TU Clausthal

Enamelling with reduced fractions of cobalt and nickel: Effect of surface roughness on enamel adhesion

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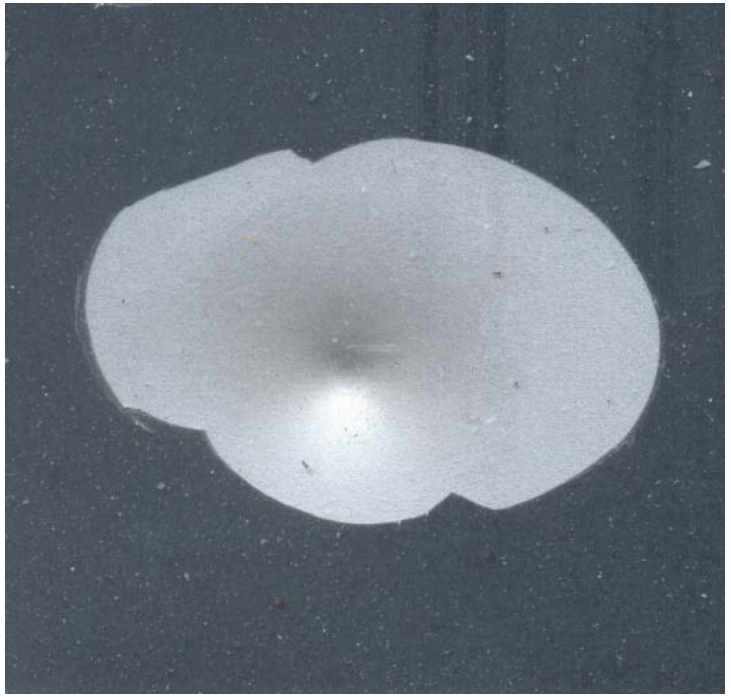
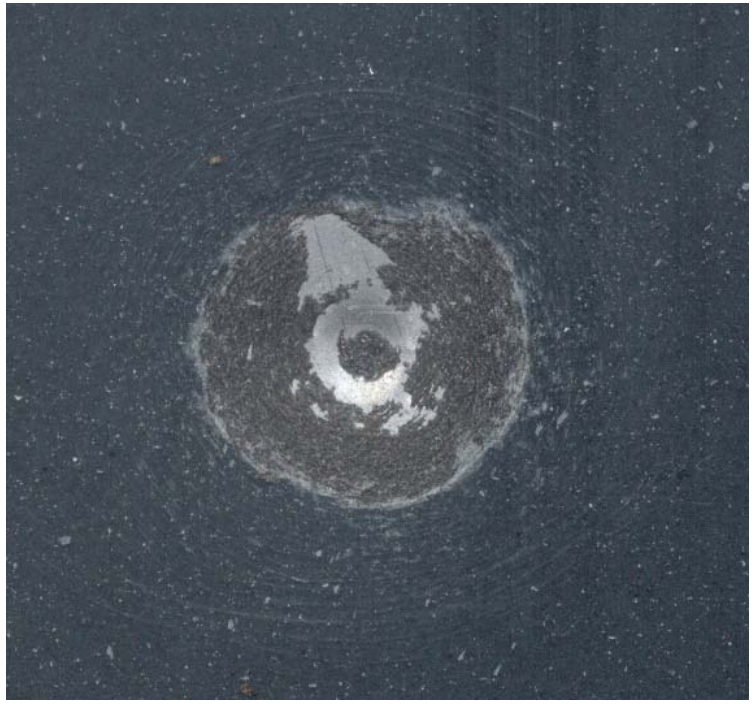
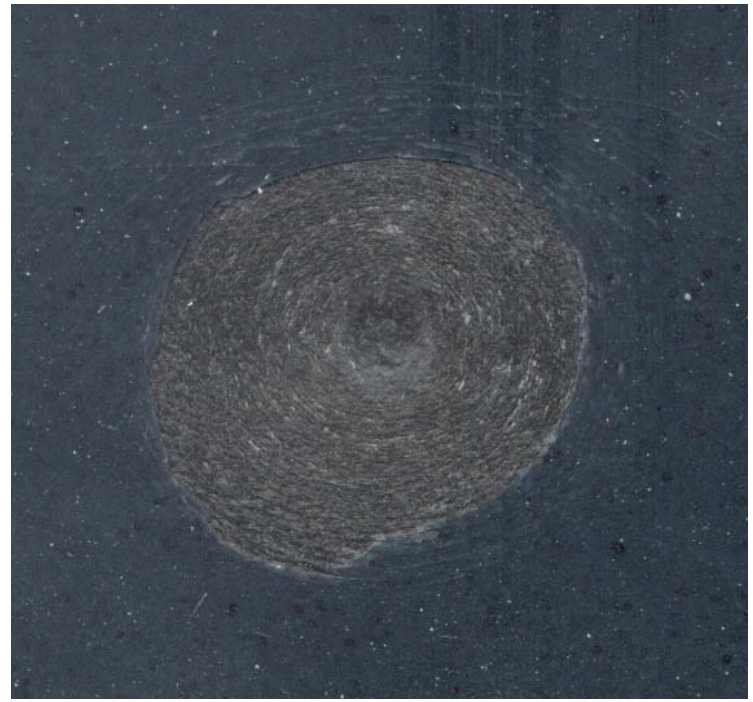






MOTIVATION

Aim of the project:

Approach for eliminating the use of adherence oxides of cobalt and nickel in ground and direct enamel

Experimental approach:

I. **Pretreatment of the steel surface (mechanical and chemical methods)**

II. **Investigations of the processes during firing conventional enamels**

III. Alternative adherence oxides and mixtures thereof (electrochemically similar to Ni and Co)

IV. Variation of the enamel composition (thermal application window)

PRETREATMENT METHODS AND ENAMELLING

- Steel sheet (d = 1.6 mm, l = 100 mm, low-carbon, Type YMVIT ULTRA, DC04ED, Tata Steel (NL))
- Degreasing
- Pretreatment procedure

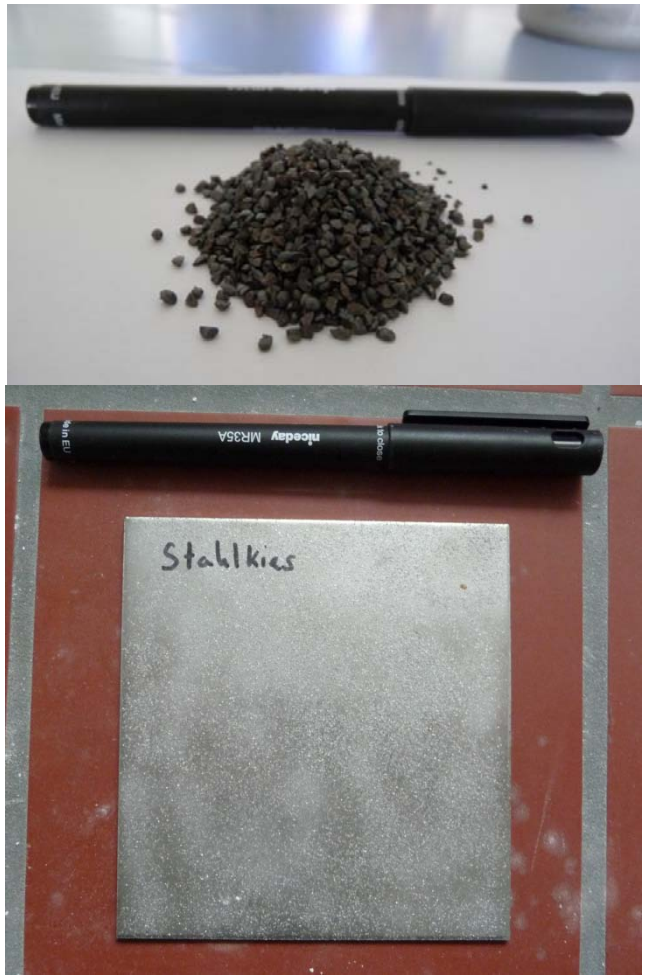
  A: Sandblasting (Corundum, steel shot, chilled cast iron)

  B: Etching in aqueous $FeCl_3$ solution (c = 2 mol/l: T = 20°C / T = 70°C for 1 h)

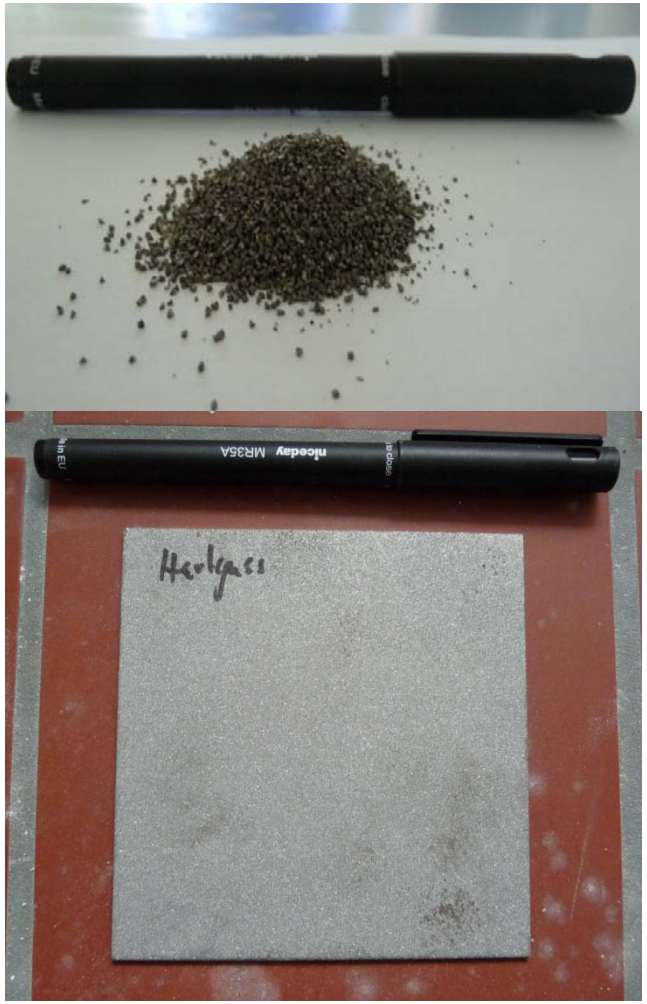
  C: TEOS (*Immersion in TEOS solution, sol-gel-chemistry route "Tetra-Ethyl-Ortho-Silane", drying at 20 °C*)
- Enamel: standard ground enamel (Wendel-Email, Germany) and mixtures thereof until Co-/Ni-free (Co100 – Co75 – Co50 – Co25 – Co0, containing adherence oxides from 100% to 0%)
- Applying the enamel: Spraying (layer thickness 200-300 µm), drying at 80 °C / 30 min.
- Firing (Parameters: T = 800 °C, t = 7 minutes, electrical furnace)
- Cooling (air)
- Testing the adherence by several methods → deep drawing (cupping test)
- Quantitative examination of the damage (scanning the surface, picture analysis via ImageJ (imagej.nih.gov/ij))

METAL PRETREATMENT: BLASTING MATERIALS

Steel shot



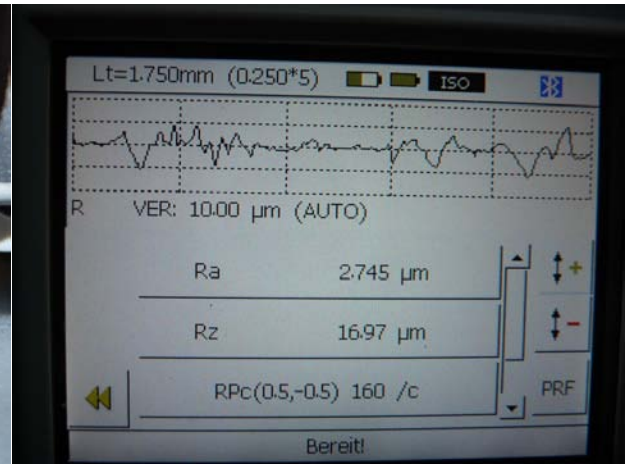
Chilled cast iron



Corundum

DETEKTION OF ROUGHNESS PARAMETERS

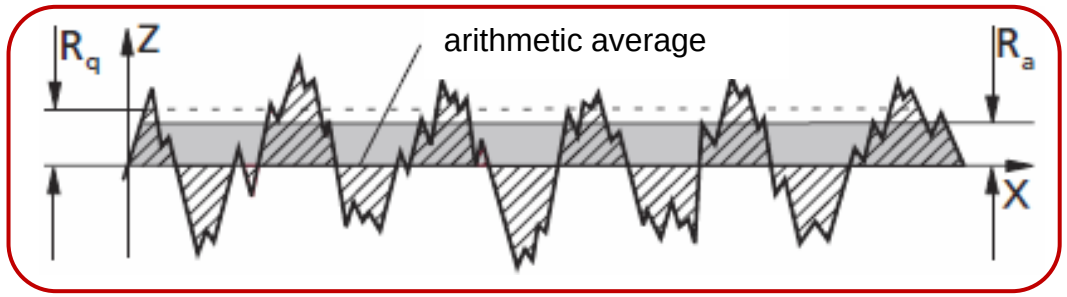


Mobile roughness measuring unit M300, Fa. Mahr GmbH,Göttingen

Profile roughness parameters:

R_a, R_q, R_z, R_p, R_v, R_k, **RP_c**, R_{sm}…



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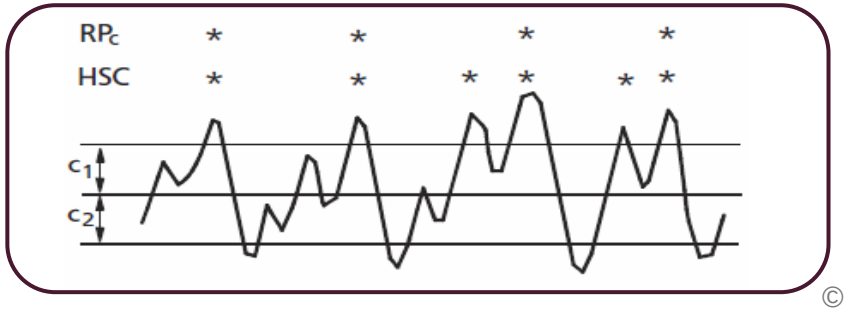

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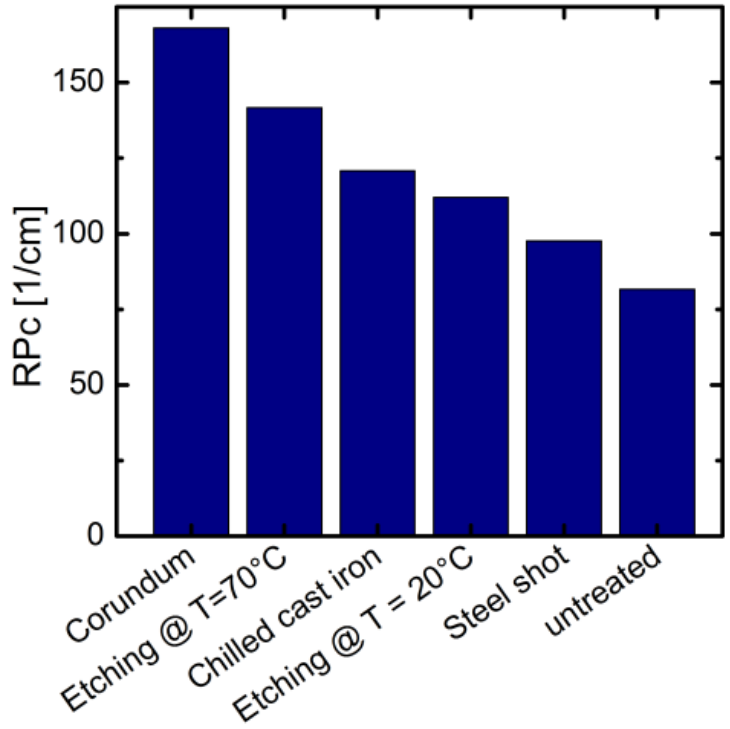
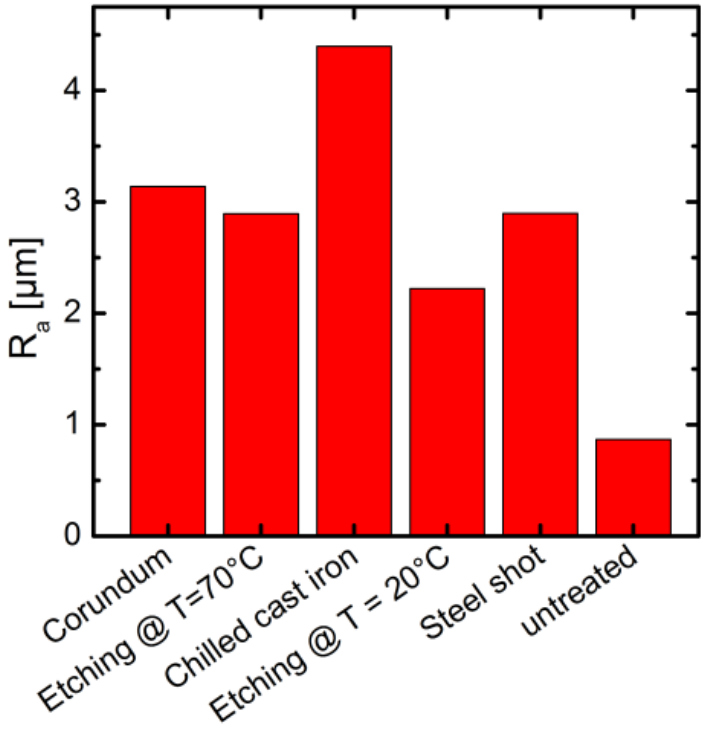
Arithmetic average, **R_a**: the mean distance of a point on the surface from the profile center line

Peak count, **RP_c**: the number of profile elements per cm that exceed a certain average level c_1 and then fall below the lower c_2

PRETREATMENT RESULTS: ROUGHNESS PARAMETERS



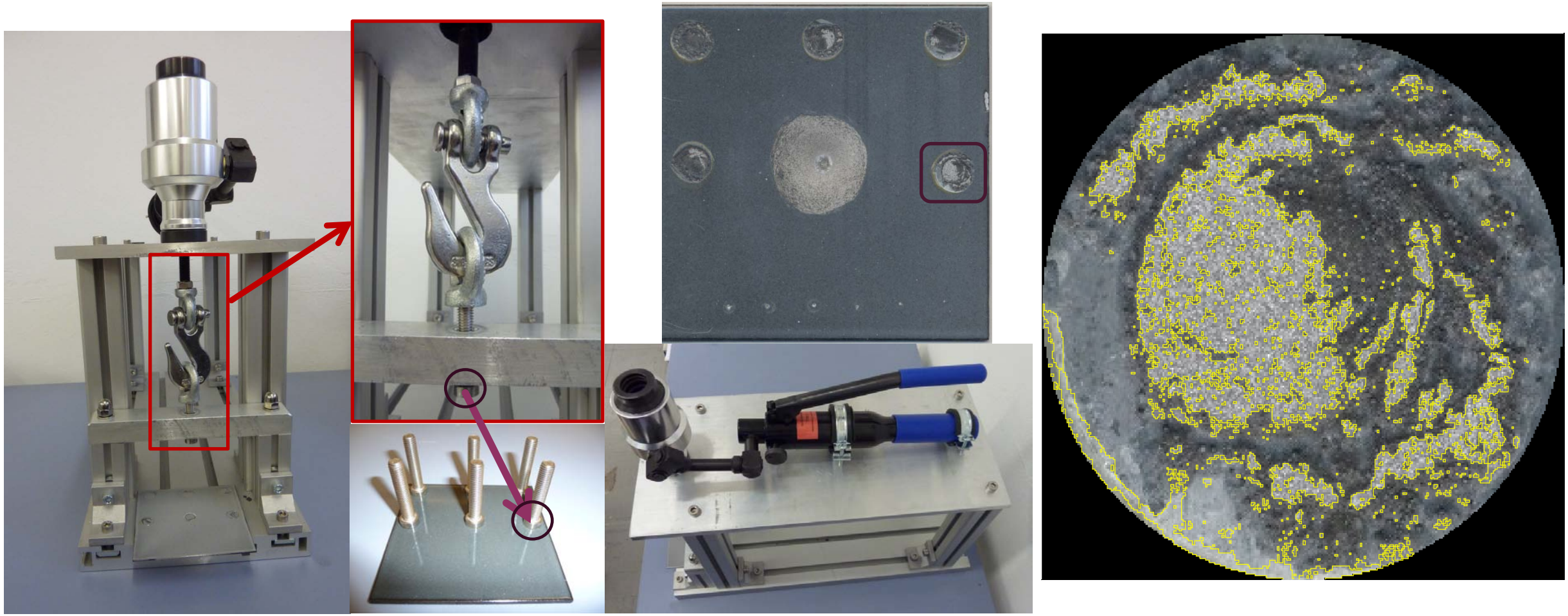
Profile peak number RPc as a function of pretreatment procedure



Surface roughness Ra as a function of pretreatment procedure

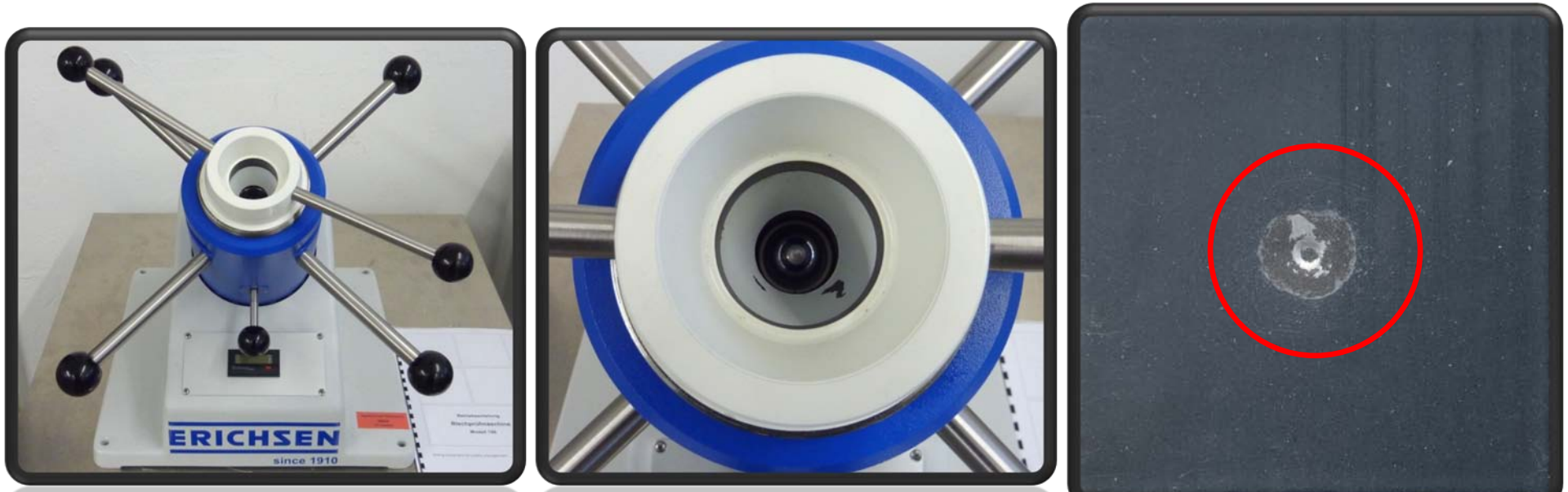
- Increase of peak counts from 80 (untreated) up to 170 cm^{-1} (Corundum blasted)
- Highest mean roughness at about 4.5 µm (chilled cast iron)
- Etching leads to significant higher roughness parameters
  - RP_c values 142 resp. 112 cm^{-1}
  - R_a values of 2.9 resp. 2.2 µm

ADHERENCE TESTING PROCEDURE: PULL-OFF TEST



- → disadvantage on steel sheet: uncertain crack initiation and crack propagation, minor differentiation of adherence

ADHERENCE TESTING PROCEDURE: DEEP DRAWING (CUPPING TEST)

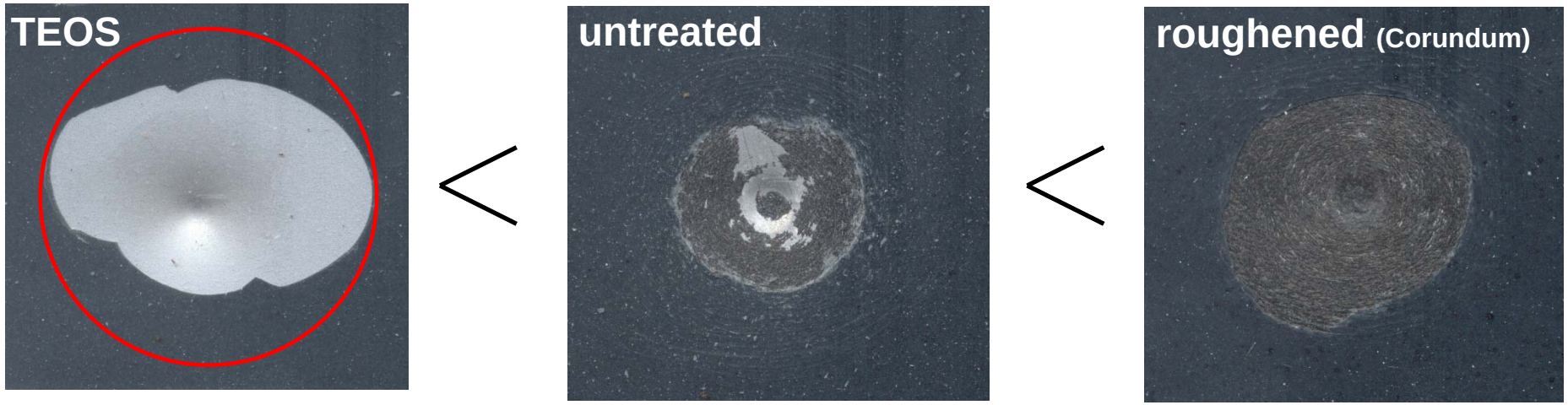


sheet metal test machine

- Deep drawing in a sheet metal testing machine
- Access to adherence by means of open metal surface fraction x (<10%: good adhesion)
- Adherence index a = 100 – x
- → Advantage: better differentiation of adherence status

RESULTS OF PRETREAMENT

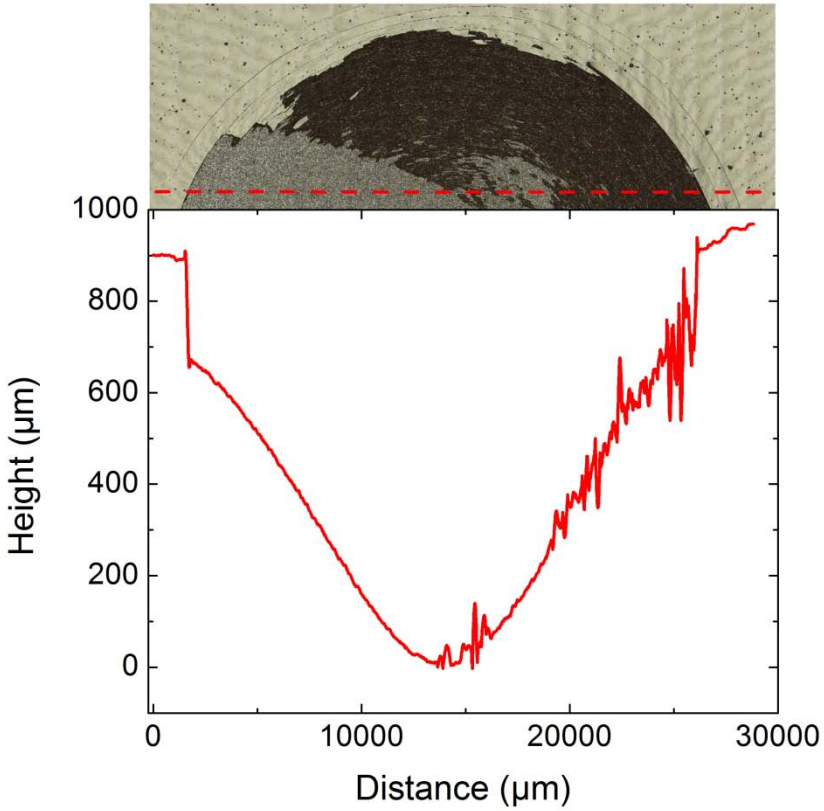
- **Coating on steel sheet**:
  - Coating with TEOS leads to a dramatic bad adherence (**no** adherence promoting layer)
- Possible causes:
  - Surface roughness is decreased due to the coating layer of SiO_2
  - Filling of the cavities decreases the number of anchor-points
  - SiO_2 layer: barrier for Oxygen inhibits oxidation of the steel surface and Fe^{2+} migration into the melt

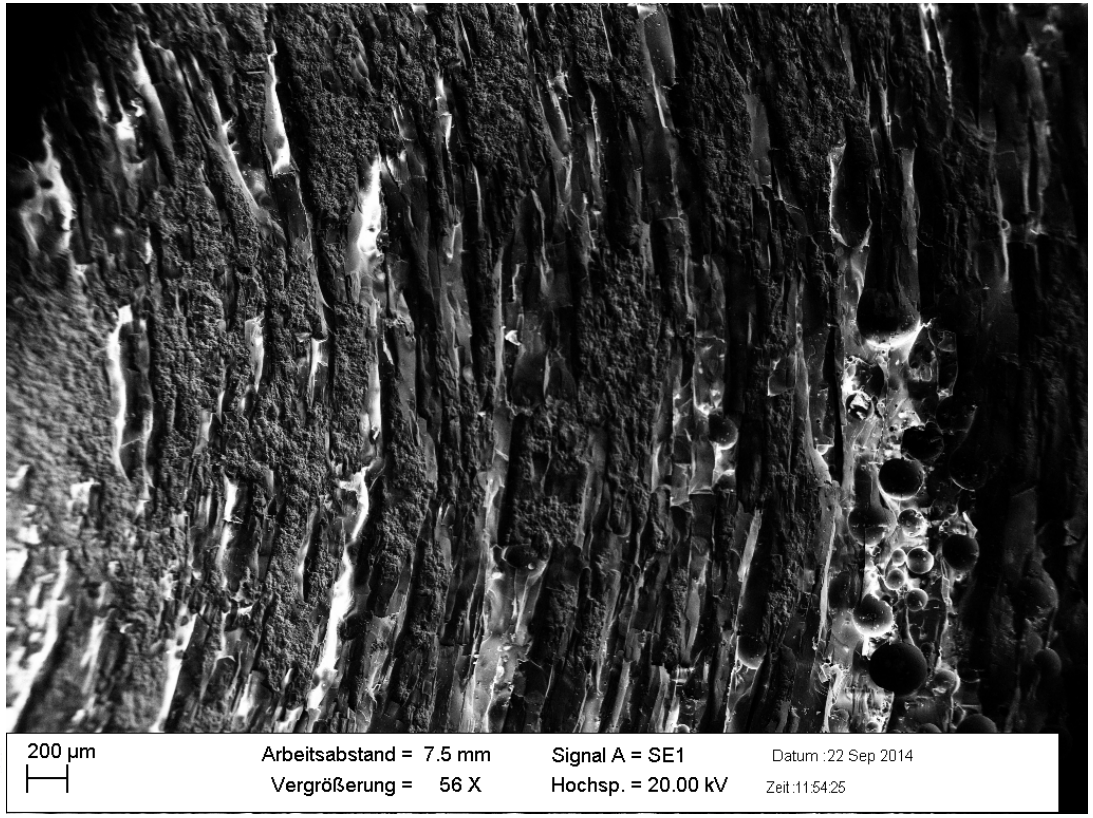


RESULTS OF PRETREAMENT: ETCHING

- Rough surface supports adherence due to an increase of mechanical interlocking
- Without CoO/NiO: no material compound can be achieved, no chemical bonding reaction

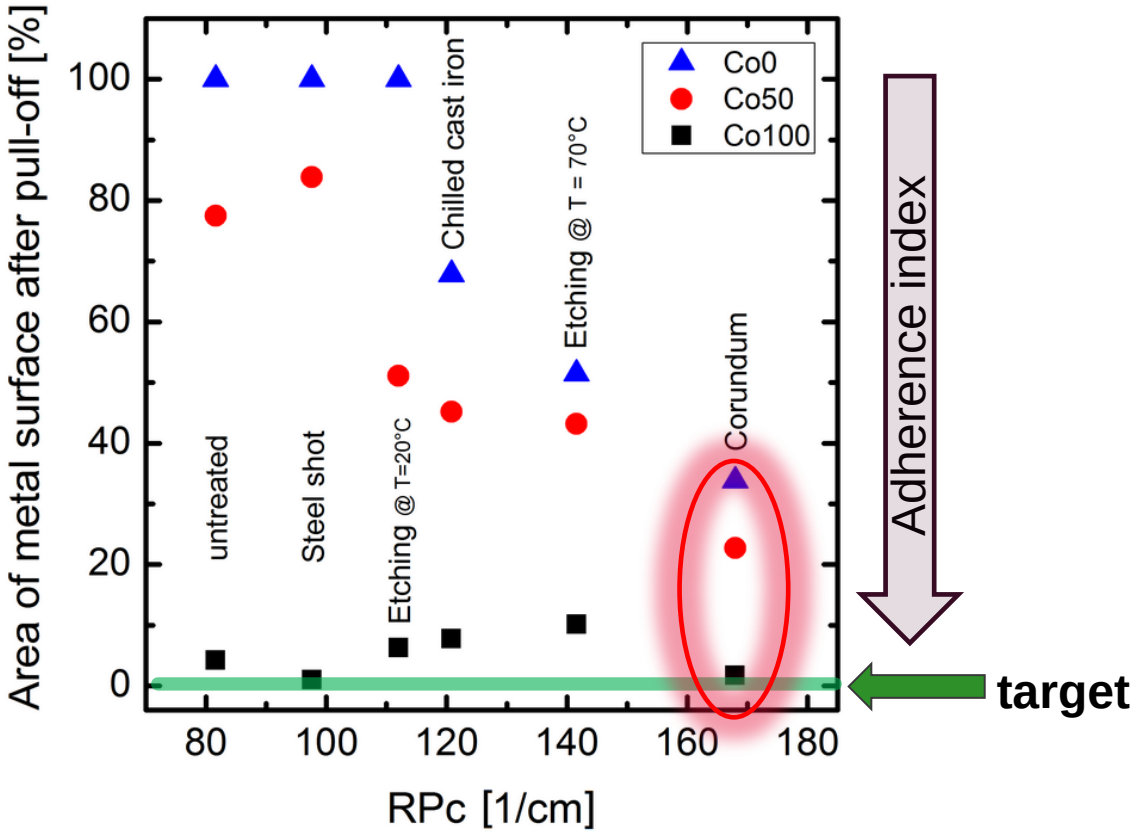
DAMAGE ASPECT: INDICATOR FOR ADHERENCE BEHAVIOR



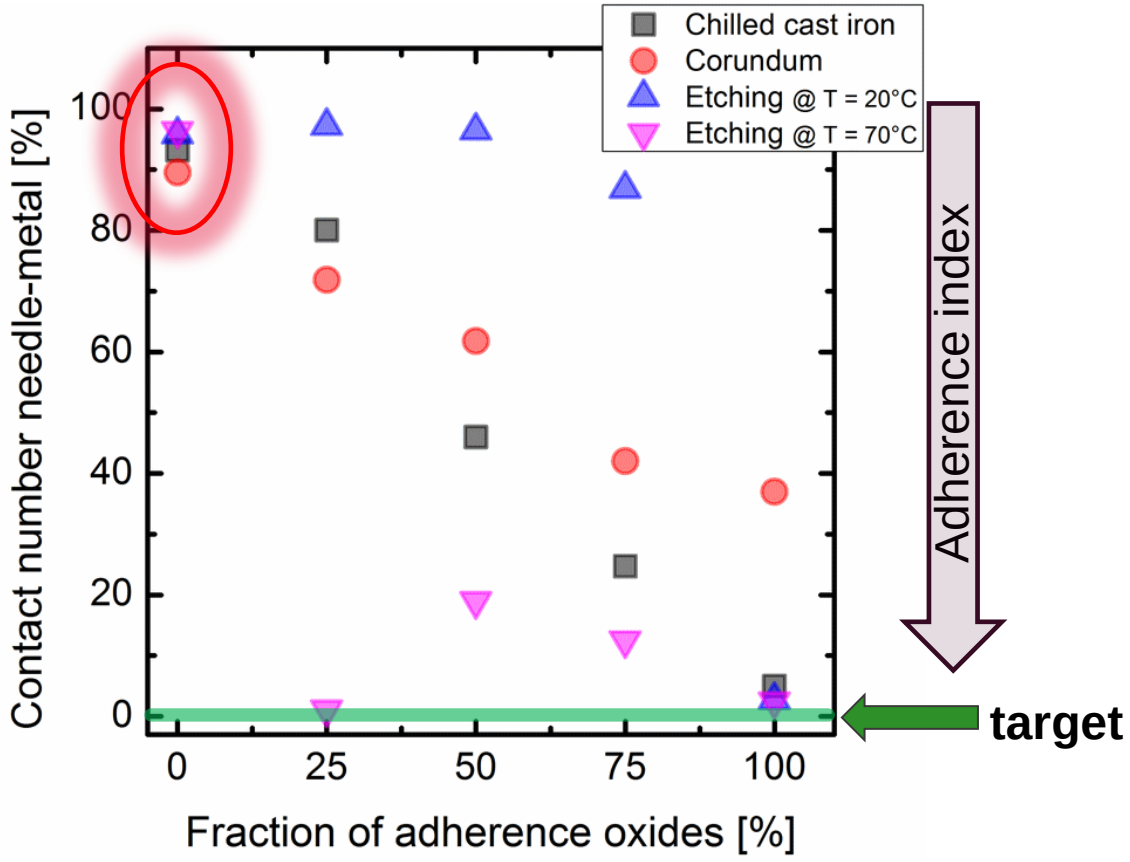


- Steep and plain edge on left side: less adherence, absence of dark colored interface
- „Flaked“ scaling (right side) of enamel layer points out a higher/better adherence behavior, presence of a dark colored interface, high iron content

RESULTS OF PRETREATMENT ON ADHERENCE INDEX



Pull-off test: adherence vs RPc,
parameter: adherence oxide content



Deep drawing test: adherence vs fraction of adherence oxide,
parameter: Pretreatment

- → Advantage of deep drawing test procedure versus pull-off test

DEEP DRAWING TEST PROCEDURE VERSUS PULL-OFF TEST

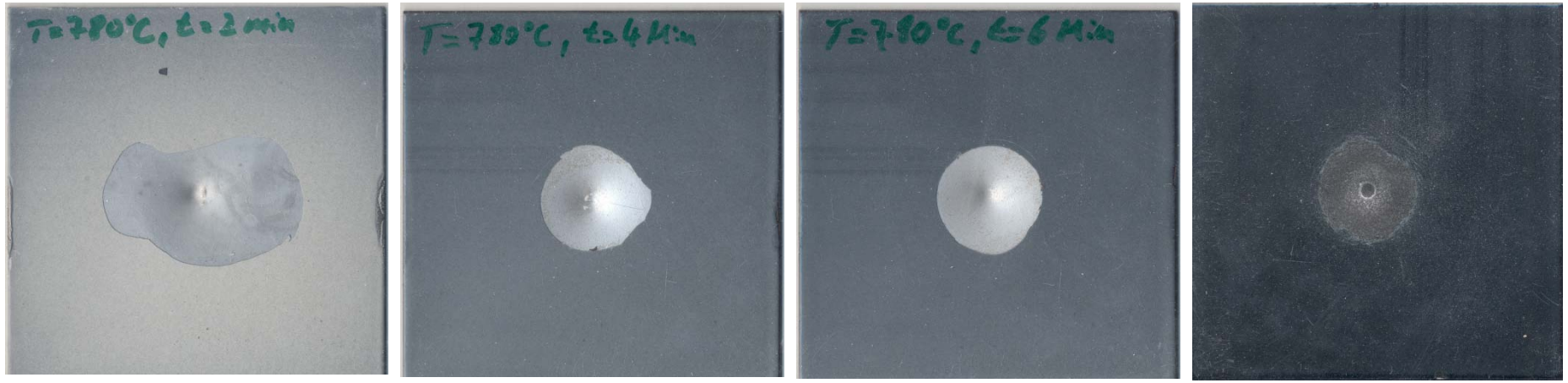
- **Results from method Pull-off test**
  - Higher surface roughness can provide a better adherence with an increase up to 60% using vitreous enamel being completely free of cobalt and nickel (blasting medium Corundum)
  - Effect of the chemical component (presence of adherence oxide) is stronger, no difference in adherence if comparing plain to rough steel surfaces

- **Results from method Deep drawing**
  - Only very small differences in adherence index between roughened and untreated steel surface
  - Mechanical roughening increases mechanical interlocking but produces no material compound (i.e. no adherence)
  - Most important is the effect of chemical interaction of adherence oxides in the melt

ENAMELLING: INFLUENCE OF TEMPERATURE

780°C

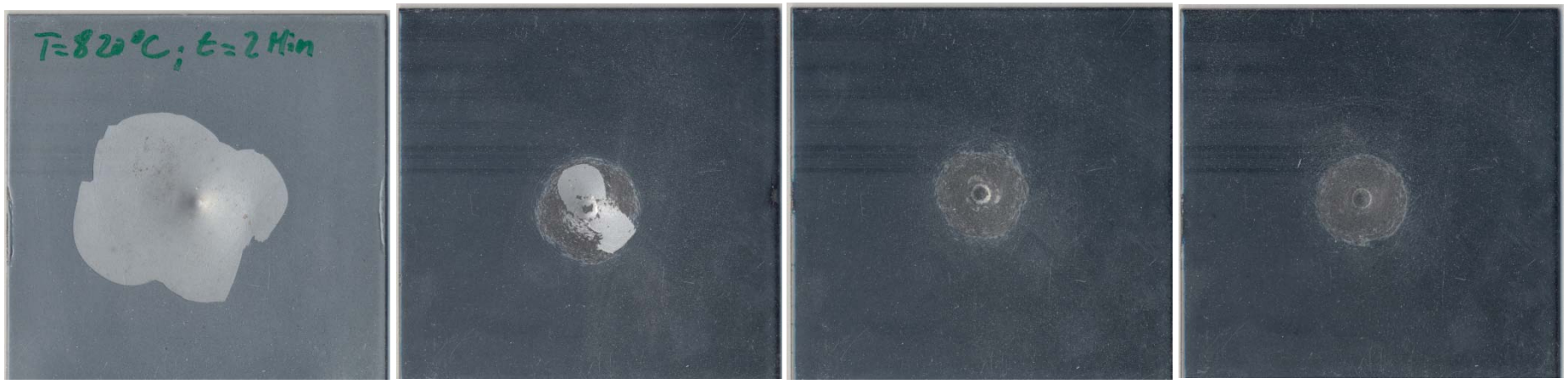
Standard ground



2 Min | 4 Min | 6 Min | 8 Min

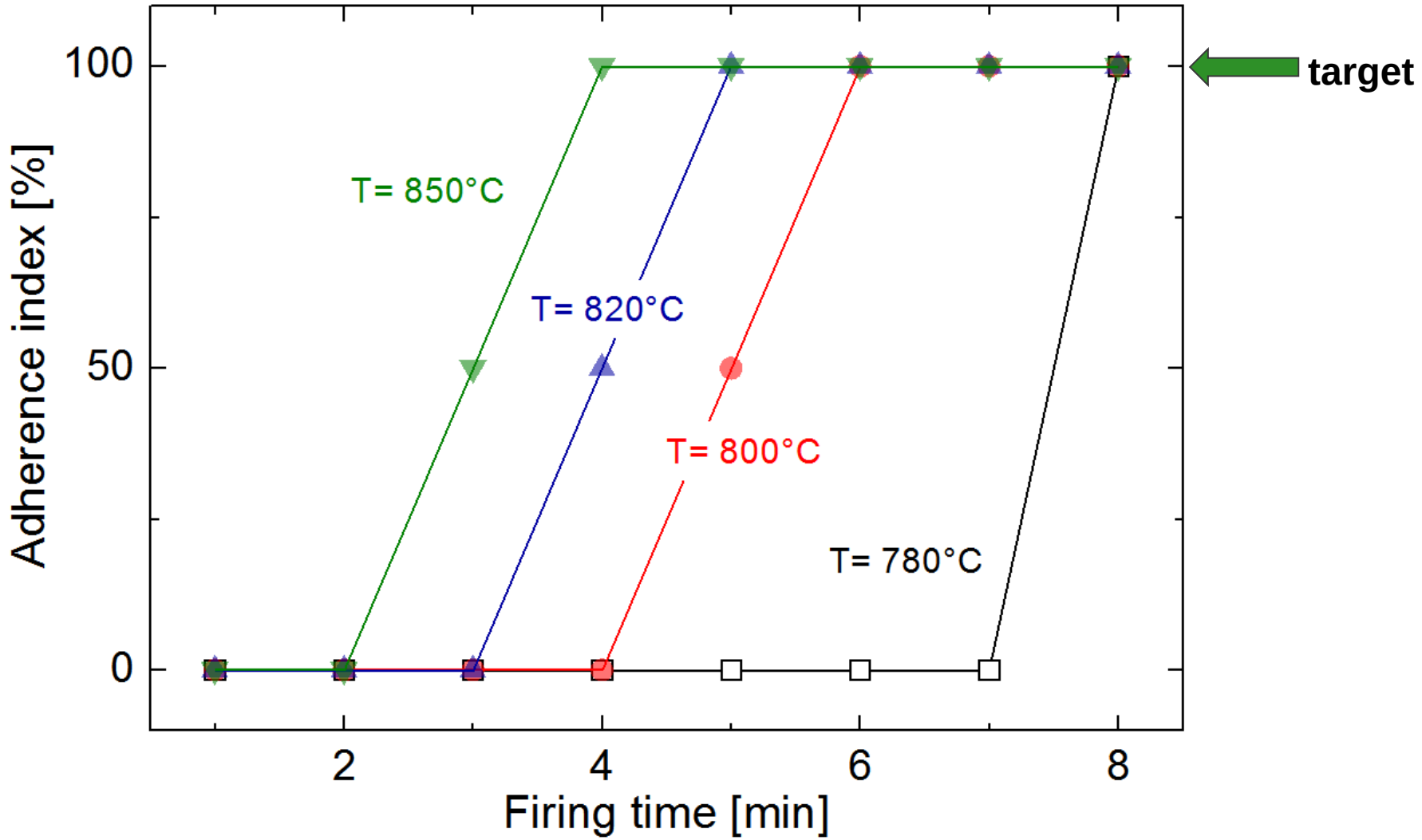
820°C

Standard ground

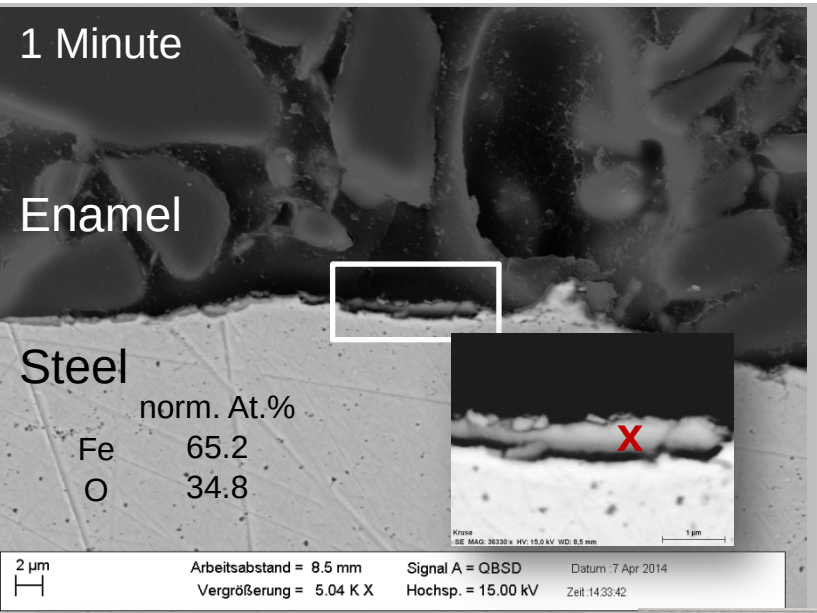


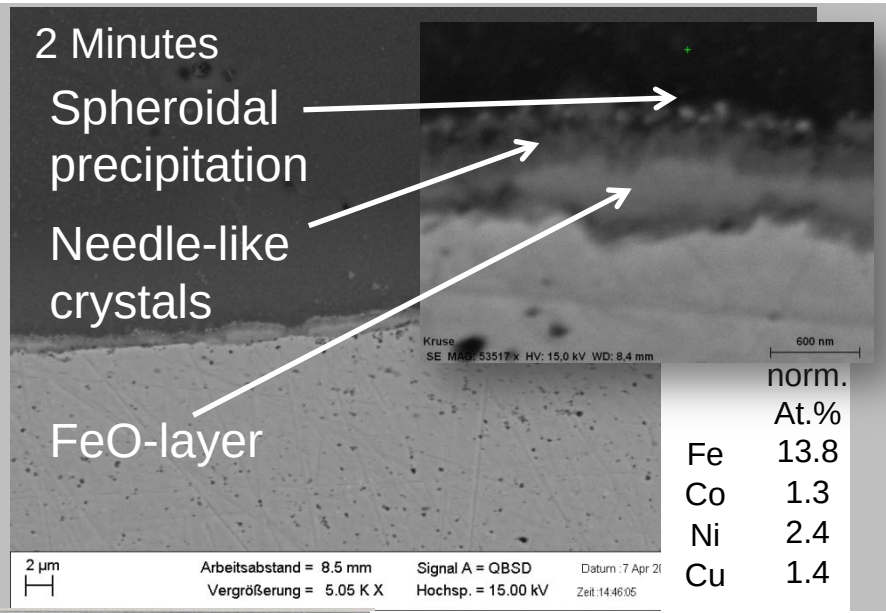
2 Min | 4 Min | 5 Min | 6 Min

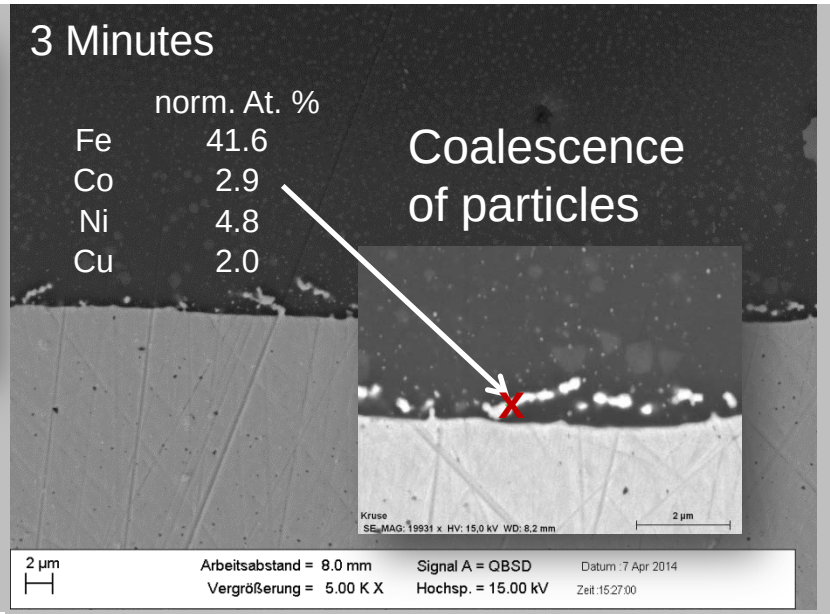
ADHERENCE ACCORDING TO TIME AND TEMPERATURE

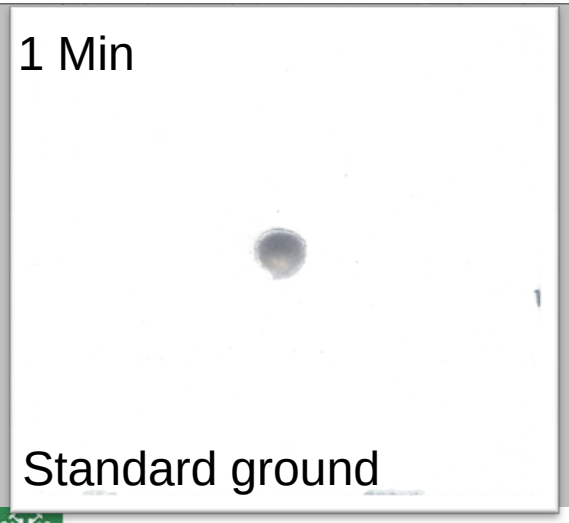


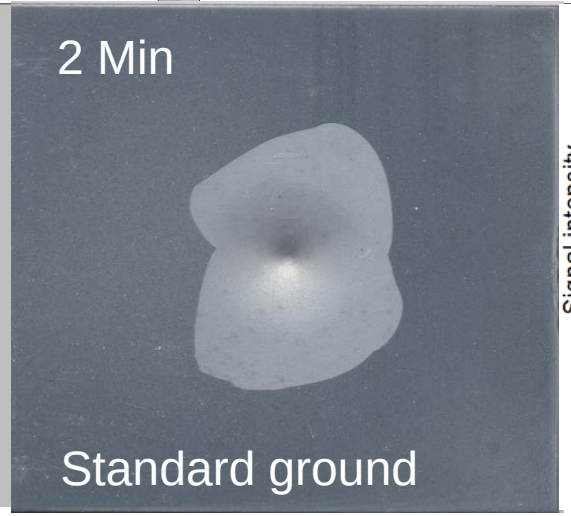
MECHANISM DURING FIRING OF CONVENTIONAL GROUND ENAMEL

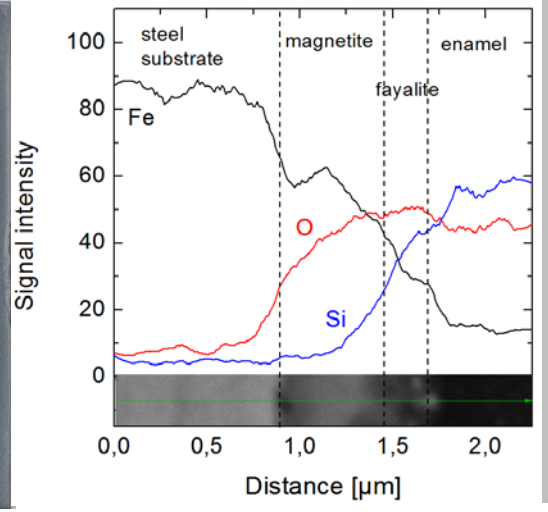


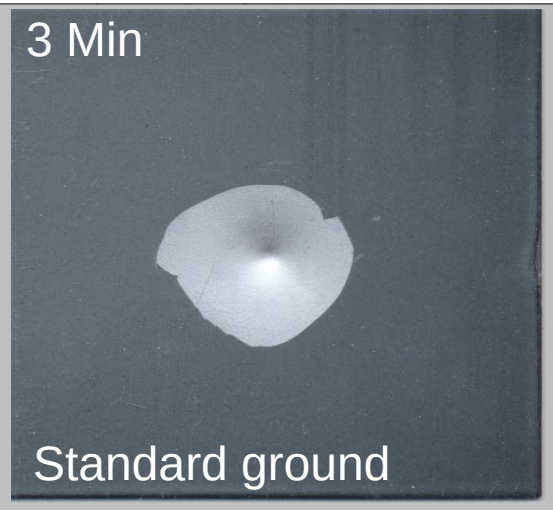




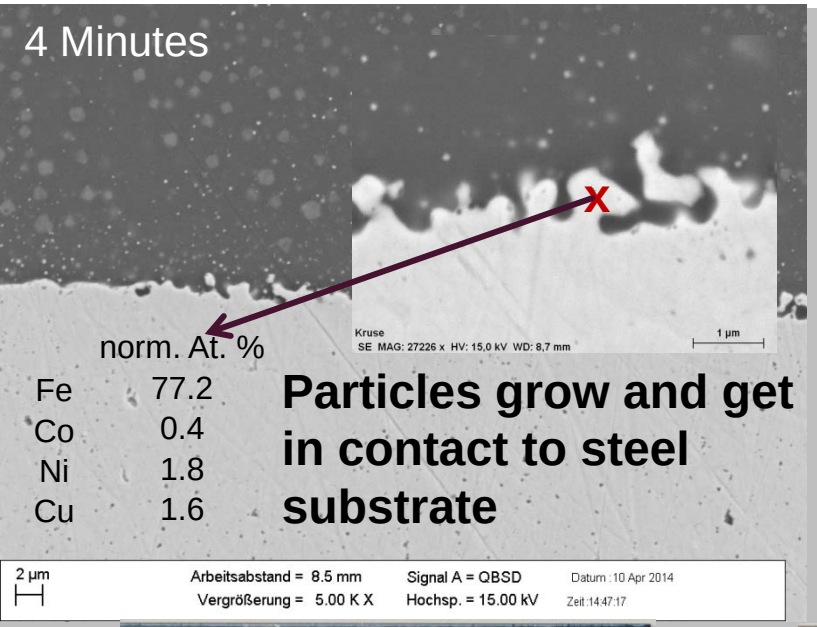


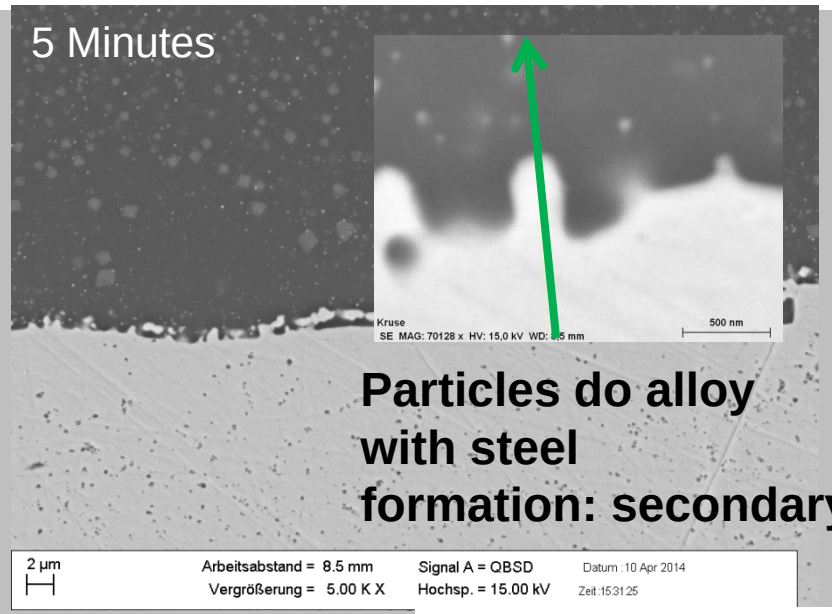


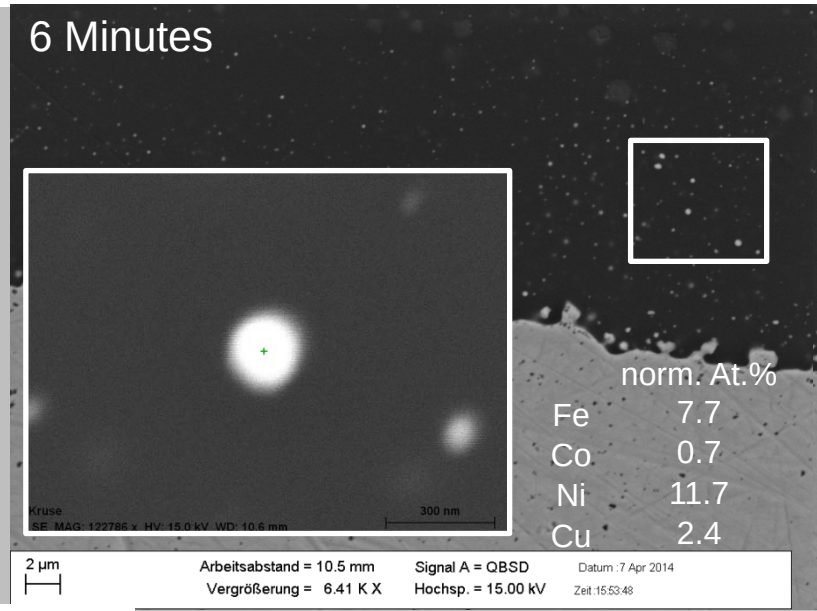


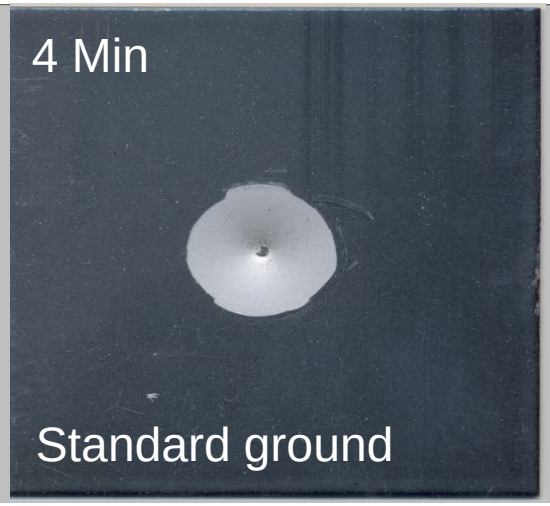


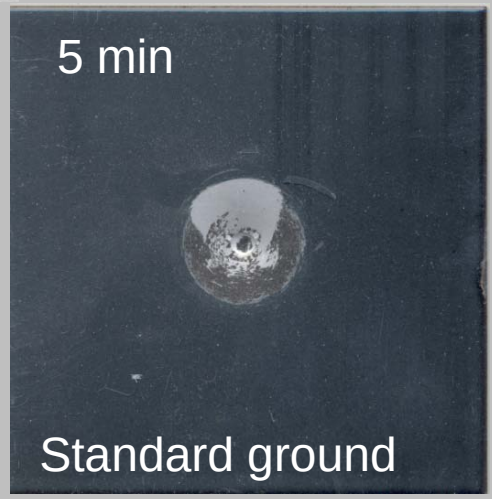
MECHANISM DURING FIRING CONT.

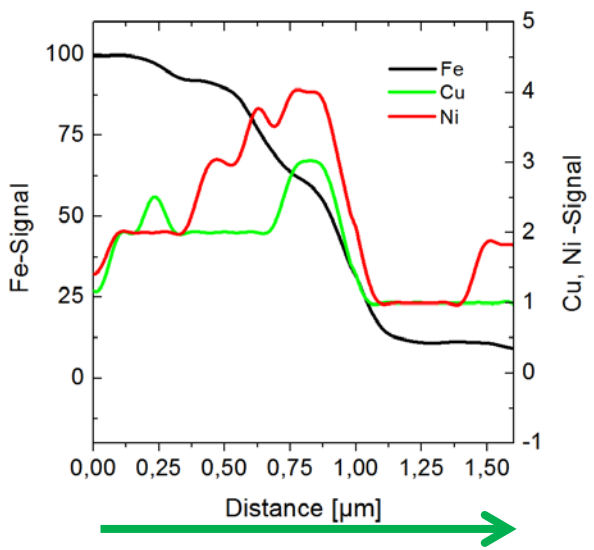


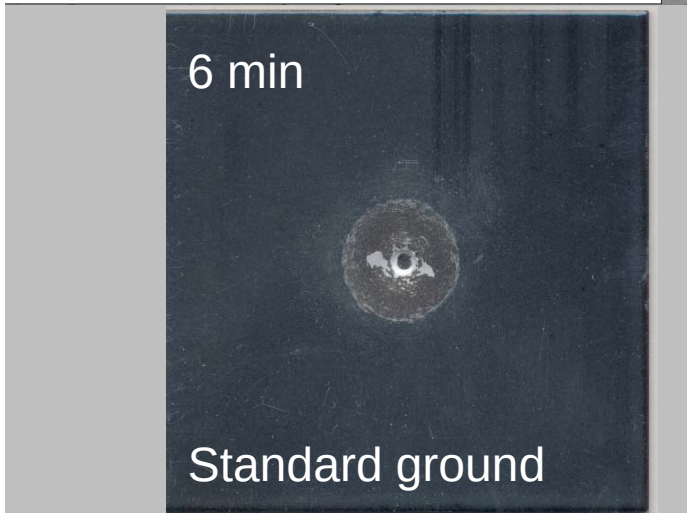












COMPREHENSION OF MECHANISMS DURING FIRING

of conventional (adherence oxides bearing) ground enamel

1. Oxidation of base metal (steel) in the initial stages of firing (Minute 1 and 2)
2. Formation of Fayalite (Fe_2SiO_4) from iron oxide and enamel (from Minute 2)
3. Dissolution of Fayalite in the glass melt
4. (Over-) saturation of iron cations in the glass melt
5. Precipitation of iron, forming alloys of Fe-Co-Ni-Cu (metal particles) (from Minute 3)
6. Growth/coarsening of micro alloys and subsequently getting in contact with base metal
7. Forming of a rough surface on steel sheet (as an **additive** event, no corrosion) → anchor-points → good adherence
8. Formation of a material compound with high surface roughness (from Minute 5)

RESULTS OF EXPERIMENTAL RESEARCH

I. Pretreatment of the steel surface (mechanically and chemically)

Good interlocking of the enamel with the steel sheet surface but
→ no formation of a material compound without adherence oxides

II. Significance of testing procedures for the adherence of enamel on steel sheet

Results and statements depend on the testing procedure:
deformation processes provide a better differentiation of the adherence index (enamel on metal) than pull-off or impact tests

III. Studies of the processes during firing of conventional enamels

Contribution to the clarification of a core aspect of the formation of metal-enamel compounds

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providing enamels

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