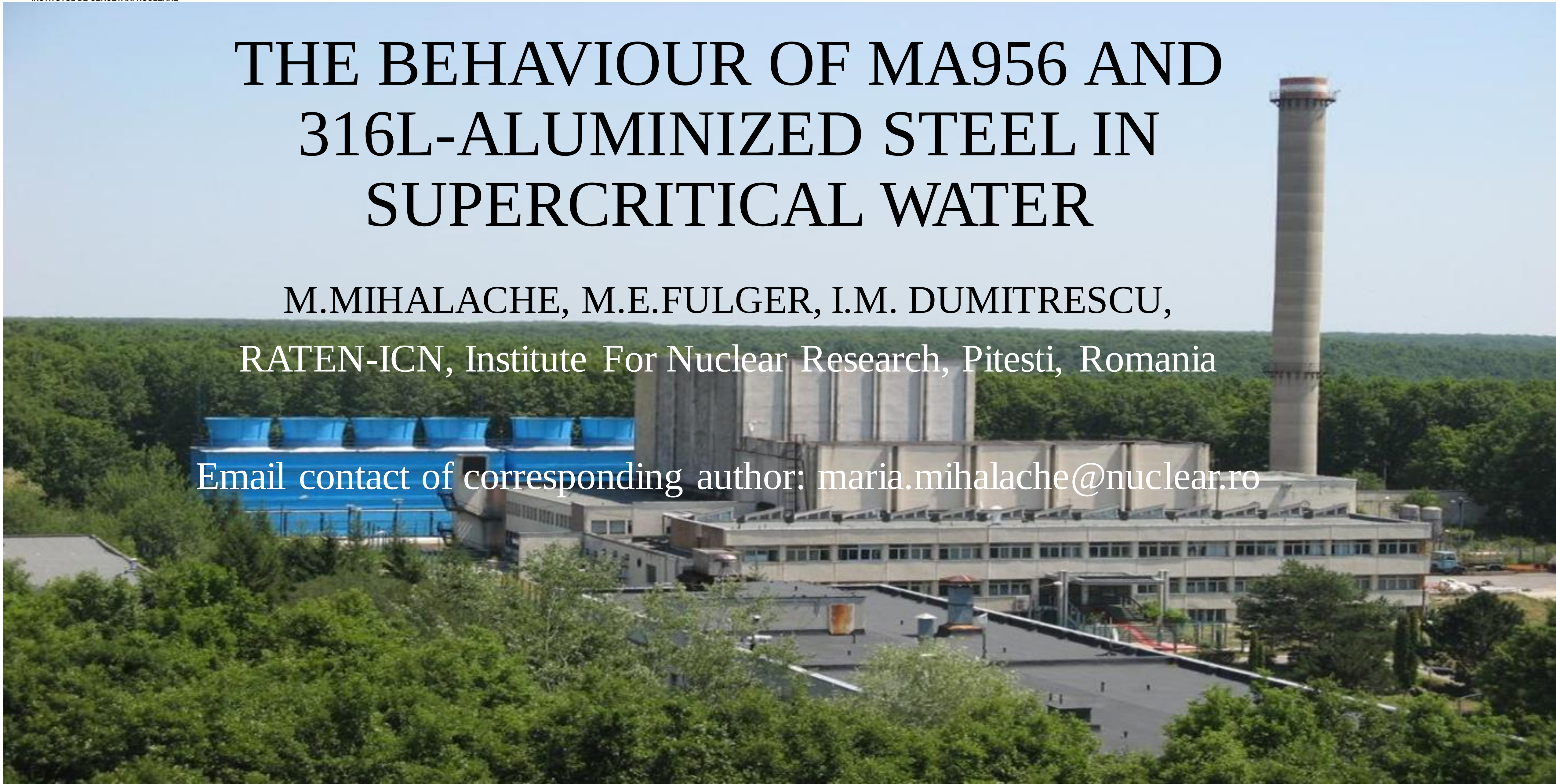
THE BEHAVIOUR OF MA956 AND 316L-ALUMINIZED STEEL IN SUPERCRITICAL WATER

M.MIHALACHE, M.E.FULGER, I.M. DUMITRESCU,

RATEN-ICN, Institute For Nuclear Research, Pitesti, Romania

Email contact of corresponding author: maria.mihalache@nuclear.ro



1. Introduction

- requirement for energy — developing GIV nuclear reactors for fission.
- GIV reactors for fission, as well as the reactors for fusion — more aggressive conditions:

  - high temperature,
  - high dose
  - high-pressure
  - extended operation period

→ coolant compatibility and weld ability - conditions for qualification as appropriated for structural materials .

- SCWR - higher thermal efficiency and simplified design

  - great attention at materials selection for using as cladding tubes or structural materials

Research, Development and Engineering
Strategic Romanian National R&D Program

Nuclear Power Programs

- ✓ Nuclear Safety;
- ✓ Fuel Channel;
- ✓ Nuclear Fuels;
- ✓ Fuel Handling;
- ✓ Management of Radioactive Wasted including Spent Nuclear Fuel;
- ✓ Environment Protection;
- ✓ Steam Generator;
- ✓ Process Systems and Equipment;
- ✓ Chemistry of NPP Circuits;
- ✓ Instrumentation and Control'
- ✓ Analysis of NPP Operating Events, Aging, Environment Qualification and Life Extension;
- ✓ Advanced Nuclear Reactors and Fuel Cycles;
- ✓ Heavy Water and Tritium

Other Programs

- Extension of TRIGA Reactor Performances;
- Irradiation Technologies and Radioisotopes;
- Applications of Nuclear Techniques;
- Informatics;
- Support for International Co-operation;

GIV advanced reactors concerns;

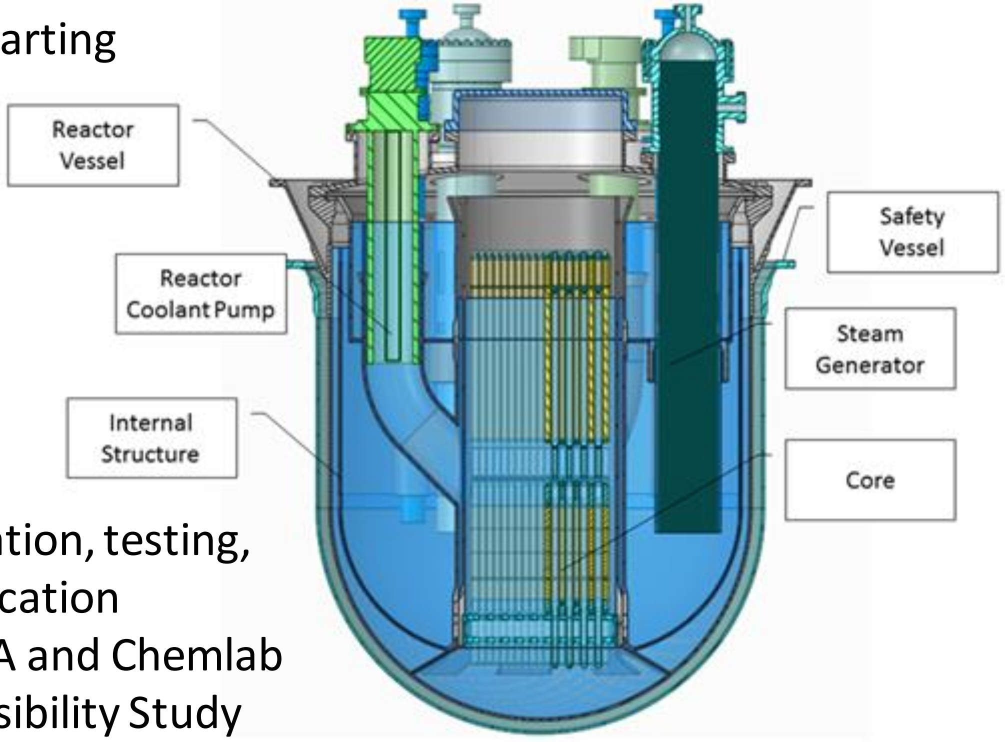
- lead ALFRED demonstrator
- Infrastructure for testing in lead:
  - ATHENA, CHEMLAB (under construction)
  - HELENA, ELF, MELTINPOT, HUB (future)

Institute For Nuclear Research-MISSION

- to provide scientific and technologic support for the Romanian Nuclear Program, especially ;
- to offer scientific and technologic support for safety and economic operation of CANDU NPP Units from Cernavoda;
- to develop technologies, methods, computer codes, experimental infrastructure, directed towards an end-product or service with applications in nuclear power plants and nuclear field.

GIV advanced reactors concerns

ALFRED Demonstrator of LFR technology
2013, December, set-up of **FALCON international consortium**
2018, pre-licensing phase starting



Infrastructure for licensing, qualification, testing, demonstration, validation and verification
- 2020 construction start for ATHENA and Chemlab
- 2019-2020, ELF and HELENA2, Feasibility Study
- 2019-2020, HandsON and Meltin'Pot, Conceptual Design

Scope of the experimental infrastructure

- **ATHENA,** large pool to test the main components in different thermal hydraulics regimes
- **ChemLab**, lab coupled with ATHENA, lead and cover gas chemistry,
- **HELENA2**, loop type facility to test components and equipment in relevant thermal-hydraulic conditions, in particular, the ALFRED hottest fuel assembly,
- **ELF**, large scale pool-type facility, to test the endurance and reliability under both forced circulation and natural circulation regimes,
- **HandsOn**, pool type experimental facility, to demonstrate the fuel handling of fuel assemblies,
- Meltin'Pot, set of facilities to investigate the fuel-coolant interaction, fuel dispersion and relocation in the coolant resulting from a severe accidental scenario, retention of fission products in lead and/or migration in cover gas, retention in lead of Polonium isotopes and influence of a gas/steam trapping on its migration.

Candidate Materials for GIV reactors for fission

- GIV nuclear systems materials requirements: Safe; Sustainable; Economical
- Gaps: fuel sheets and structural materials
- Structural materials requirements :
  - High operating temperature (up to 700°C)
  - High Neutron Flux Exposure (up to 200 dpa)
  - Extremely corrosive environment (SCW, LM…)
  - Operation life (>60 years)
- 316L SS and improvements (N, Al, Si or protective Cr based Layers - structural materials candidate for lead or SCW GIV reactors - EUROTRANS FP6, FP7) or ferritic ODS steels (TiO_2, Y_2O_3 additions)
- 15-15Ti, T91, MANET, OPTIFER, 1.4914 ferritic/martensitic steels candidate for fuel sheets in lead or SCWR GIV

Objectives of study

• Testing and comparison the behaviour of 304L SS, 316-Al, MA956 (reinforced with yttrium and titanium oxides), in stagnant SCW at 550^{o}C temperature and 25MPa pressure up to ~2300 exposure hours;

•Assessment of oxidation kinetics (dissolution or oxidation?);

•Protectiveness assessment of oxide films formed on surface (morphology, stratification and chemical analyses of oxides evaluated optical, by SEM and EDS techniques);

•Diseminating RATEN ICN (Institute for Nuclear Research)activity on P12 “advanced reactors and fuel cycles” and P9 “Circuits Chemistry” National Programs

Materials tested

The manufacturing processes:

- austenitic (ferritic?) 316 - Al steel

- mechanical enhanced with -mechanically alloying (MA) with 4.5%Al ;
- hot isostatic pressing process (HIP) - 3 hours at 1105°C ,100MPa

- MA956 ferritic ODS steel,

- mechanical alloying,
- extrusion hot rolled plate,
- heat treatment 1300°C;

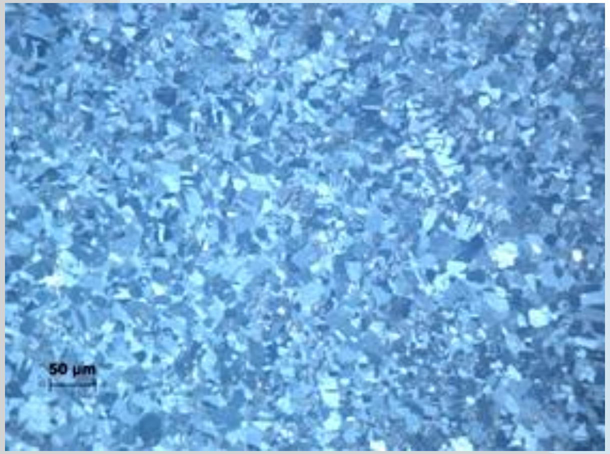
- 304 L (A/SA -240 commercial plate)

Chemical composition

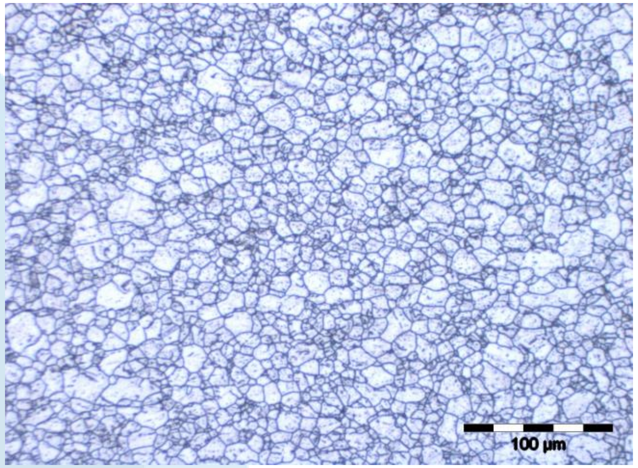
Element	Percentage by Weight Maximum Unless Range is Specified		
	316 Al	MA956	304L
Iron	balance	balance	balance
Chromium	15.75	20	18-20
Nickel	16.90	0.04	8-10
Manganese	0.69	0.11	1.00
Nitrogen	-	-	0.1
Silicon	0.23	0.07	0.75
Molybdenum	1.00	-	-
Aluminium	3.25	4.44	-
Y_2O_3	-	0.40	-
TiO_2	-	0.61	-

Basic microstructural characterisation (SEM, optical microscopy)

GRAIN MICROSTRUCTURE:

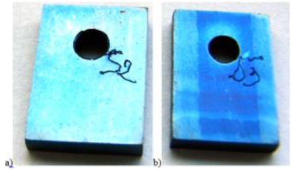


304L

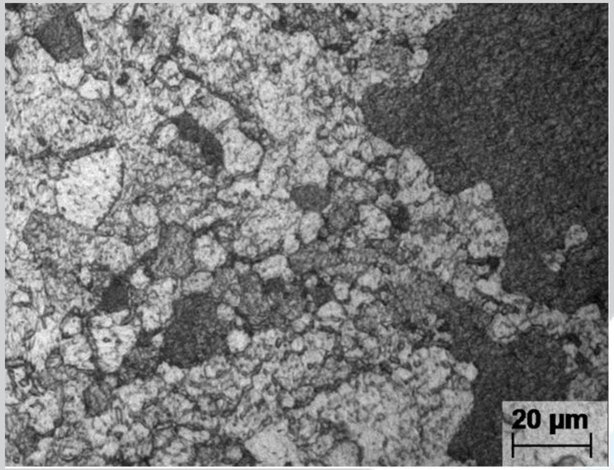


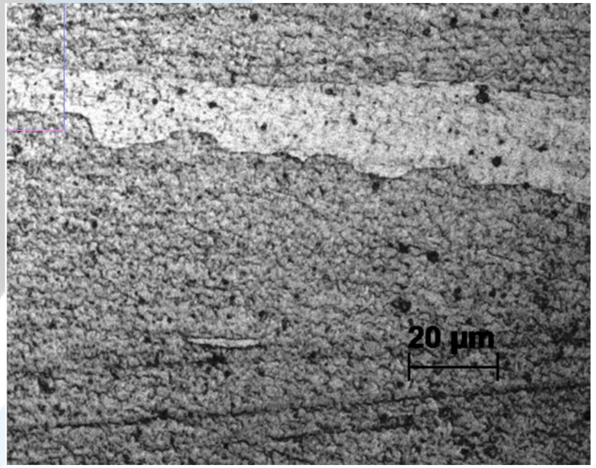
316 - Al

- 304L –austenite
- 316-Al - 3.2% aluminum – ferrite? phase, small grains, higher mechanical properties

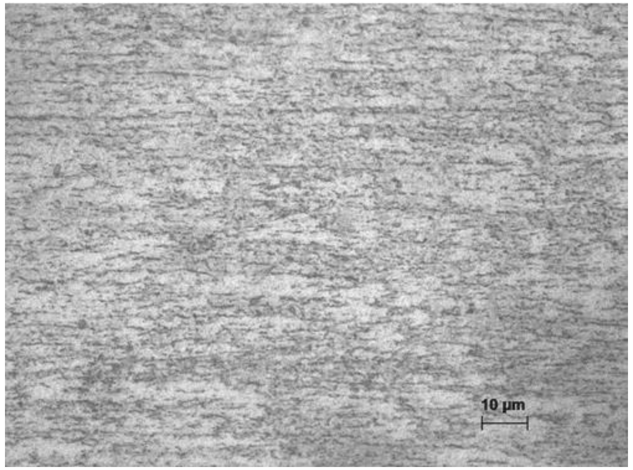


MA956 coupons - a) transverse b) longitudinal





a) MA956



b)

-MA956 - nonuniform structure can be seen, very large ferrite grains containing a fine structure are present, two grains sizes : smaller and larger grains, non-uniform distributed particles that promote grain boundaries in ODS steel and high mechanical properties

Coolant compatibility tests

Testing conditions:

- demineralised supercritical water
- temperature = 550°C
- pressure = 25 MPa
- pH = 6
- conductivity = 0.4 mS/cm².

Assessment methods:

Gravimetric Analysis

- Weight gain measurements

Oxide surface analysis

- SEM
- EDS

Cross-sectional oxide layers

- Backscattered electrons (BSE)

Supercritical Static Autoclave

GRAVIMETRIC ANALYSIS

Oxidation kinetics in static demineralized SCW

1. 304L

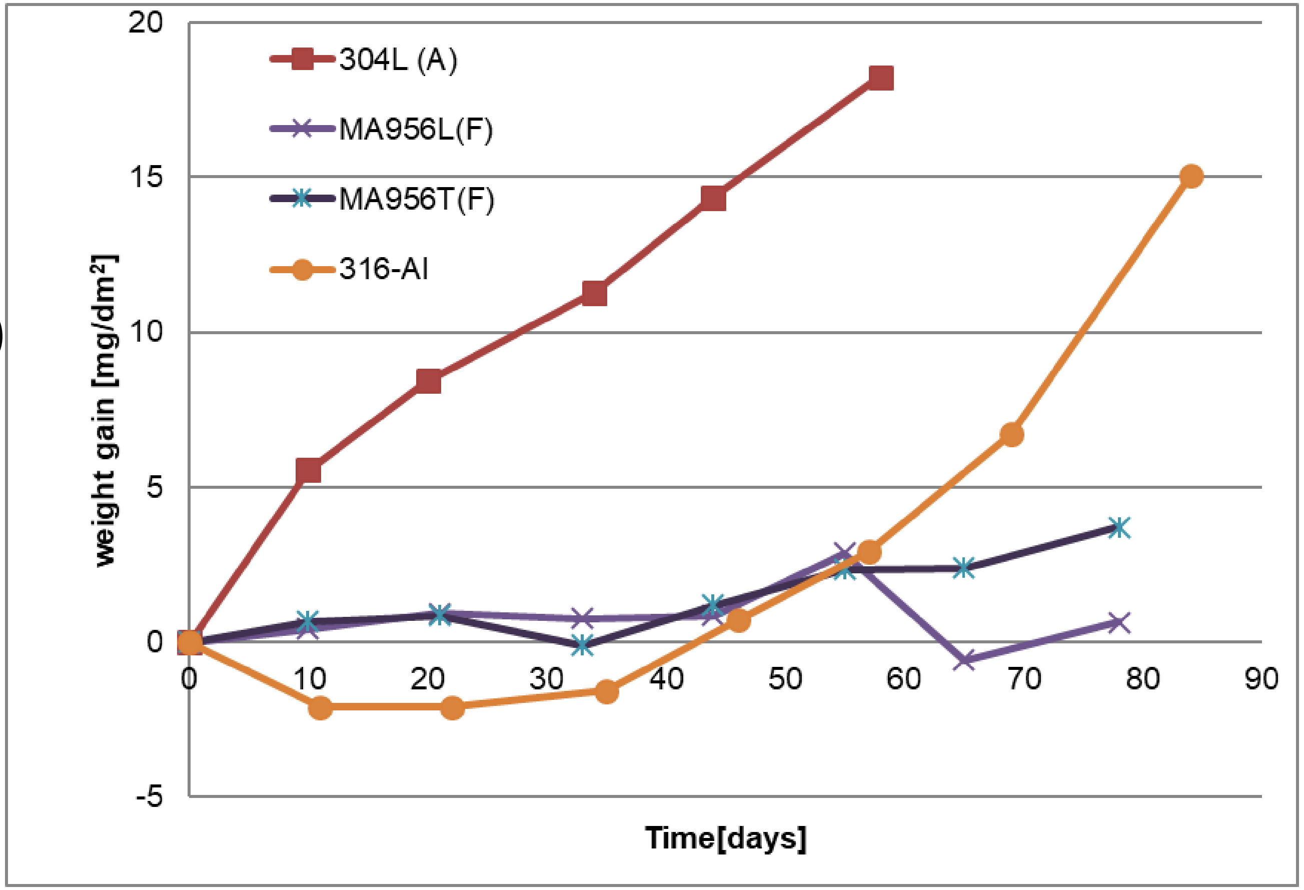
- weight gain - oxidation

2. 316- Al

- weight loss up to ~ 40 days (dissolution)
- weight gain after ~ 40 days (oxidation)

3. MA956

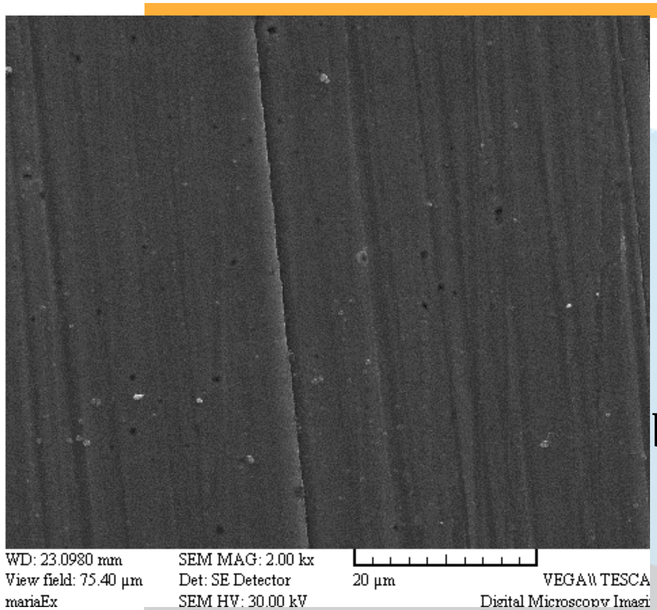
- dissolution with oxidation alternating up to 80 exposure days or
- Oxidation with small weight gain up to 80 exposure days – maybe thin oxide was developed;

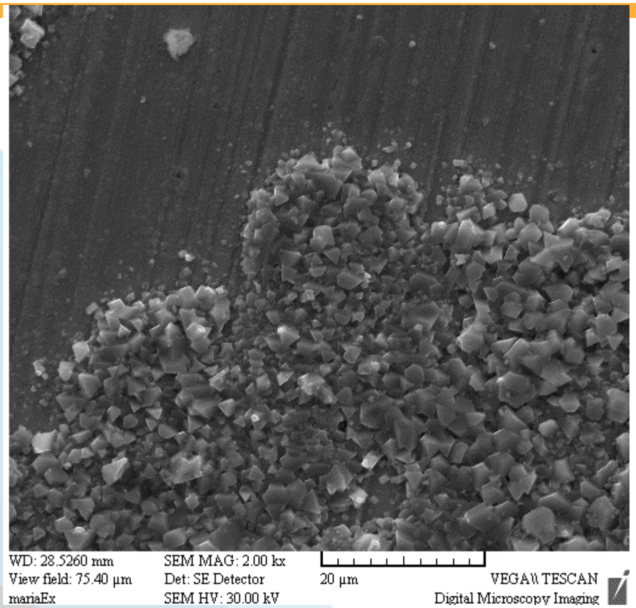


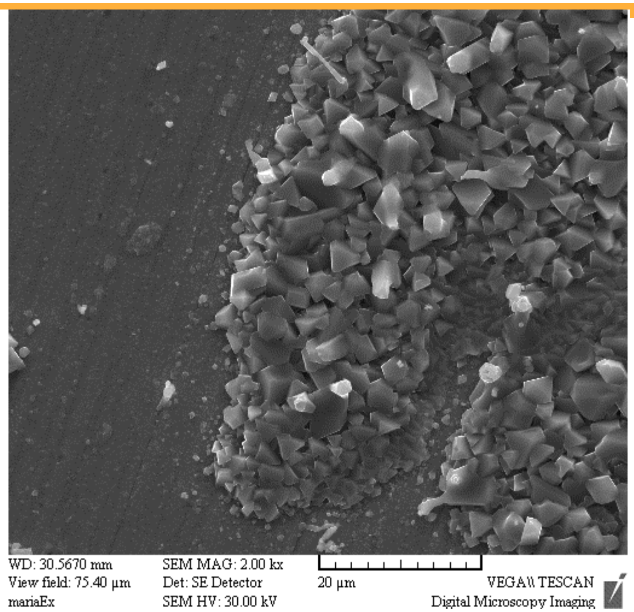
Comparative oxidation kinetics in SCW (550°C, 25MPa) of MA956 alloy, 304L, 316-Al

RATEN ICN PITEŞTI
INSTITUTUL DE CERCETĂRI NUCLEARE

OXIDE MORPHOLOGY MA956

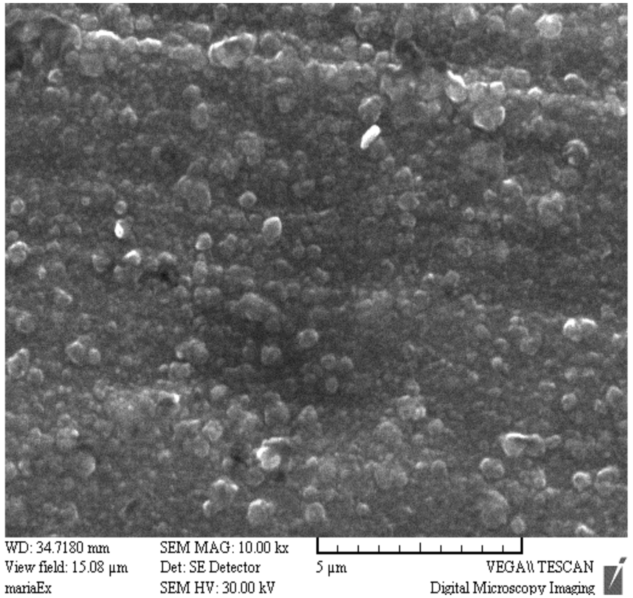
a)


b)


c)


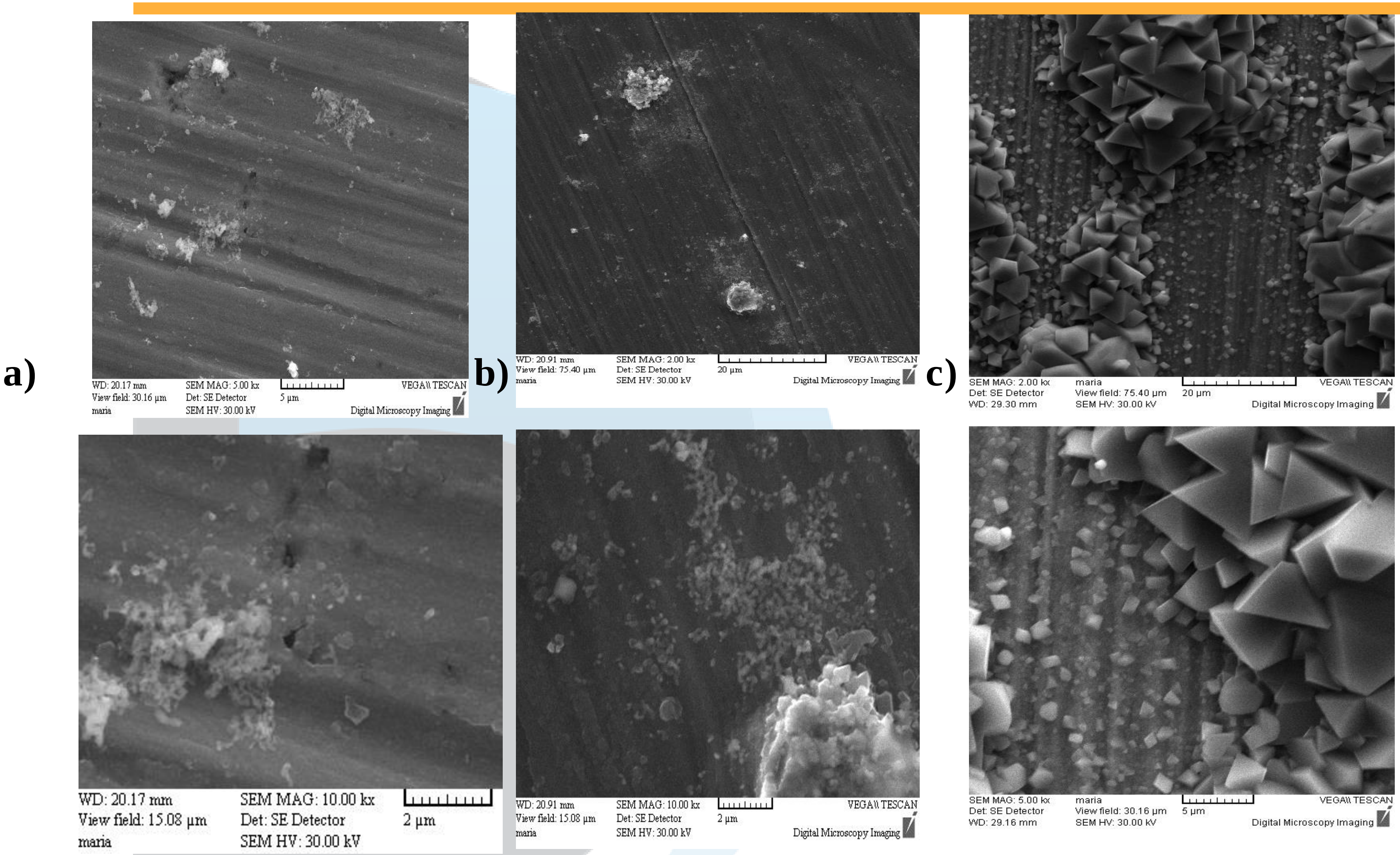
Aspects of oxides on MA956 after
a) 10 days,
b) 33 days
c) 54 exposure days

- two oxide layers: one inner with small crystallites and an external layer composed from large crystallites;
- inner oxide contains small pores or pits, but a detail image displays a compact and dense aspect.
- outer oxide layer contains groups of larger crystallites with sharp edges and porous oxide morphology, up to 2 microns in diameter, and the crystallites sizes become larger in time and also the covered surface extents with exposure time.



Aspects of inner oxide layer

OXIDE MORPHOLOGY 316-AI

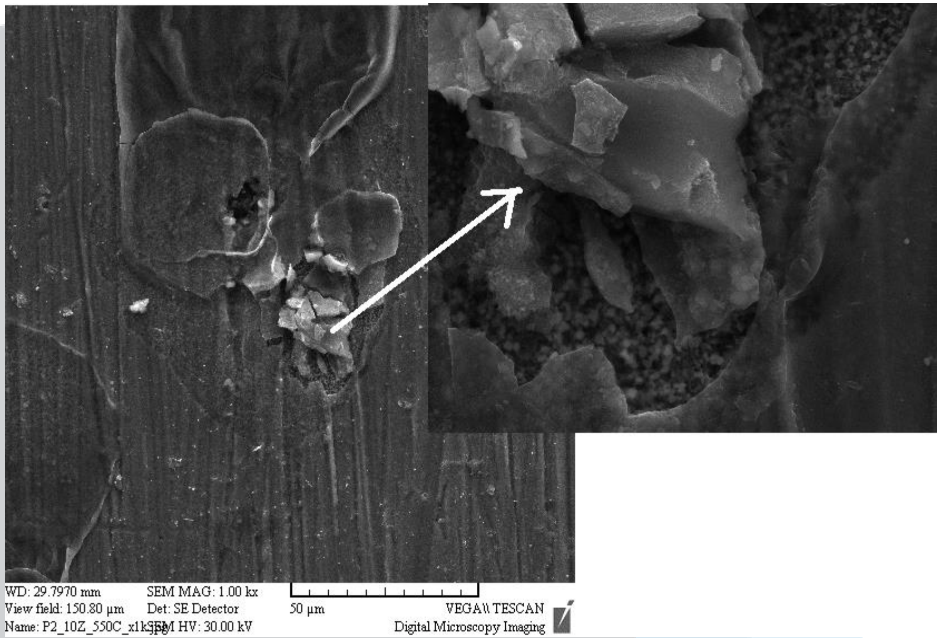


Aspects of oxides after a) 10 , b) 39, c) 84 exposure days

- two oxide layers: inner layer with small crystallites (pores and cracks) and external layer composed from fine crystallites (39 days);
- outer oxide layer contains large crystals after 84 exposure days, and the crystallites sizes become larger in time.

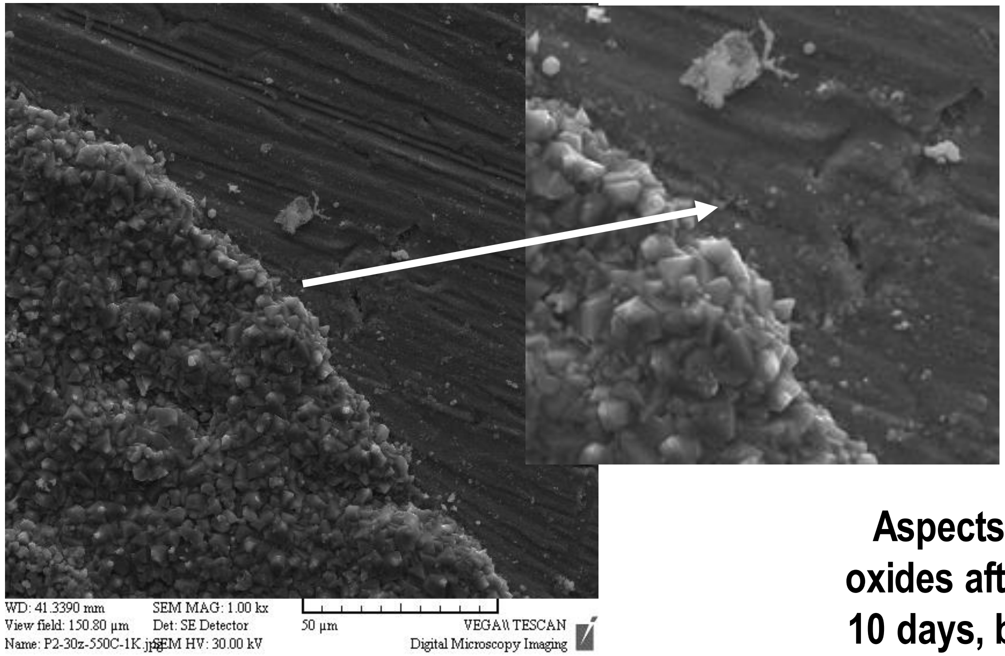
OXIDE MORPHOLOGY 304L SS

a)



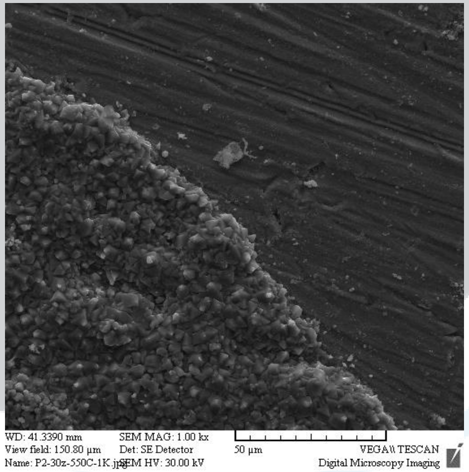
oxide islands containing broken amorphous oxides under which there are visible smaller oxide crystallites

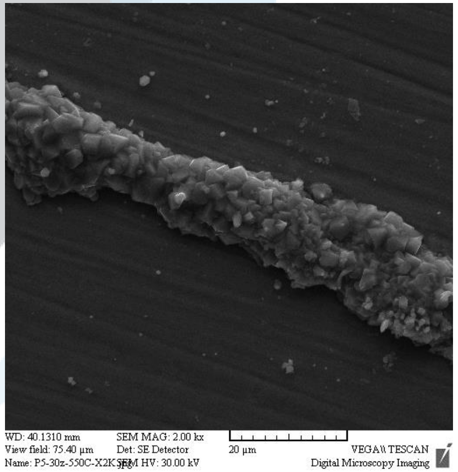
b)

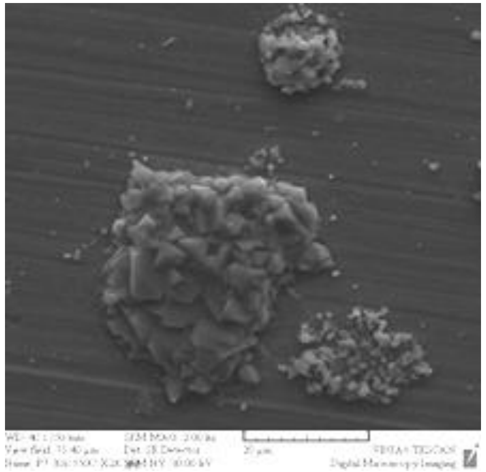


the surfaces are not entirely covered by oxide crystallites

Aspects of oxides after a) 10 days, b) 33 days

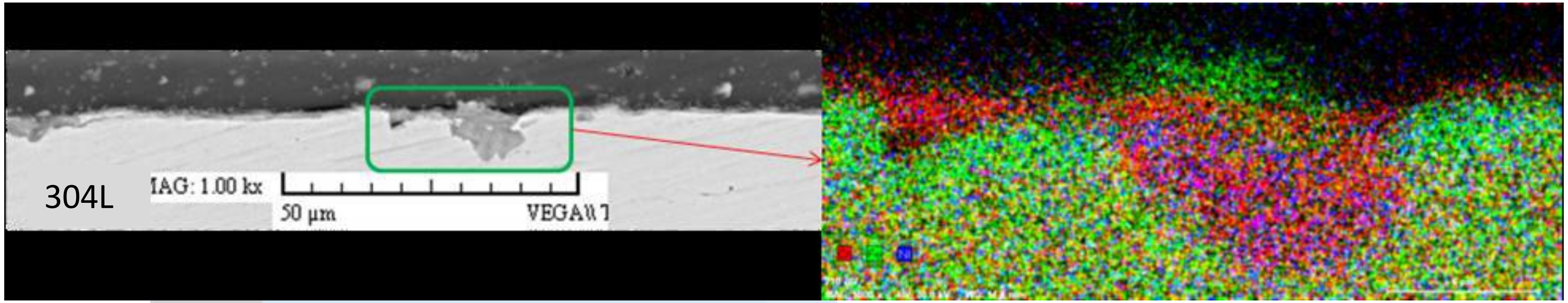


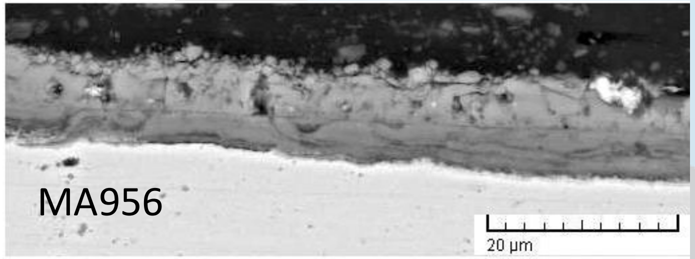


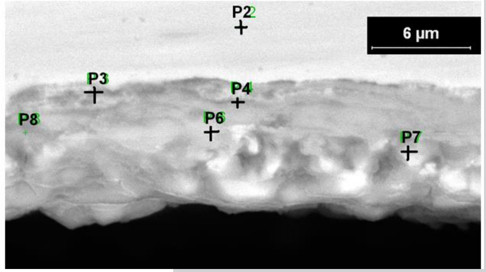


Aspects of oxides 33 days are dependent on surface preparation unpolished, #600 (rows) and #1200 (cauliflower islands)

OXIDE STRUCTURE (BSEI,EDS)





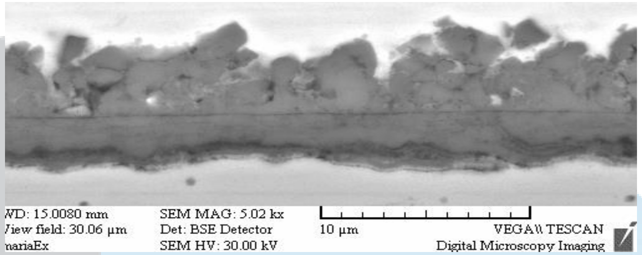


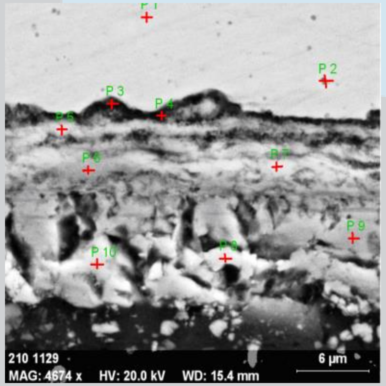
	Fe	Cr	Al	Mn	Ti	O	Cu	Si	C
P 2	72.8	19.8	4.6	0.9	-	-	1.3	-	0.7
P 3	44.1	30.2	9.3	0.8	0.7	13.0	1.3	-	-
P 4	29.6	39.9	7.2	1.0	0.4	18.4	1.8	0.7	1
P 6	36.0	37.1	3.7	1.1	0.5	17.4	2.5	-	0.7
P 7	68.3	3.8	1.5	0.5	-	16.1	7.2	-	0.8
P 8	33.0	40.9	4.5	1.5	0.9	9.6	4.6	0.3	0.8

The 304L steel displays an undesired internal oxidation [4], very dangerous for structural components.

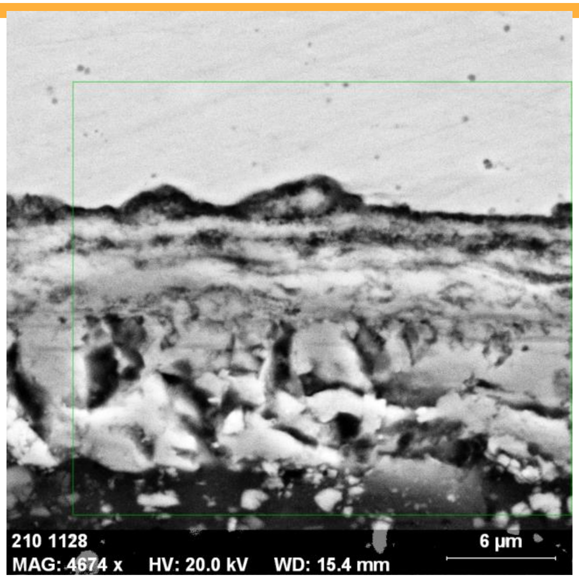
On MA956, EDS microanalysis confirmed the presence at metal – oxide interface of (Fe, Cr , Al) oxide layer (P3, P6 and P7) that protects the surface

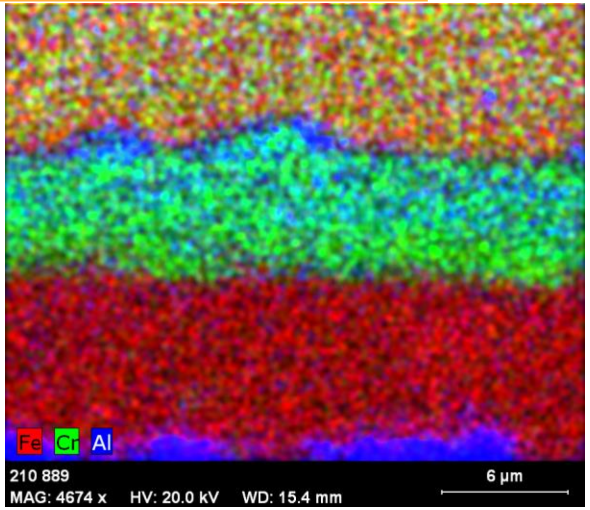
OXIDE STRUCTURE (BSEI,EDS) – MA956





Spectrum	O	Al	Cr	Mn	Fe
P 1	-	4.88	21.31	0.89	72.91
P 2	-	18.63	17.78	0.84	62.74
P 3	17.64	24.21	18.41	0.95	28.11
P4	23.89	20.51	26.54	0.41	46.57
P5	27.56	7.16	47.67	1.29	16.85
P6	26.56	4.37	44.88	1.16	23.02
P 7	29.51	5.18	46.49	0.99	17.83
P 8	20.95	1.53	1.04	0.76	75.72
P9	24.65	1.45	1.56	0.40	71.94
P 10	22.84	1.02	1.35	0.75	74.05

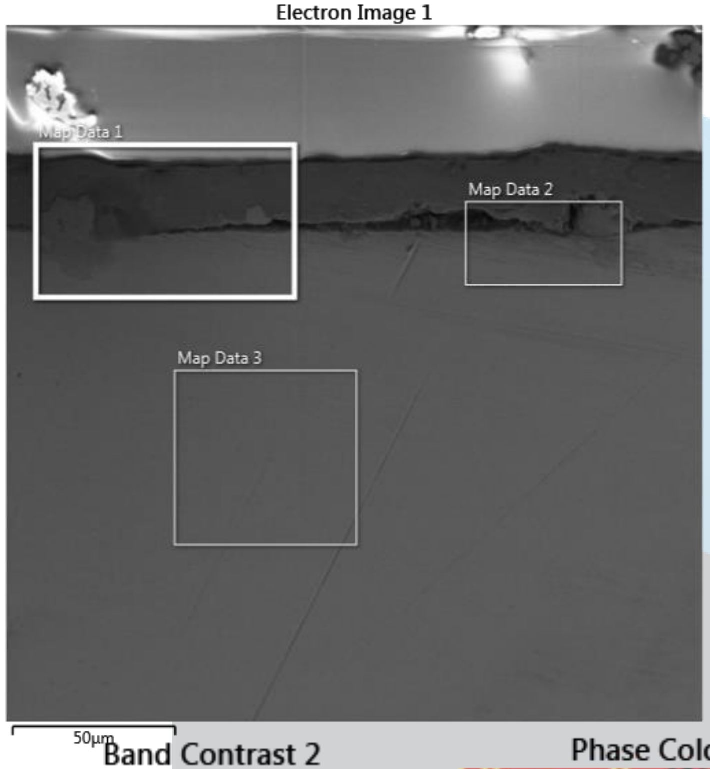


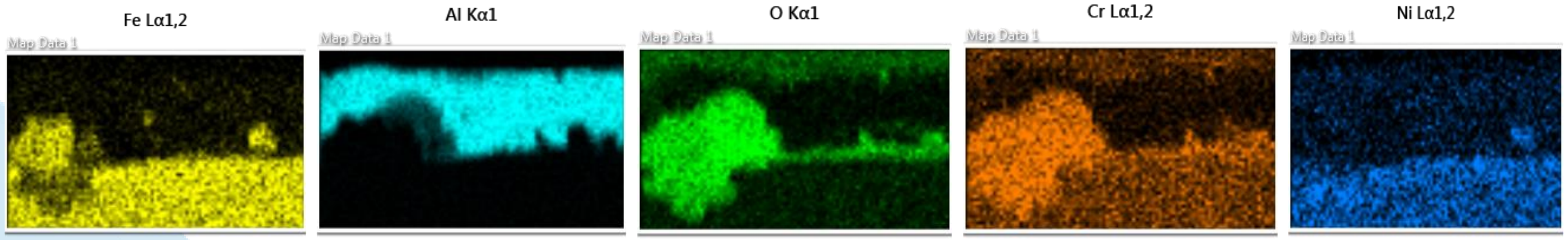


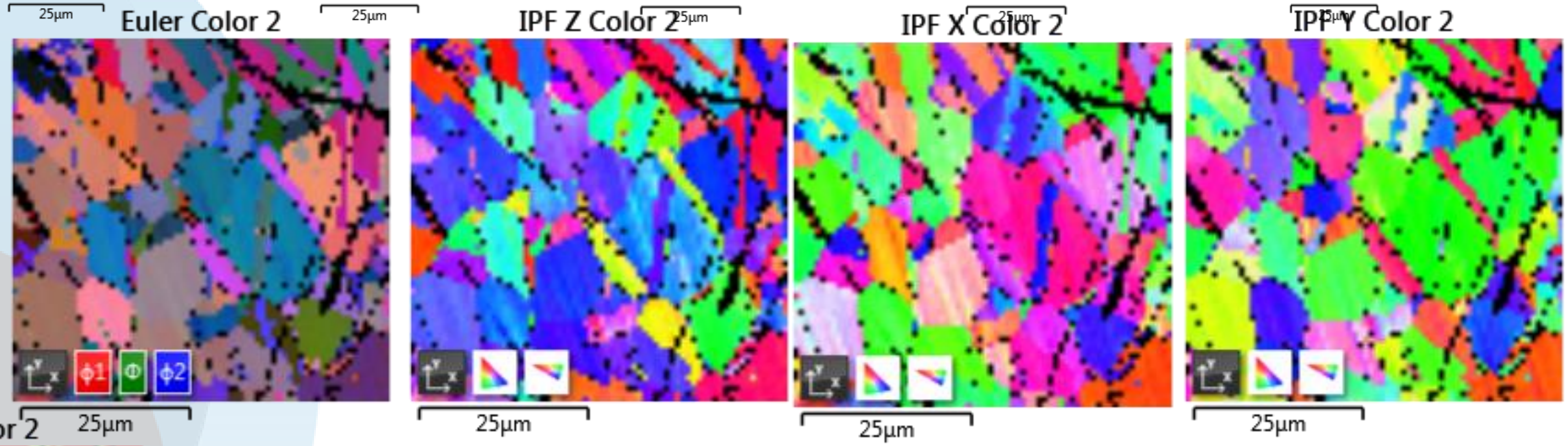
EDS microanalyses confirms the presence of aluminium enriched oxide (20-25% Al) at the metal-oxide interface, the next layer with a high content of chromium (45% Cr, 25% Fe and 30% O) and composition of external layer: 70-75% Fe, 20-25% O - magnetite.

78 exp. days: an aluminium enriched layer at the interface metal-oxide; external layer preponderantly by iron oxides and under iron oxide layer - a layer composed from chromium oxide containing aluminium enriched surfaces

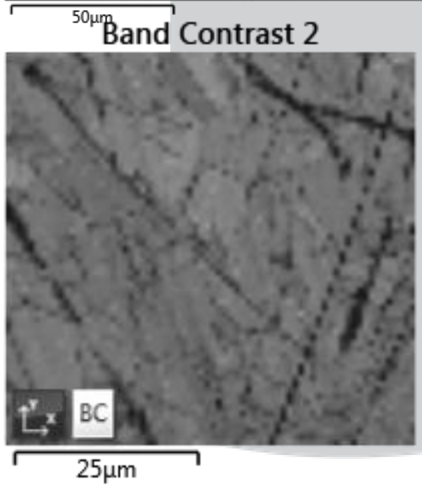
OXIDE STRUCTURE (BSEI, EDS, EBSD) – 316 Al

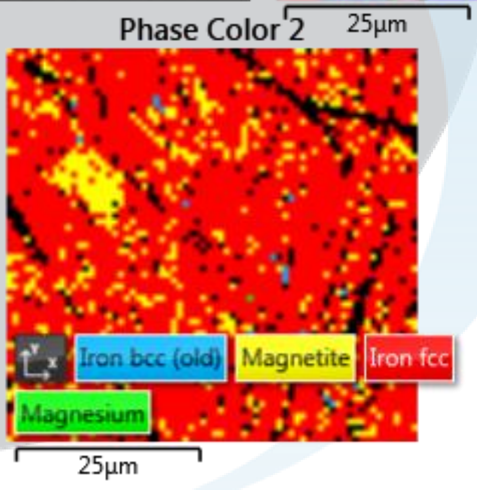






EBSD - Euler (COM) și Miller maps directions OxOy; OxOz; OyOz, (Map data 3), 84 exp. days





SE image, EBSD crystallographic phases (Map data 3), 84 exp. days

EDS:

- External Aluminium layer (3-25 microns)
- Fe-Cr-O layer
- Enriched Nickel layer

EBSD:

- inside grains, at grain boundaries precipitates (compounds magnetite like – yellow)
- Ferrite presence in matrix (red)

Conclusions

1. On 304L stainless steel the oxides grow slower, at the end of experiments after 56 days, only few islands interconnected could be visualized. The oxide layer seems to be a thin and apparently protective chromium oxide film, but also internal oxidation zones are present in, as packages on surface. When the chromium oxide layer is broken, the iron exit through the surface and forms the oxides on the surface. The iron migration creates an nickel enriched zone that oxidizes.
2. On 316-Al, a double layer are formed on surface: an external Aluminum layer (3-25 microns – 80 days), internal Fe-Cr-O layer, the substrate become Nickel enriched. Aluminum presence in 316 Al produces ferrite crystallographic phase of matrix
3. MA956 could lose in weight in the first stage of exposure followed by a weight gain, the threshold being at 40 exposure days. On MA956 a duplex oxide is formed on surface: an compact inner oxide with atomic contrast lines placed parallel with metal-oxide interface (2-3 microns – 80 days) found as chromium oxide containing aluminium enriched surfaces - and an outer porous layer – iron oxide - containing small pores and cracks at surface (5-6 microns – 80 days).
4. The corrosion kinetics are different: 304L manifests oxidation with weight gain but undesirable internal oxidation zones, 316 Al manifests dissolution with weight loss up to 40 days followed by oxidation for longer exposure time, but aluminium oxide layer is desirable to protect the surface in GIV, and MA956 maintains a very small weight gain after 80 days of exposure.
5. The behaviour of materials depends on microstructure at surface (grain shapes and size, surface preparation, etc …)
6. The candidate materials may be improved at exposure in SCW by microstructure improvement, surface preparation, etc. and with small amount of some alloying elements additions or coatings, but have to be fully experimentally characterized in conditions as close possible to operation conditions.

RATEN ICN - INSTITUTE FOR NUCLEAR RESEARCH, Pitesti, ROMANIA