MASS TRANSPORT THROUGH A LAYER OF OXIDATION PRODUCTS
THE PROCESS OF THE SCALE FORMATION
TAMANN (1920)

\[
\frac{1}{2} X_2 + Me \rightarrow MeX
\]
THE SCHEME OF CLASSICAL PFEIL EXPERIMENT (1929)

Air

SiO$_2$

Fe

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Air

Scale

SiO$_2$

Fe
EXAMINATION OF PARTICULAR REACTANT CONTRIBUTIONS TO THE TRANSPORT PROCESS OF MATTER THROUGH THE SCALE

- The marker method
- The two-stage oxidation method
- The examination of self-diffusion coefficients
- The scratch method
- The pellet method
The location at which the following reaction takes place:

\[
\frac{1}{2} X_2 + Me \rightarrow MeX
\]
THE MARKER METHOD

Oxidant

Marker

Metal

The range of high temperatures

\[
\begin{align*}
\text{Me} &\quad 1-y \\
X &\quad 2 \\
\text{Me} &\quad \text{Marker}
\end{align*}
\]

\[
\begin{align*}
\text{Me} &\quad 1+y \\
X &\quad 2 \\
\text{Me} &\quad \text{Marker}
\end{align*}
\]

\[
\begin{align*}
\text{Me} &\quad 1\pm y \\
X &\quad 1\pm z \\
\text{Me} &\quad \text{Marker}
\end{align*}
\]
THE MARKER METHOD

Favourable conditions for correctly performing the marker experiment:

• The surface of examined metal or alloy is smooth
• The marker does not react with the metallic ground, oxidant or with substances which are compounds that constitute the scale
• Before beginning the oxidation process, contact between marker and surface of examined material is saved
• The formed scale is compact, single-phase and strictly adheres to the metallic core
• Oxidation time is selected so that the thickness of the scale will be at least one order of magnitude larger than the marker
THE MARKER METHOD

1. Oxidant
2. Oxidant
3. Oxidant
4. Oxidant

- Metal
- Scale

Marker
Cross-section of the sulfide scale formed on Co

\[ T = 700 \, ^\circ\text{C}, \quad p(S_2) = 10^{-2} \, \text{Pa} \]
Cross-section of the sulfide scale formed on Co

$T = 860 \, ^\circ\text{C}, \quad p(S_2) = 10^{-1} \, \text{Pa}$
RBS Spectra (^{4}\text{He} - 2 \text{ MeV}); Nb sample with Au marker

Before sulfidation

After sulfidation
The marker method – MoS$_2$

The marker in the form of evaporated Au islands on the surface of Al foil – correct experiment
The marker in the form of evaporated Au islands on the surface of Al foil – uncorrect experiment
The marker as the Pt paste – correct experiment
FORMATION MECHANISM OF A THREE-LAYERED SCALE IN THE AREA OF FLAT SURFACES

- External compact layer
- Intermediate porous layer
- Internal porous layer
- Metal

Diagram showing the formation mechanism with layers labeled as:
- External compact layer
- Intermediate porous layer
- Internal porous layer
- Metal

Chemical reaction:

\[ \text{Me}^+ + \text{e}^- + X_2 \rightarrow \text{Me} \]
DISSOCIATION CRACKS IN THE SULFIDE SCALE ON Cu-9%Zn, FORMED DURING A TWO-STAGE SULFIDATION PROCESS
CROSS SECTION OF THE SULFIDE SCALE GROWN ON COPPER, OBTAINED AT 444 °C

The compact layer of the scale

The porous layer of the scale

marker

Cu

Reaction time: 25 s

Reaction time: 9 min.
THE MARKER METHOD
Marker does not adhere to the metal core

A - A
THE MARKER METHOD
The wire as a marker is strongly wrapped around the metal
THE MARKER METHOD – OXIDATION OF OXIDE

X₂ diffusion

Me diffusion

Me and X₂ diffusion
The relationship between the external thickness and internal part of the oxide layer ($\text{Me}_c\text{X}_d$)

$$\frac{d \cdot a - b \cdot c}{b \cdot c}$$
THE MARKER METHOD

Oxidation from Cu$_2$O to CuO

\[ \text{Cu}^{+2} + 2e^- + \frac{1}{2}O_2 \rightarrow \text{CuO} \]

\[ \text{Cu}_2\text{O} \rightarrow \text{CuO} + \text{Cu}^{+2} + 2e^- \]
THE MARKER METHOD

Oxidation from Cu₂O to CuO

CuO

50 %

50 %

CuO

Au Markers

Cu₂O

Cu²⁺

e⁻

O₂

Cu₂O → CuO + Cu²⁺ + 2e⁻

Cu²⁺ + 2e⁻ + \( \frac{1}{2} \)O₂ → CuO
THE MARKER METHOD

Oxidation from CoO to Co$_3$O$_4$

\[ 4 \text{CoO} \rightarrow \text{Co}_3\text{O}_4 + \text{Co}^{+n} + n\text{e}^- \]

\[ \text{Co}^{+n} + n\text{e}^- + \frac{2}{3}\text{O}_2 \rightarrow \frac{1}{3}\text{Co}_3\text{O}_4 \]
THE TWO-STAGE OXIDATION METHOD

OUTWARD LATTICE DIFFUSION OF METAL

The ideal case
(lack of atoms X and *X mixing)

The real case
(atoms X and *X mixing)

C(*X) – concentration of the radioactive isotope of oxidant (tracer)
THE TWO-STAGE OXIDATION METHOD

INWARD DIFFUSION OF OXIDANT THROUGH GRAIN BOUNDARIES

The ideal case
(lacks of atoms X and *X mixing)

The real case
( atoms X and *X mixing)

C(*X) – concentration of the radioactive isotope of oxidant (tracer)
THE TWO-STAGE OXIDATION METHOD

SIMULTANEOUS DIFFUSION OF BOTH REACTANTS

Slow mixing of atoms X and *X

Fast mixing of atoms X and *X

C(*X) – concentration of the radioactive isotope of oxidant (tracer)
The concentration profile of Cu, O\(^{16}\) and O\(^{18}\) inside the sample, formed during oxidation of Cu\(_2\)O at 1273 K under oxygen pressure 10\(^5\) Pa.
Tracer concentration in the MeX compound, deposited onto its surface - lattice diffusion

\[ c = \frac{c_0}{2 \sqrt{\pi D t}} \exp \left( -\frac{x^2}{4 D t} \right) \]

\[ \ln c = \ln \left( \frac{c_0}{2 \sqrt{\pi D t}} \right) - \frac{x^2}{4 D t} \]

c – tracer concentration at distance \( x \) from crystal surface,
c_0 – tracer concentration on the surface before beginning of heating,
t – heating time
D – tracer diffusion coefficient
EXAMINATION OF TRACER DIFFUSION COEFFICIENTS

Tracer concentration in the MeX compound, deposited onto its surface - grain boundary diffusion

\[ \ln c = - \left( \frac{2 \left( \frac{D_v}{D_g} \right) \sqrt{d}}{\sqrt{\pi} D_v t} \right) \cdot x + \text{const} \]

- \( c \) – tracer concentration at distance \( x \) from crystal surface,
- \( t \) – heating time
- \( D_v \) – the lattice diffusion coefficient
- \( D_g \) – the grain-boundary diffusion coefficient
THE SCRATCH METHOD

Inward diffusion

Outward diffusion

Mutual diffusion
THE PELLET METHOD (WAGNER)

The range of metal loss

\[ \text{Ag}_2\text{S} + \text{e}^- \rightarrow \text{Ag} + \text{S} \]
THE MODIFIED PELLET METHOD

\[ \text{Ag} \rightarrow \text{Ag}_2S \rightarrow \text{Ag} \]

\[ \text{S} \rightarrow \text{Ag}_2S \rightarrow \text{Ag}_2S \rightarrow \text{Ag}_2S \]

\[ ^{35}\text{S} \rightarrow \text{Ag}_2S * \rightarrow \text{Ag}_2S \rightarrow \text{Ag}_2S * \]

\[ \text{Ag} \rightarrow \text{Ag}_2S \rightarrow \text{Ag} \]

\[ \text{S} \rightarrow \text{Ag}_2S \rightarrow \text{Ag}_2S \rightarrow \text{Ag}_2S \]
THE MECHANISM OF W/ZrC COMPOSITE FORMATION

Temperature: 1400 °C
Time: 1.5 h
THE END