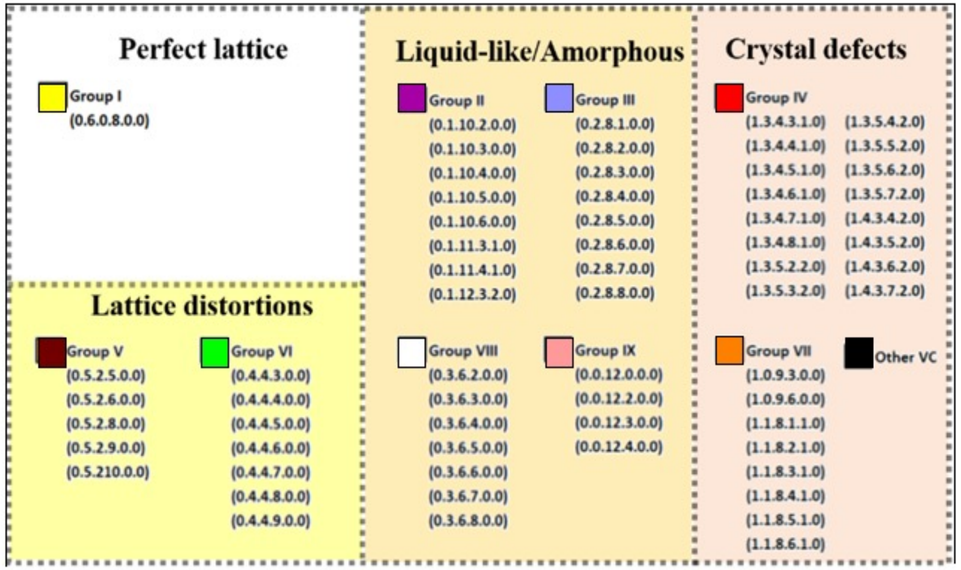


Polycrystal Al

pH 13







Al

2. Corrosion in water solution

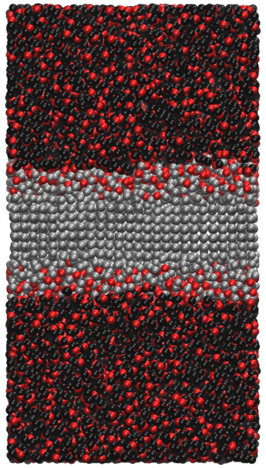
2b. With coating

T = 363K
pH = 1, 13

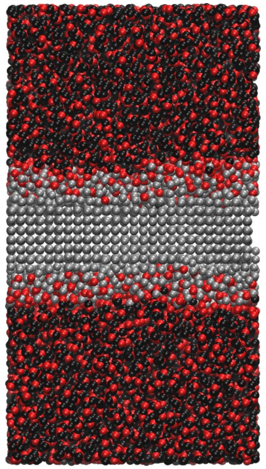
Al 2b Al / Al oxide corrosion

- T=363K t=1ns

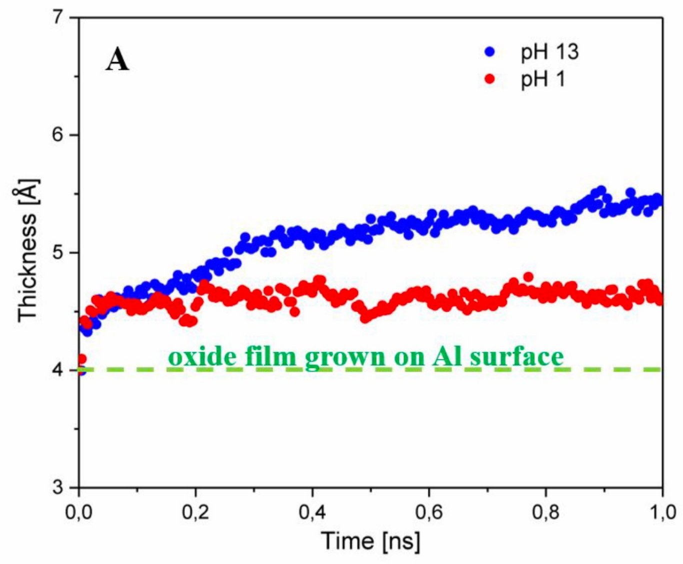
pH 1



pH 13



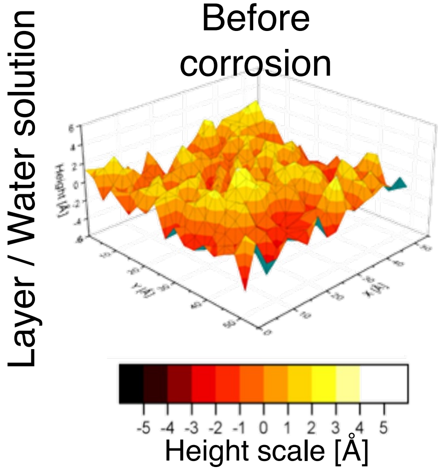
Thickness change

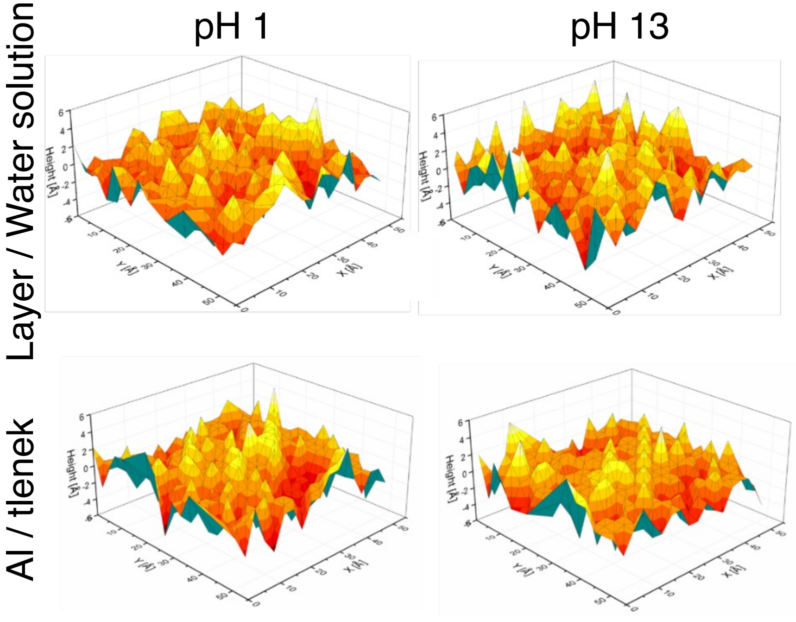


Layer thickness increase

Coating	pH	thickness increase [Å]
Without coating	1	0.2
	13	2.1
Oxide layer	1	0.5
	13	1.6

Surface topography





Roughness: Al / Layer

pH	Ra [Å]	Rz [Å]
1	1.13	6.92
13	1.16	6.62

Roughness: Layer / Water solution

pH	Ra [Å]	Rz [Å]
Before corrosion	1.18	7.82
1	1.54	8.26
13	1.47	7.79

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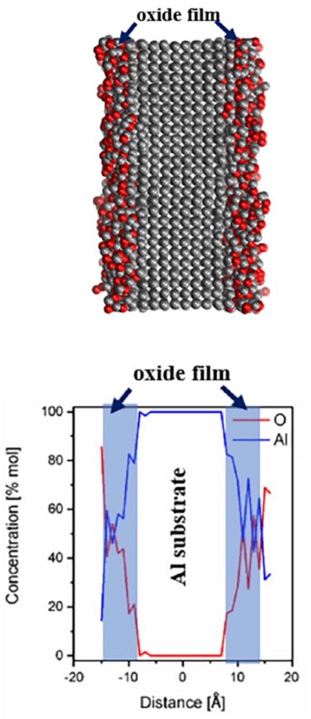
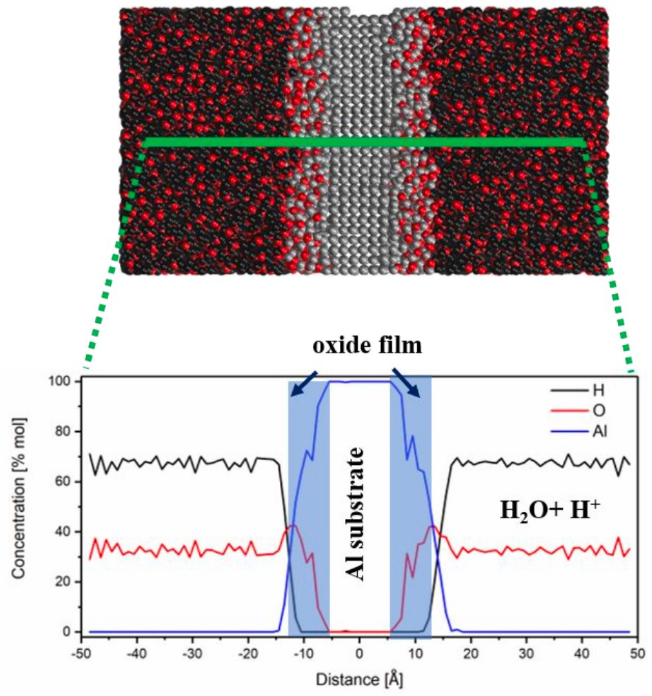
Al 2b Al / Al oxide corrosion - concentration profiles

- T=363K t=1ns

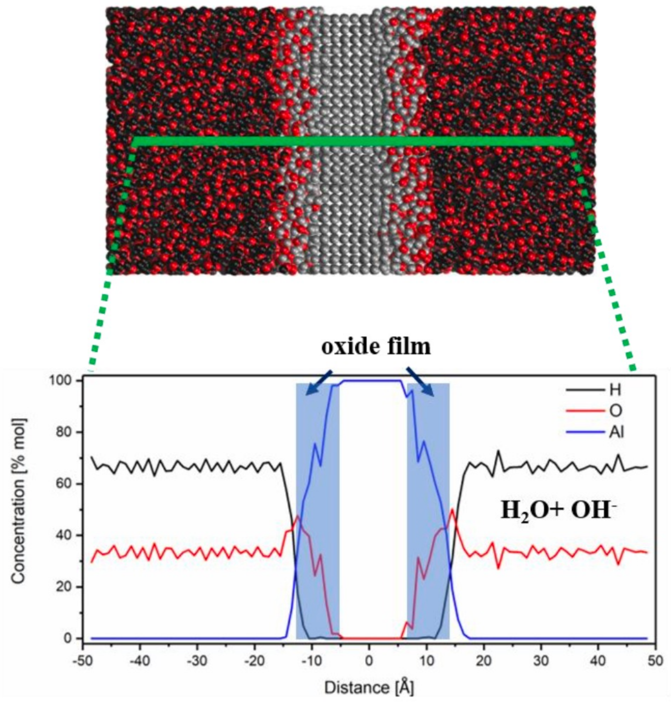
Before corrosion



Acidic solution, pH 1



Alkaline solution, pH 13



Chemical composition

pH	H [% mol]	O [% mol]	Al [% mol]
Before corrosion	0.0	38.6	61.4
1	1.9	32.3	65.8
13	7.1	34.6	58.2

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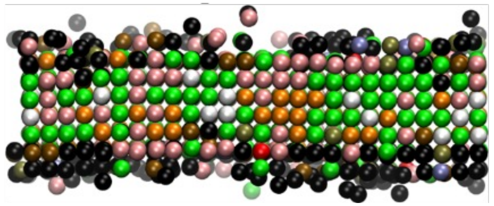
Al 2b Al / Al oxide corrosion - Voronoi analysis

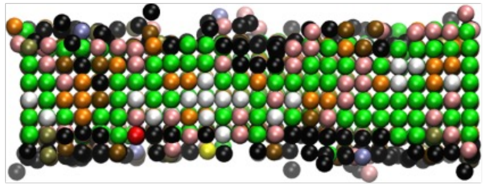
- T=363K t=1ns

Substrate

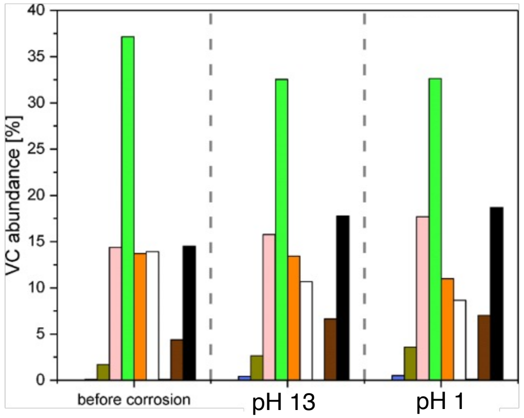
pH 13

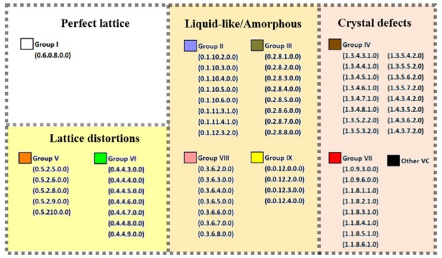


pH 1

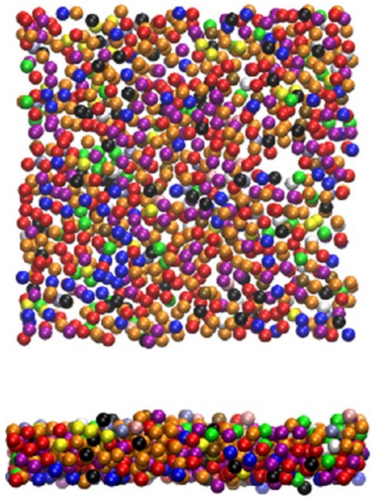


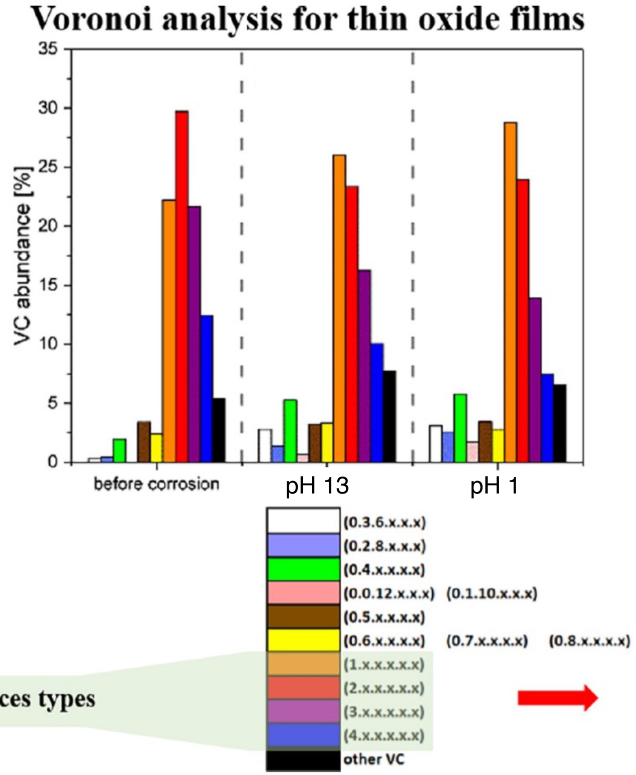
Monocrystal Al / Oxide

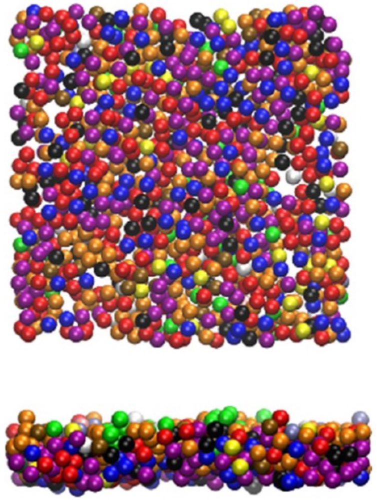




Thin Layer







Oxide-type structure

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Conclusions

- Oxygen density is crucial during the thermal oxidation of Al, increasing the oxygen density accelerated the oxidation process significantly.
- Low adsorption energy of benzotriazole to the substrate with Al oxide, agreement of DFT results with ReaxFF-MD
- Different corrosion mechanisms depending on the pH of the solution used
- The oxide layer reduces the corrosion process of the Al substrate

Research in progress

- Continuation of MD simulations corrosion for Al and Al-Mg alloys with deposited coatings (benzotriazole) in water solution
- Continuation of DFT calculations of adsorption energy of deposited coatings on Al and Al-Mg substrates
- Experimental corrosion tests for Al and Al-Mg alloys with applied protective coatings

Thank you for your attention