AKADEMIA GÓRNICZO-HUTNICZA
IM. STANISŁAWA STASZICA W KRAKOWIE
AGH UNIVERSITY OF SCIENCE
AND TECHNOLOGY

METHODS OF STUDYING SCALE MORPHOLOGY, CHEMICAL AND PHASE COMPOSITION

http://home.agh.edu.pl/~grzesik

Most often used methods to study scales

- visual observation with the naked eye (photographs, macrophotographs)
- microscopic observations:
  - optical microscopy
  - electron microscopy (SEM, TEM, HRTEM)
  - atomic force microscopy (AFM)
- X-ray diffraction (XRD)
  - low angle diffraction (XRR)
  - diffraction using a fixed incidence angle (GIXD)
- electron diffraction
  - backscattered electron diffraction (EBSD)
  - electron diffraction of a chosen region in TEM (SAED)
  - electron diffraction X-ray spectroscopy (EDXS)
- spectroscopic methods
  - infrared absorption spectroscopy
  - Raman spectroscopy
- mass spectrometry (SIMS, SNMS)
- X-ray photoelectron spectrometry (XPS)
- Auger electron spectrometry (AES)

Observations of the naked eye

A type of observation, where additional equipment is not used, e.g.: magnifier, microscope, etc.
In corrosion studies it is mostly used to initially determine the state of the surface of materials that undergo corrosion. For scientific-technical documentation of visual observation, photographs are used, specifically macrophotographs.

Fragment of a power plant boiler screen partially covered with a protective coating after a certain exploitation time

Valve steel sample oxidized in cyclic conditions

Types of microscopic observations in corrosion studies

- scale surface observations (at room temperature or at reaction temperature)
- observations of oxidized sample cross-sections (metallographic cross-sections or fractures)
- observations of the metallic core surface under the scale

Applications for surface observations

- nucleation process studies
- determining the scale growth mechanism
- investigating the influence of the substrate surface on the procedure of product growth in the initial reaction stages

Applications for cross-section observations

- Scale microstructure studies
- Investigations on the texture of the crystals constituting the scale

Applications for metallic core observations

- studies on internal oxidation processes
- analysis of precipitation formation on intergranular boundaries of the metallic substrate
- determining substrate degradation resulting from corrosion processes

Stages of sample preparation for microscopic observations

For scale surface observations:

- collecting samples
- in some cases, additional spraying of the sample surfaces with carbon or gold (for SEM observations)

For fracture observations:

- collecting samples
- breaking the samples, possibly after cooling it first in liquid nitrogen
- spraying carbon or gold on the sample surfaces

For cross-section observations:

- collecting samples
- mounting samples in resin
- grinding, polishing and sometimes sample etching
- spraying carbon or gold on the sample surfaces

For metallic core/internal surface of the scale:

- collecting samples
- detaching the scale from the metallic sample, e.g. using adhesive tape
- spraying carbon or gold on the sample surfaces

Metallographic cross-section preparation

Collecting samples – samples are collected from locations, at which the presence of corrosion effects are assumed (corrosion products, cracks, damages, etc.). It is important to ensure that the sample does not overheat, because this could change the local structure of the material. The optimal frontal area of a sample is 1-4 cm^2.

Mounting in resin – samples are submerged in thermosetting or chemically hardened resin (in the case of fragile materials or those that can be overheated).

Grinding and polishing – grinding is carried out on cooled grinding discs (sandpapers). As the grain gradation changes from larger to smaller the grinding direction must be changed by 90°. In order to obtain a surface with mirror shine, the sample is mechanically and then sometimes electrolytically polished. Mechanical polishing is performed with the help of rotating discs covered with felt dampened by a slurry of polishing compounds (e.g. aluminum oxide or diamond).

Etching – this is used to reveal the structure of materials, grain boundaries, etc. It can be carried out chemically or electrolytically. In this process, the differences in the dissolution of individual phases or their coloration as a result of oxidation.

Microscopic material studies

Data obtained from microscopic observations, without which it would would be impossible to prepare a complete description of the oxide scale formation mechanism on metals:

- morphological build of oxidation products
- texture
- size and shape of the crystals
- porosity

Optical microscopy

Microscope – an apparatus used to observe small objects, usually invisible to the naked eye. **Optical microscope** – a type of microscope that uses light traveling through the optical system consisting of a set of a few to several dozen optical lenses.

Build of an optical microscope:

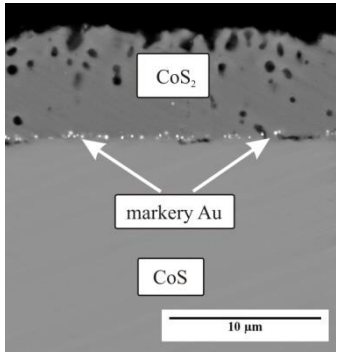
1. Eyeglass;
2. Revolver;
3. Object-lens;
4. Macrometric screw;
5. Micrometric screw;
6. Small table;
7. Light source;
8. Condenser;
9. Arm of the microscopy

Scanning electron microscope (SEM)

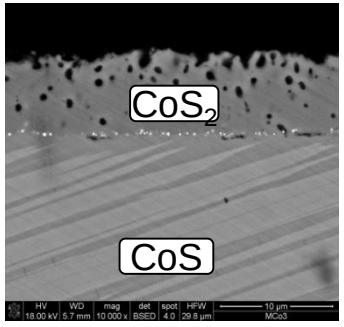
A type of electron microscope that allows for topography observations of a studied material in a nanometric to micrometric scale. The initial beam in this microscope is an electron beam.

SEM – examples of techniques

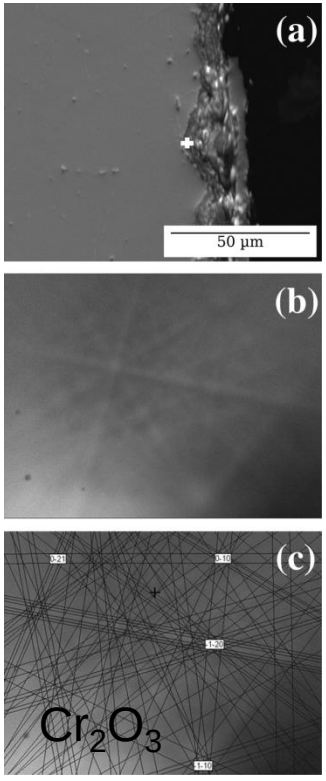
SEI



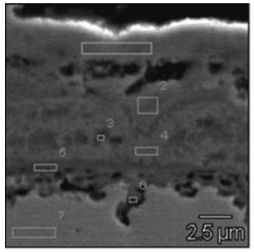
BSE



EBSD

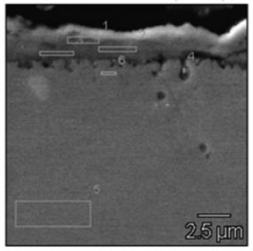


EDS



X2CrNiMo17-12-2

	Si-K	Cr-K	Mn-K	Fe-K	Ni-K	Mo-L
pt1	2.9	18.9	1.1	64.5	11.8	0.8
pt2	2.9	33.1	1.9	40.6	19.4	2.2
pt3	2.7	38.3	2.3	41.9	12.7	2.1
pt4	2.2	31.5	2.3	33.3	28.6	2.0
pt5	2.9	59.3	1.0	31.7	3.2	1.8
pt6	5.4	41.7	3.1	34.8	13.4	1.6
pt7	1.1	18.8	1.6	67.0	10.4	1.0



Super 304H

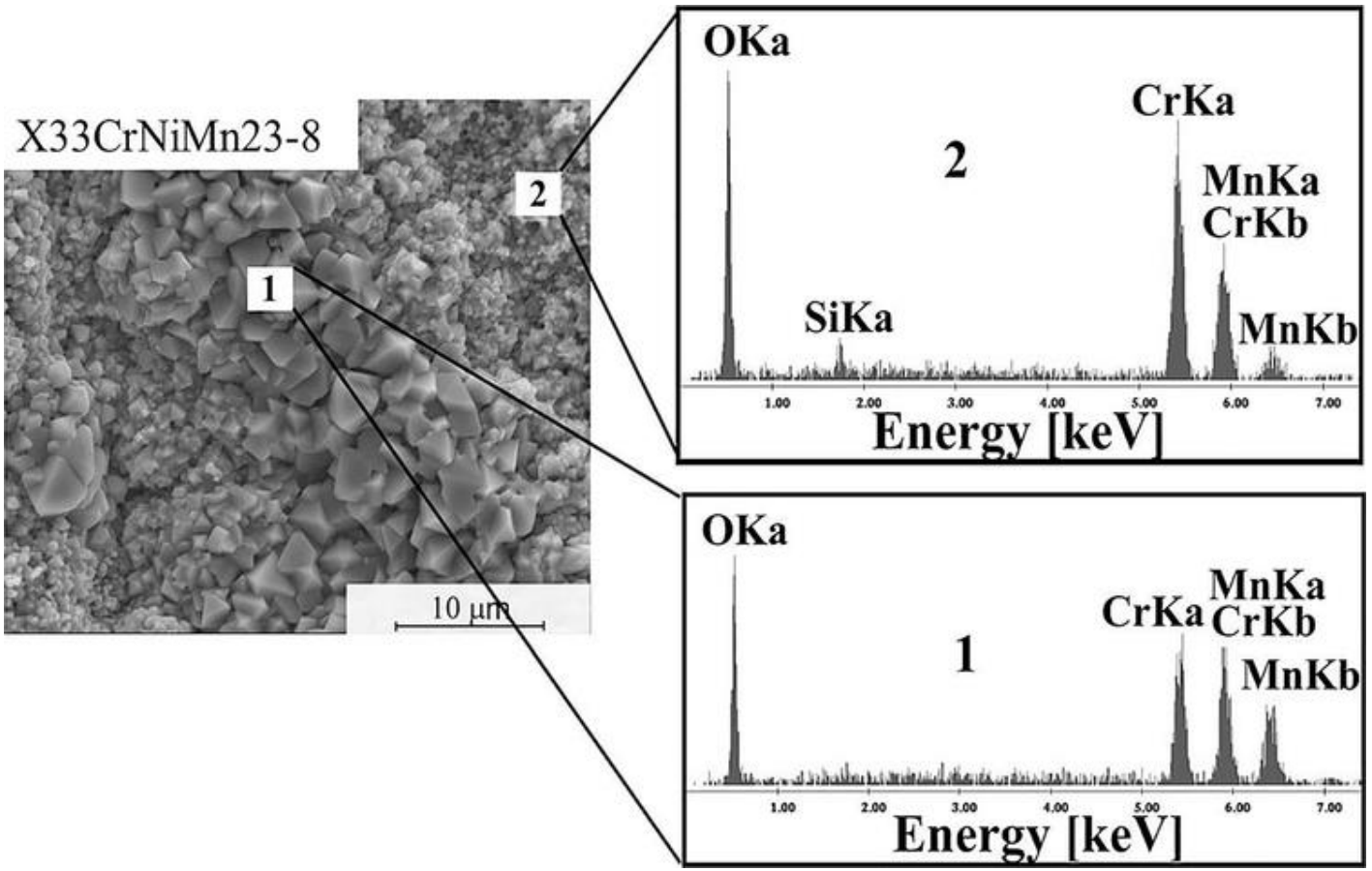
	Si-K	S-K	Cr-K	Mn-K	Fe-K	Ni-K	Cu-K
pt1	4.8		37.9	2.9	54.3		
pt2	3.1		72.7	4.3	20.0		
pt3	1.5	0.4	72.4	2.5	23.1		
pt4	3.6		15.2	0.5	69.5	9.4	1.7
pt5	0.8		20.1	0.7	68.4	7.9	2.1
pt6	0.9	0.4	14.3		70.6	10.4	3.4

B. Kościelniak, G. Smoła, Z. Grzesik, A. Hernas, High Temperature Materials and Processes, 37(4), 341-350 (2018)

Z. Grzesik, G. Smola, Ochrona przed Korozją, 57, 147-149 (2014)

EDS – examples of techniques

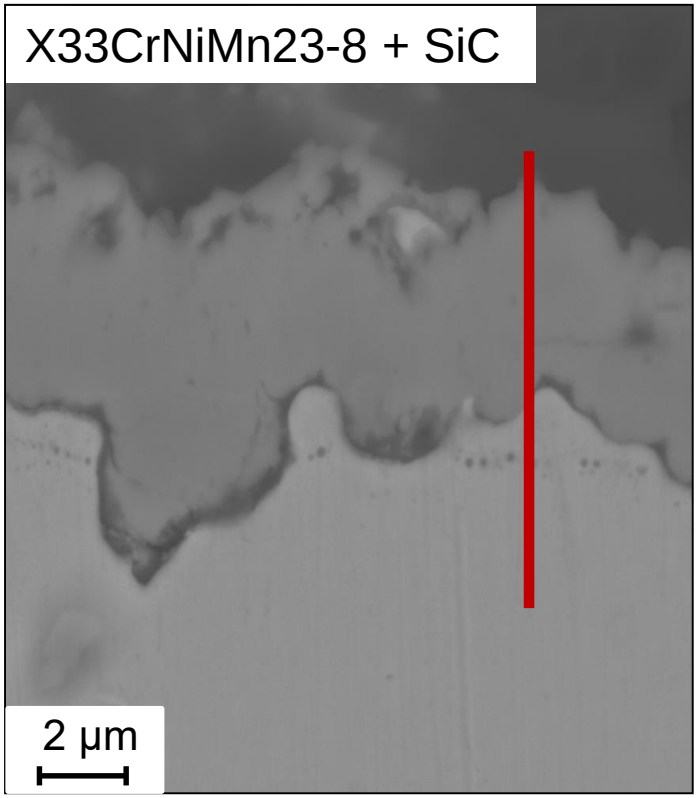
SEM microphotograph of the surface of a scale grown on X33CrNiMn23-8 steel covered with a SiC coating after 100-hr oxidation at 1173 K in air and EDS point analysis

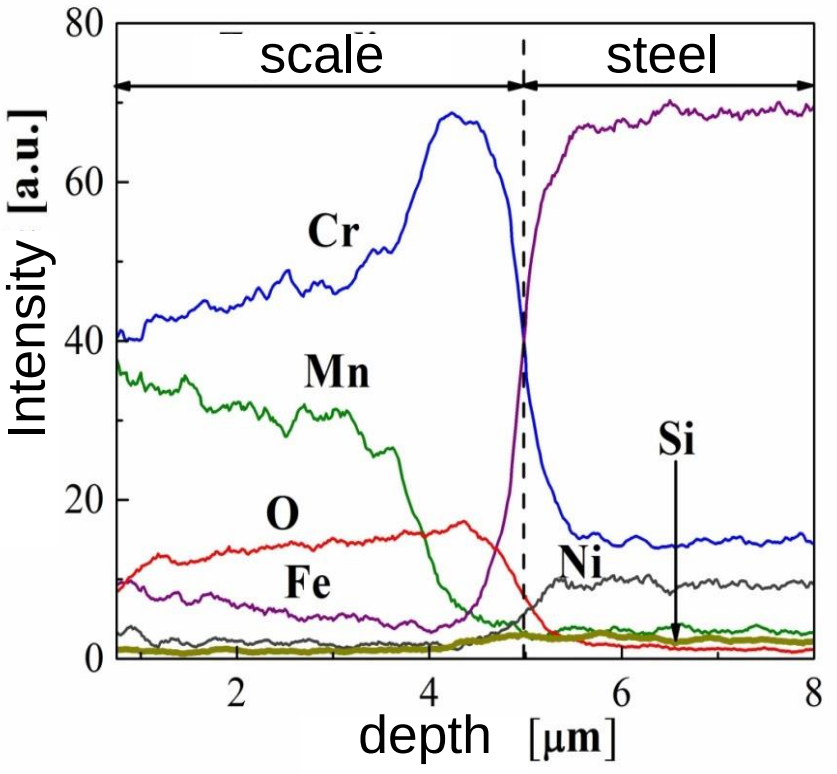


R. Gawel, K. Kyziol, Z. Jurasz, Z. Grzesik, Corrosion Science, 145, 16-25 (2018)

EDS – examples of techniques

SEM microphotograph of the cross-section of X33CrNiMn23-8 steel covered with a SiC coating after 100-hr oxidation at 1173 K in air and EDS line scan of element distribution

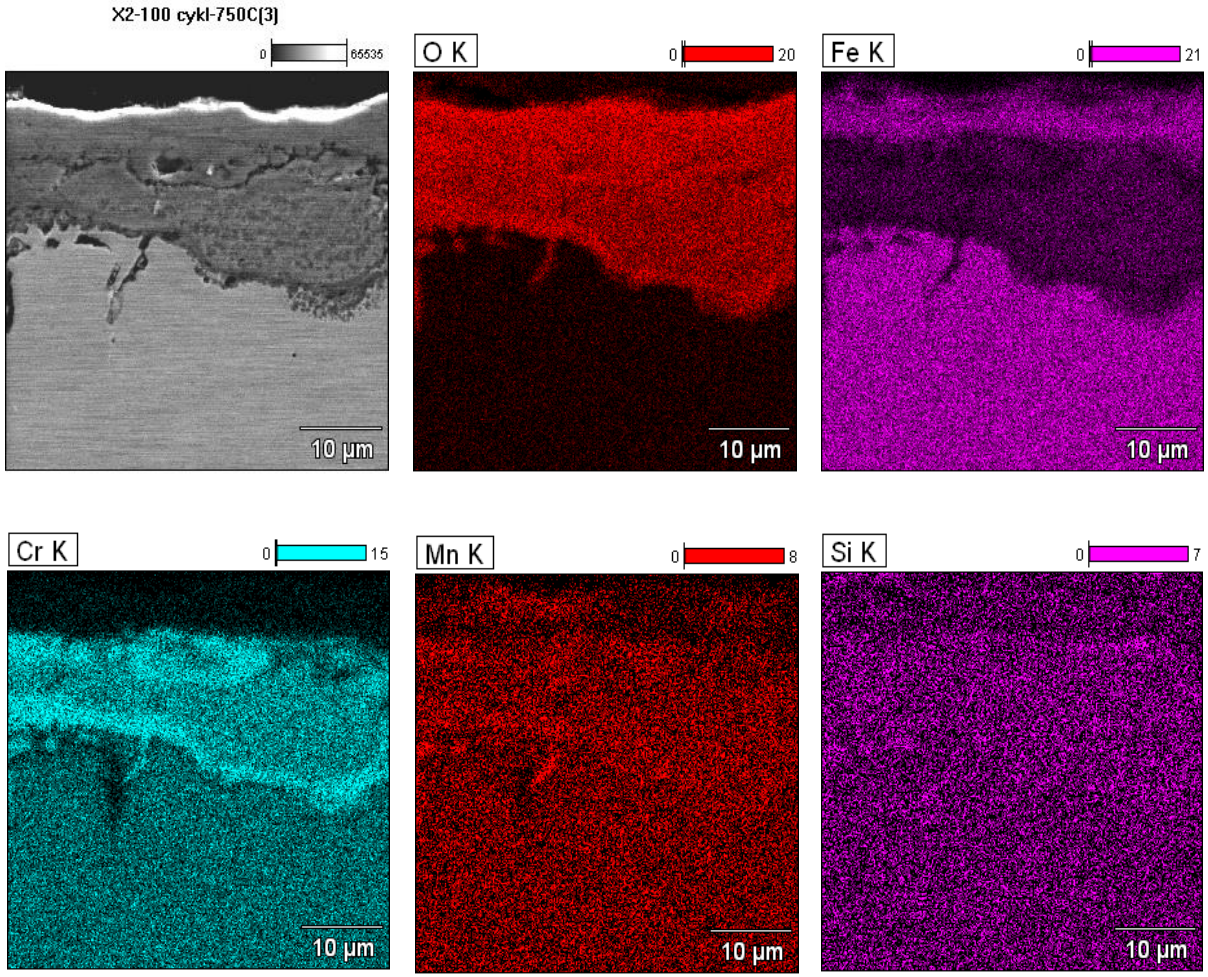




R. Gawel, K. Kyziol, Z. Jurasz, Z. Grzesik, Corrosion Science, 145, 16-25 (2018)

EDS – examples of techniques

EDS map of element distribution on the cross-section of X2CrNiMo17-12-2 steel cyclically oxidized for 200 h in O_2-50%H_2O atmosphere at 750°C



X-ray diffraction (XRD)

The XRD technique provides information about the crystal structure and phase composition of studied materials using the diffraction of X-ray waves phenomenon on crystalline planes.

Advantages:

- non-destructive technique, uses small sizes of samples
- enables identification of the structure and phases inside the material
- enables quantitative determination of the concentration of phases in the material
- allows for determining the grain sizes and their orientation
- allows for measurements of stresses in the surface layers of crystals
- low-angle X-ray diffraction for analysis of thin layers

Disadvantages:

- it does not allow for determining chemical composition
- complex diffraction patterns obtained from multiphase materials make it difficult to identify each individual phase.

Transmission electron microscopy (TEM)

In the TEM technique electrons travelling through a thin (order of a few 100 nanometers) sample are registered.

Advantages:

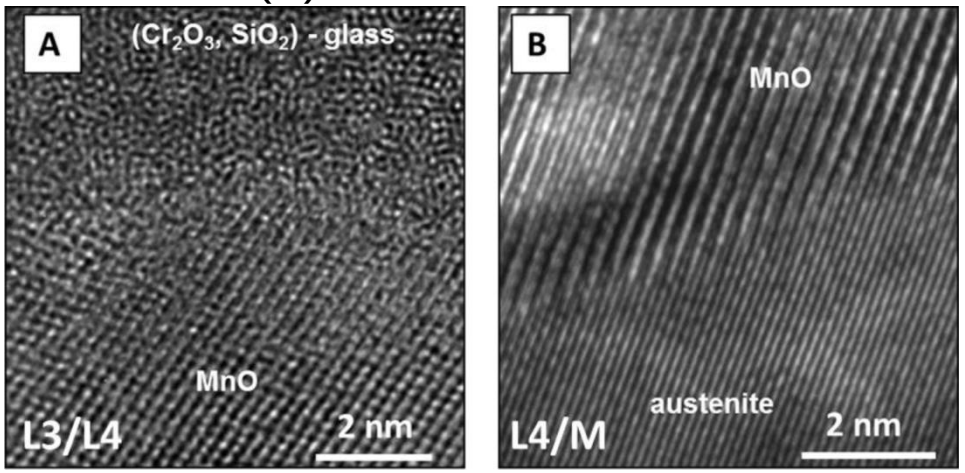
- analysis of grain/crystallite/particle size,
- analysis of material with defects, their placement and distribution of precipitation
- phase identification in microregions
- analysis of local orientation of microregions

Disadvantages:

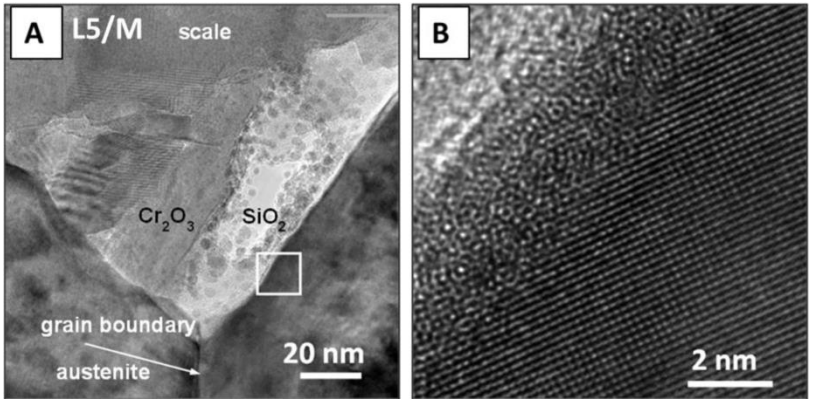
- difficulty in preparing samples

High resolution transmission electron microscopy (HRTEM)

HRTEM pictures of boundaries between (A) glass phase and MnO, and (B) MnO and austenite



TEM picture of oxide precipitates on the grain boundary of Sanicro 25 steel and HRTEM picture of the selected region



B. Rutkowski, Rutkowski, A. Gil, A. Czyrska-Filemonowicz , Corrosion Science 102 (2016) 373–383

Atomic force microscopy (AFM)

Atomic force microscope – a type of microscope with a scanning probe that enables obtaining a picture with a resolution the order of a single atom by using interatomic interaction forces.

Picture of Si surface
with (111) orientation

http://archiwum.wiz.pl/1999/99092500.asp

Auger electron spectroscopy (AES)

AES – a variant of electron spectroscopy consisting of analyzing the Auger electron energy distribution.

Advantages:

- enables obtaining information on elements present at the surface (it can analyze all elements except H and He)
- allows for determining the type of chemical bonds
- enables calculation of element concentrations
- possibility of point measurements.
- possibility of obtaining maps of element and chemical compound surface distribution.

Disadvantages:

- presence of thermal effects
- very high background level in the pattern

Mass spectrometry (MS)

MS – a technique based on measuring the ratio of mass to electrical charge of a given ion.

Capabilities:

- identification of chemical compounds and their mixtures,
- determination of chemical compound structures,
- determination of chemical (element) composition,
- determination of the isotope composition of analyzed substances,
- determination of the composition of complex mixtures of compounds with large molar masses.

Secondary ion mass spectrometry (SIMS)

- This is a method of studying **surfaces of solids** placed in a vacuum, which interact with a primary ion beam.
- Due to the interaction between ions from the primary beam and atoms from the studied material, atomization of the sample takes place (destructive method).
- Due to the atomization of the sample, electrons, atoms, groups of atoms (clusters), positive and negative ions, and clusters with a charge are emitted.
- The *SIMS* method consists of gathering and analysis using a secondary ion mass spectrometer that provides information on the composition of the investigated material.

As a result of these studies 3 type of data can be obtained:

a) **Mass spectrum** – isotope composition
b) **Profile analysis** – isotope distribution in relation to depth
c) **Surface picture analysis** – isotope surface distribution

X-ray photoelectron spectrometry (XPS)

XPS – a variant of electron spectroscopy consisting of analyzing the kinetic energy distribution of photoelectrons emitted as a result of exciting the sample with characteristic radiation in the range of soft Roentgen radiation.

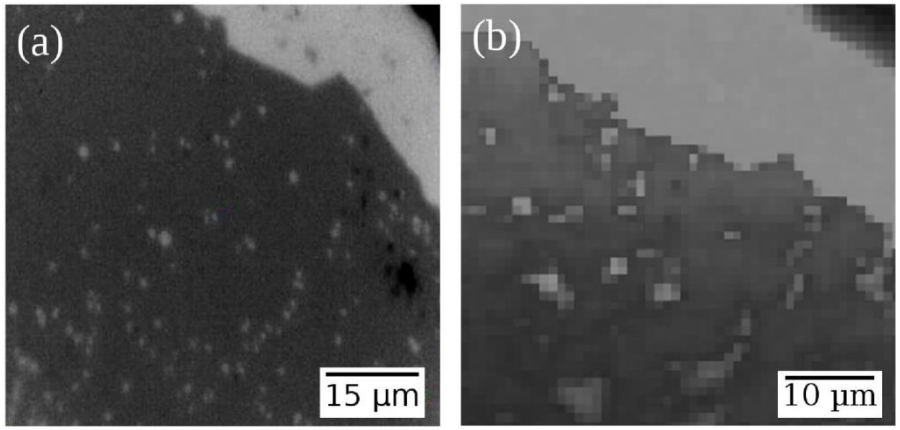
Advantages:

- enables detection of quantitative analysis of all elements with 0,1–1%at. sensitivity (with the exception of hydrogen)
- allows for determining the type of chemical bonds, which the elements at the surface exhibit
- Ion etching can be used to increase the measurement possibilities

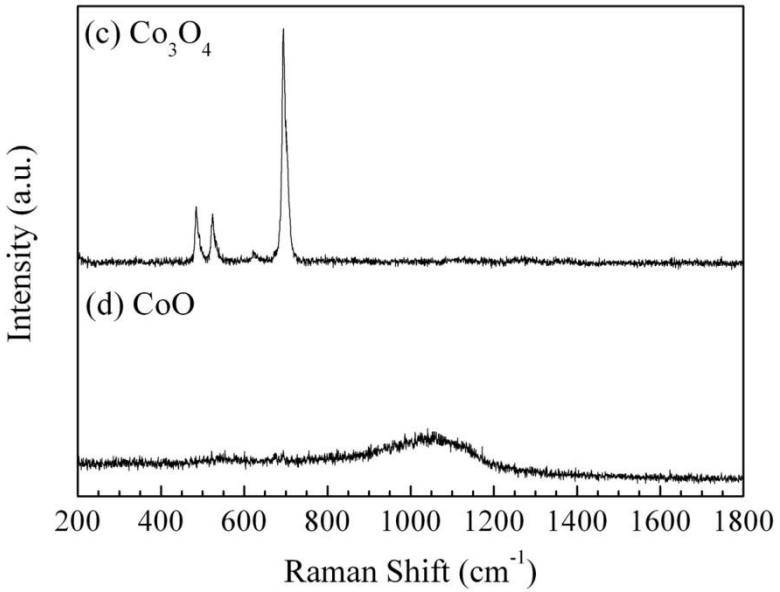
Disadvantages:

- presence of thermal effects
- A large surface is analyzed due to the difficulties in concentrating a X-ray beam and, as a consequence, an averaged result from a large surface is obtained.

Example of applying Raman spectroscopy to study CoO oxidation at 1173 K



Raman spectroscopy – a spectroscopy technique consisting of measuring non-elastic photon dispersion.

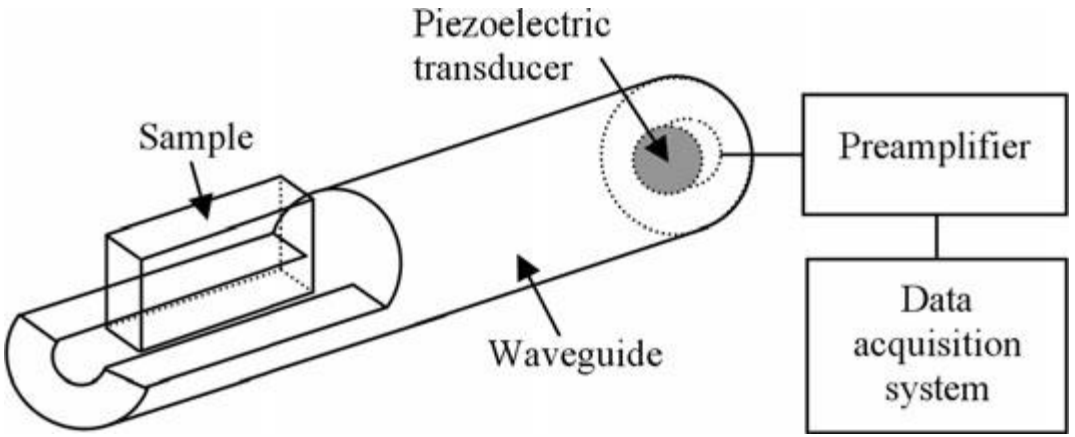


a) picture from an optical microscope;
b) Raman map of the analyzed region;
c) Raman spectrum obtained from the light region;
d) Raman spectrum obtained from the dark region

M. Żyła, G. Smoła, A. Knapik, J. Rysz, M. Sitarz, Z. Grzesik, Corrosion Science, 112, 536-541 (2016)

Analysis of the level of stresses in the scale using the acoustic emission method

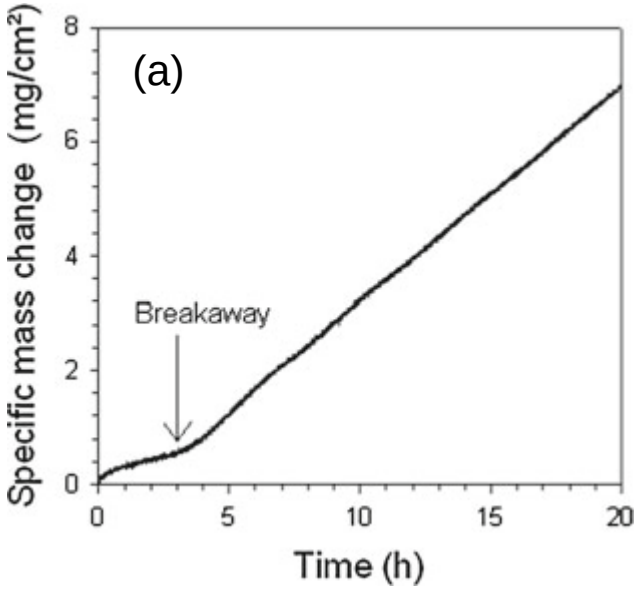
In the acoustic emission method acoustic wave intensity accompanying scale formation processes is measured.

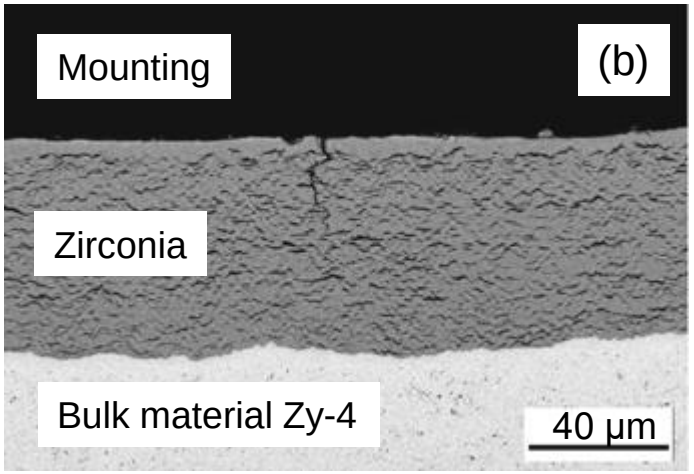


Schematic illustration of a typical apparatus for acoustic emission measurements.

V. Parry, M.T. Tran, Y. Wouters, Oxid Met 79 (2013) 279–288

Analysis of the level of stresses in the scale using the acoustic emission method

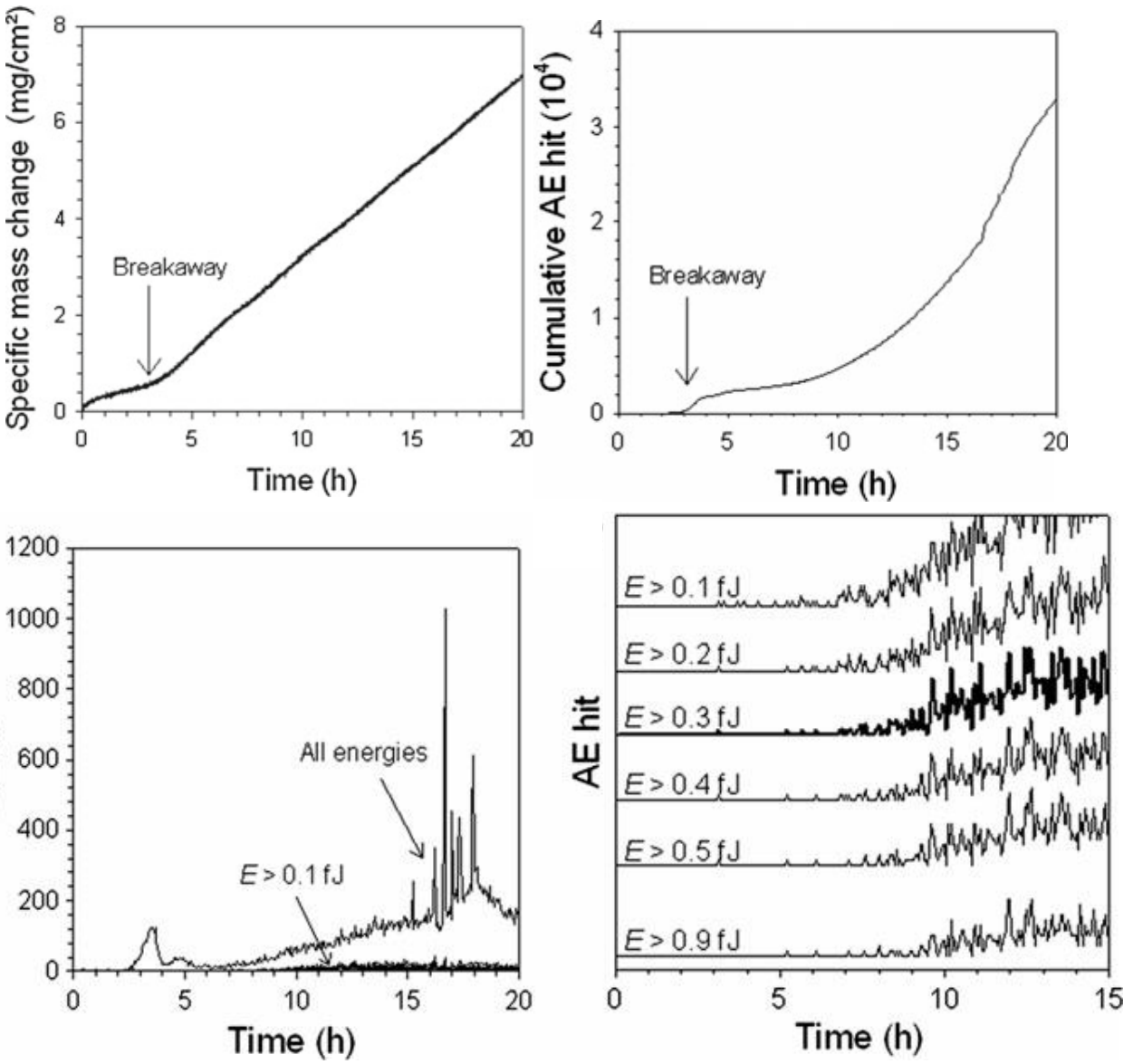




Oxidation kinetics (a) and SEM picture of Zr-4 cross-section after 20-hr oxidation at 700 ^{o}C in Ar/O_2 atmosphere, p(O_2) = 150 mbar (b)

V. Parry, M.T. Tran, Y. Wouters, Oxid Met 79 (2013) 279–288

Analysis of acoustic emission during Zr-4 alloy oxidation



V. Parry, M.T. Tran, Y. Wouters, Oxid Met 79 (2013) 279–288

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THE END