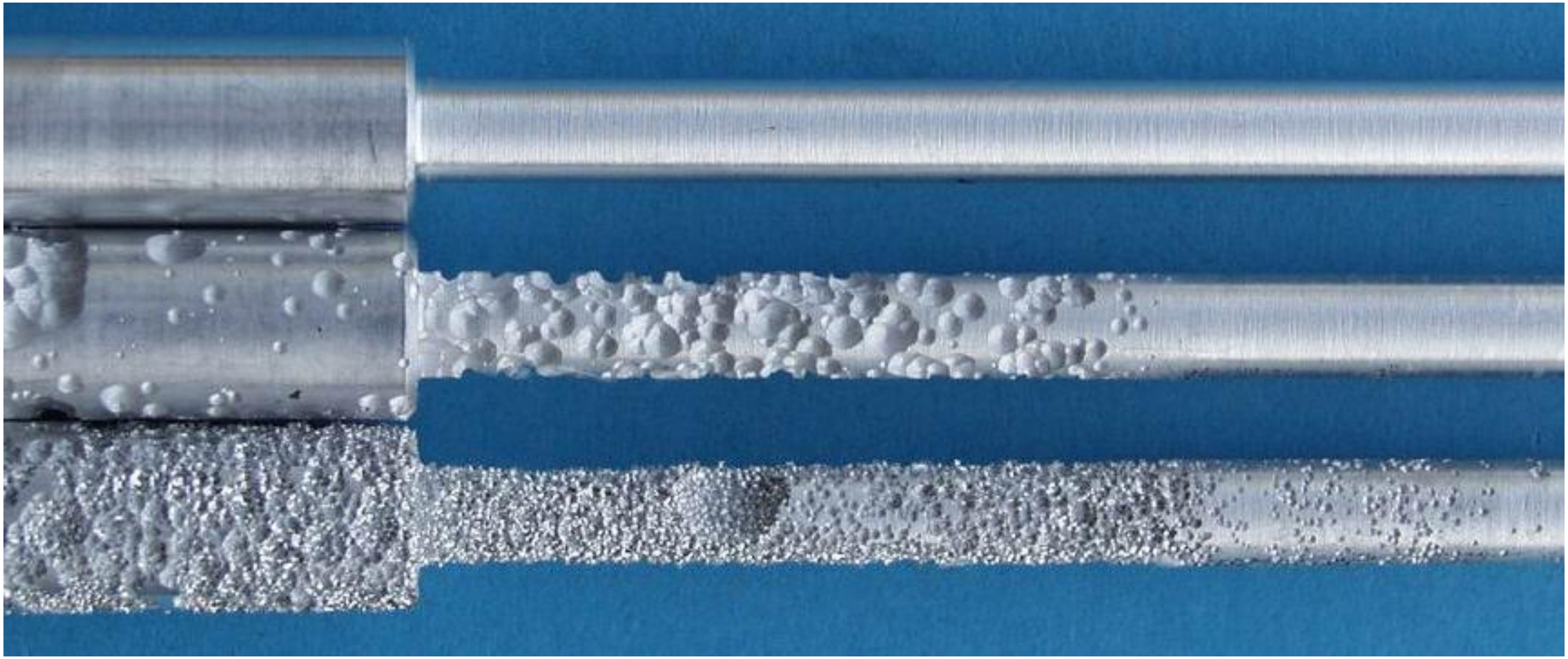
Susceptibility of aluminium alloys to alcoholate corrosion in alcohol blended biofuels – technological influences

K. Bauer, G. Andersohn, H. Kaufmann, T. Troßmann



Agenda

- Alcoholate corrosion of aluminium
- Technical temperature threshold
- Influences on initiation and propagation of alcoholate corrosion
  - Fuel composition
  - Temperature
  - Water content
  - Cyclic mechanical loading
- Conclusion

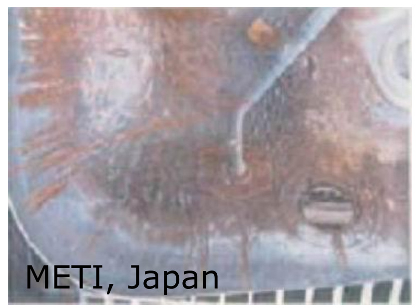
Corrosion mechanisms of metals in oxygenated fuels

Electrochemical corrosion depending on material and fuel composition

due to dissolved water
(e.g. low water content)

pitting corrosion of X90CrMoV18 in an E10 gasoline blend

due to separated water
(high water content)



corrosion at the bottom of a tank
after phase separation of water

Chemical corrosion
"dry corrosion", chemical
alcoholate corrosion

concerns alcohol containing fuels,
in particular Al-, Mg-alloys and lead

„dry" alcoholate corrosion of a cast Al-alloy in an E10 gasoline blend

Alcoholate corrosion of aluminum

- Refers to the chemical corrosion of metals in the presence of fuel alcohol containing fuel blends
- Alcohols can react with aluminium alloys, lead and magnesium with the formation of alkoxide or alcoholate corrosion products

$$3C_2H_5OH + Al \rightarrow (C_2H_5O)_3Al + 3/2H_2 \qquad (1)$$

$$(C_2H_5O)_3Al + 3H_2O \rightarrow Al(OH)_3 + 3C_2H_5OH \qquad (2)$$

$$(C_2H_5O)_3Al \rightarrow Al_2O_3 + 6C_2H_4 + 3H_2O \qquad (3)$$

(1) alcoxides (alcoholate) get hydrolyzed (2) or decomposed (3)

Damaging process may progress rapidly and is accompanied by an increase in pressure due to hydrogen formation

Alcoholate corrosion of Al

Aim of the investigation

Investigation of major influences on the alcoholate corrosion of aluminum alloys, like

- **Material composition**
- **Fuel composition**
  - Ethanol content
  - Water content
- **Temperature**
- **Cyclic mechanical loading**

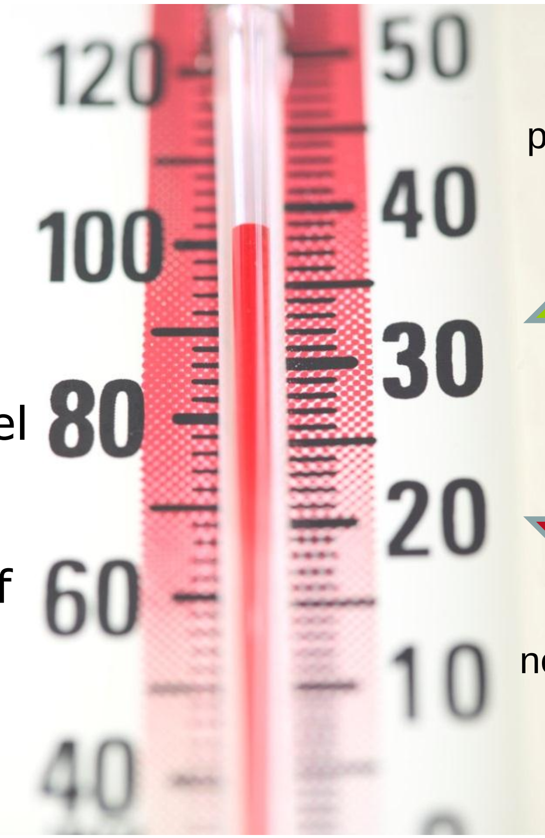
Technical temperature threshold

TECHNISCHE UNIVERSITÄT DARMSTADT

- Defined as a guidance level (not a characteristic material value) for a specific alloy

- For a given level and type of alcohol of a fuel blend

- Illustrates the effect of technical parameters and processes on the susceptibility to alcoholate corrosion



positive effect

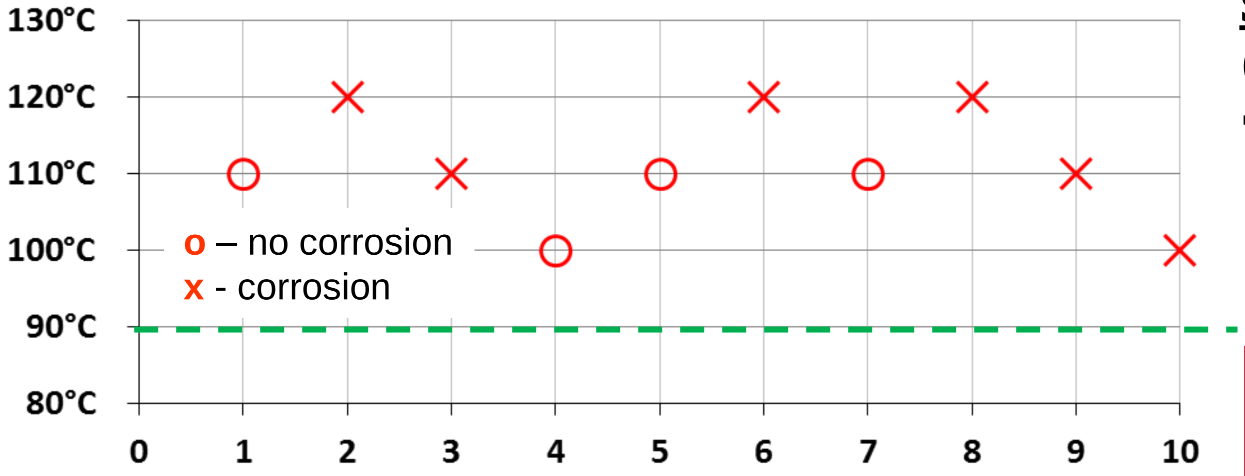
- **water**
- defect free coatings (e.g. anodisation, NiP, solgel…)
- mixing sequence
  fuel + EtOH + water
- mixing of fuel in ambient air
- steric complex or long chained alcohols
- …

negative effect

- wear, scratching
- detrimental microstructural features
- aggressive impurities
- coating defects
- higher surface/volume ratio
- mixing sequence
  EtOH + water + fuel
- time
- **mechanical loads**
- …

Test conditions and deduction of the technical temperature threshold

- Preparation of fuels (e.g. reference fuel + SeccoSolv EtOH)
- Testing of partially immersed samples (168 h) in pressure tight vessels with protection against explosions
- Pressure signal is used as indicator for alcoholate corrosion
- Test sequence according to stair case method (n > 10)

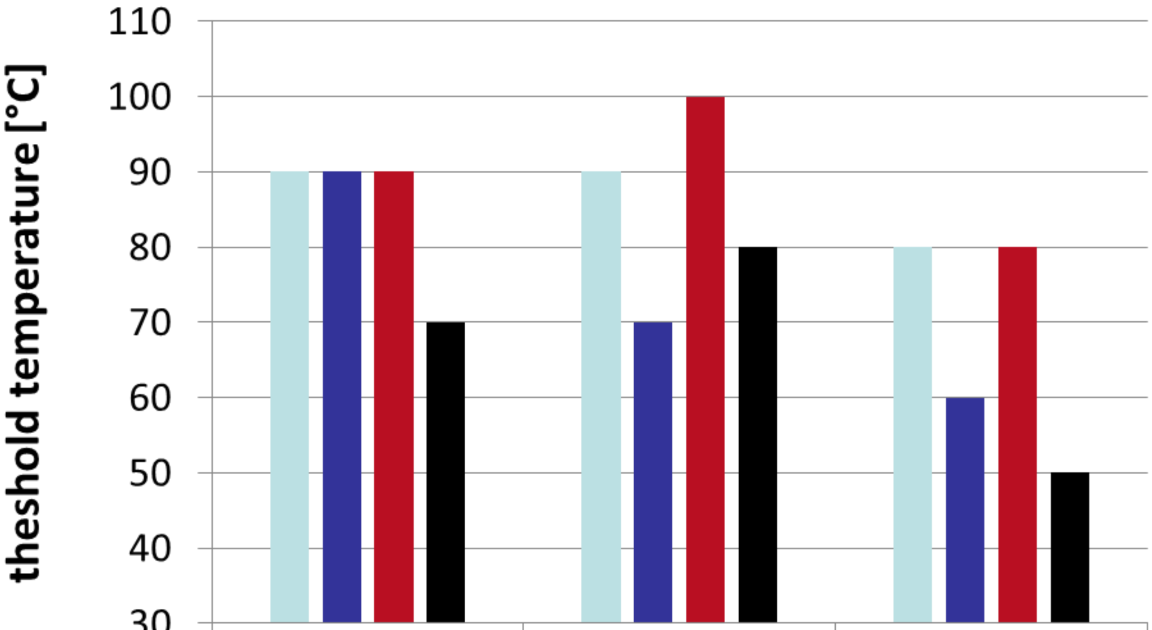


Stair case method:
(step width = 10 °C)
➔ stabilization on an average level, scatter can be calculated

T-Threshold ($T_{Psurvival90\%}$ – 10°C)

Technical temperature threshold

Influence of EtOH-content



	E10	E20	E85
Al99,5	90	90	80
AlSi9Cu3	90	70	60
AlMn1	90	100	80
Alusil	70	80	50

Observations:

- **Al99,5 / AlSi9Cu3** drop of threshold with increasing EtOH-content
- **AlMn1 / Alusil** highest threshold for E20, lowest E85
- Lowest overall threshold for cast **Alusil / E85**

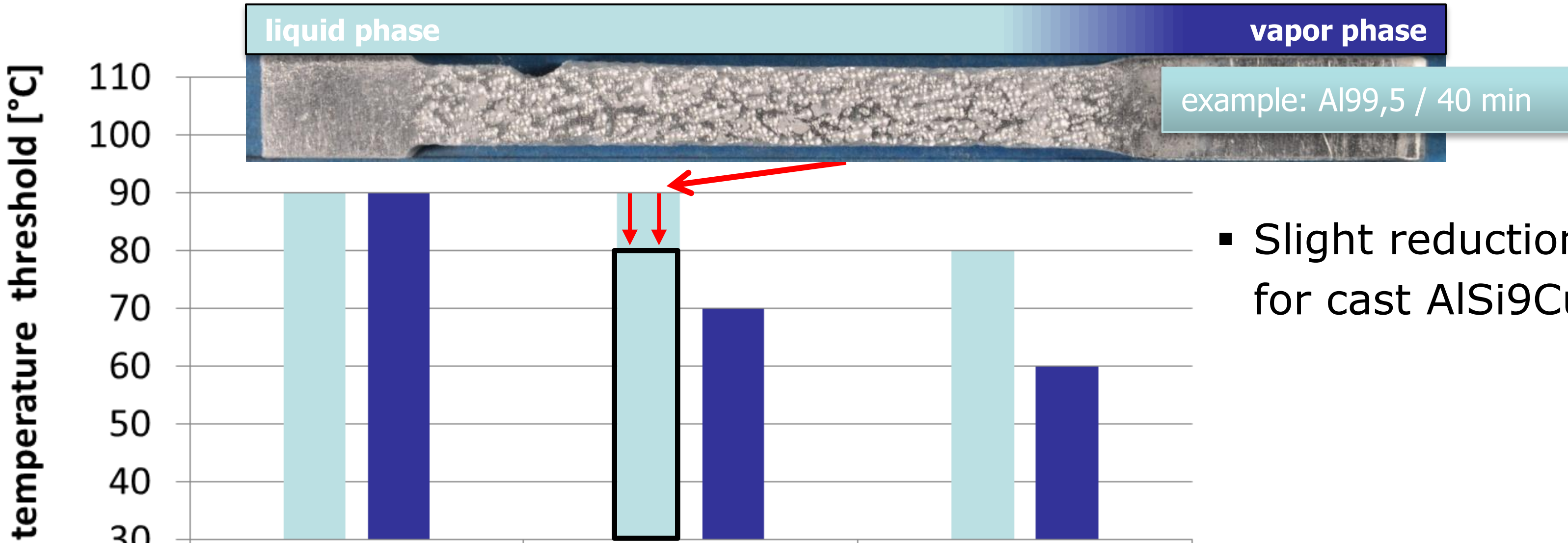
Technical temperature threshold

Influence of increased testing time, surface/volume ratio

TECHNISCHE UNIVERSITÄT DARMSTADT

- Increased surface area: 1 → **4 specimens in one test vessel**
- Increased testing time: 168 → **336 h** (2 weeks)

⇨ **Slight reduction of temperature threshold**



	E10	E20	E85
Al99,5	90	~~90~~ ⇨ 80	80
AlSi9Cu3	90	70	60

- Slight reduction for cast AlSi9Cu3

MPA IfW Fraunhofer LBF SzM

Technical temperature threshold

Influence of water-content

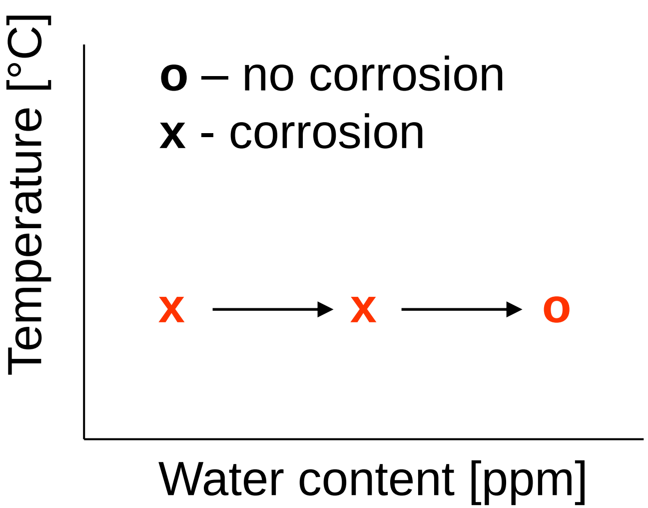
Starting temperature:

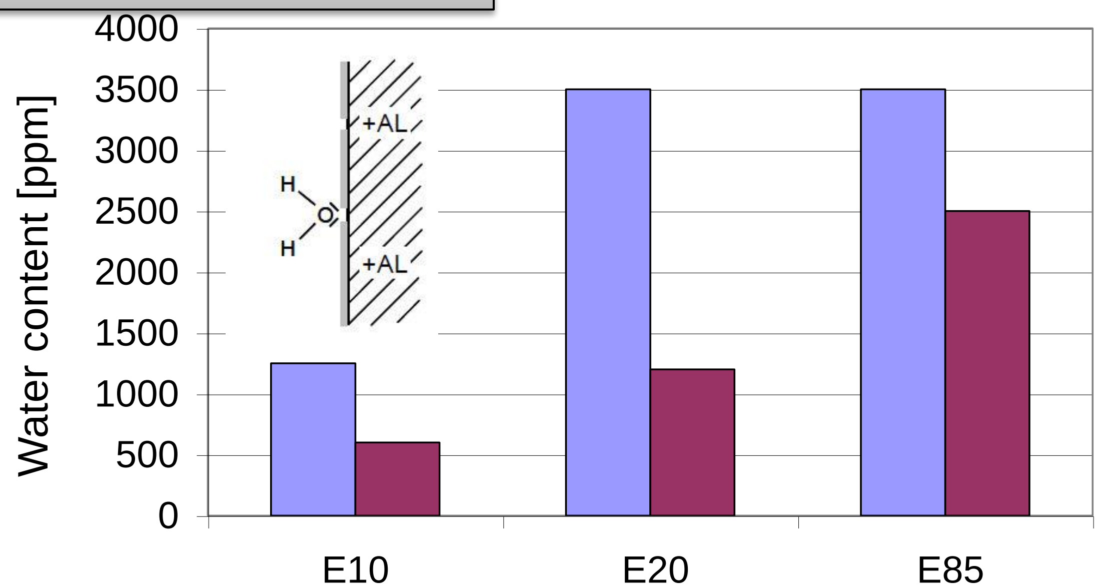
10 °C above the highest temperature level with **assured** alcoholate corrosion ➔ water addition, until no alcoholate corrosion occurs at this temperature level.

Starting temperature:

Al99,5	AlSi9Cu3
E10: 130°C	E10: 120°C
E20: 130°C	E20: 110°C
E85: 120°C	E85: 100°C

⇨ **Inhibition of alcoholate corrosion by water additions is possible, but....**

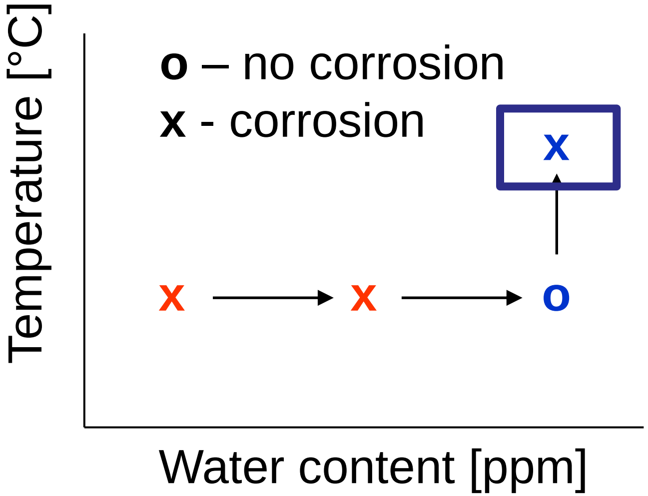




Technical temperature threshold
Influence of water-content

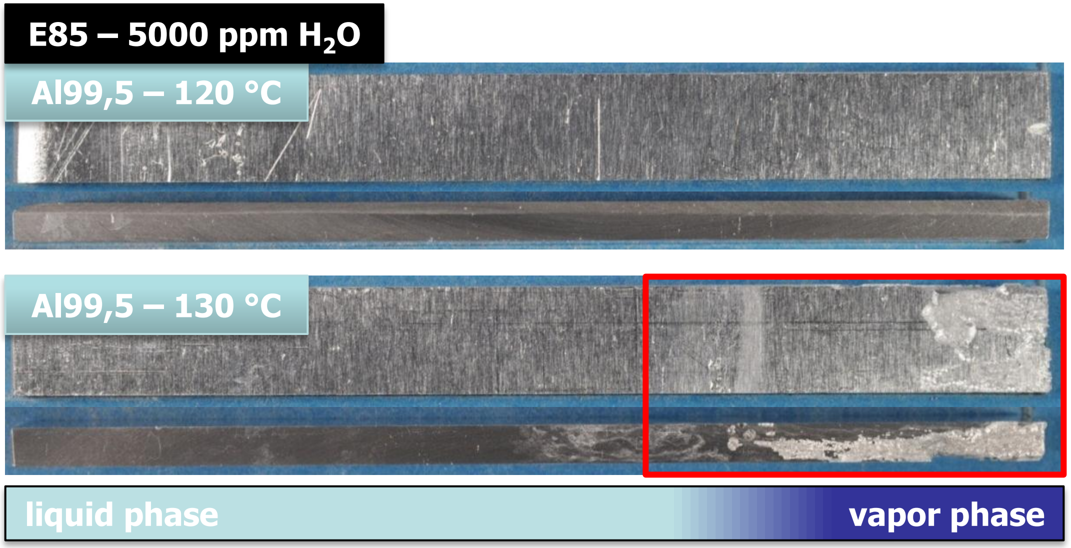
<u>Increase of temperature for the water-inhibited fuel</u>

⇨ **Alcoholate corrosion!**



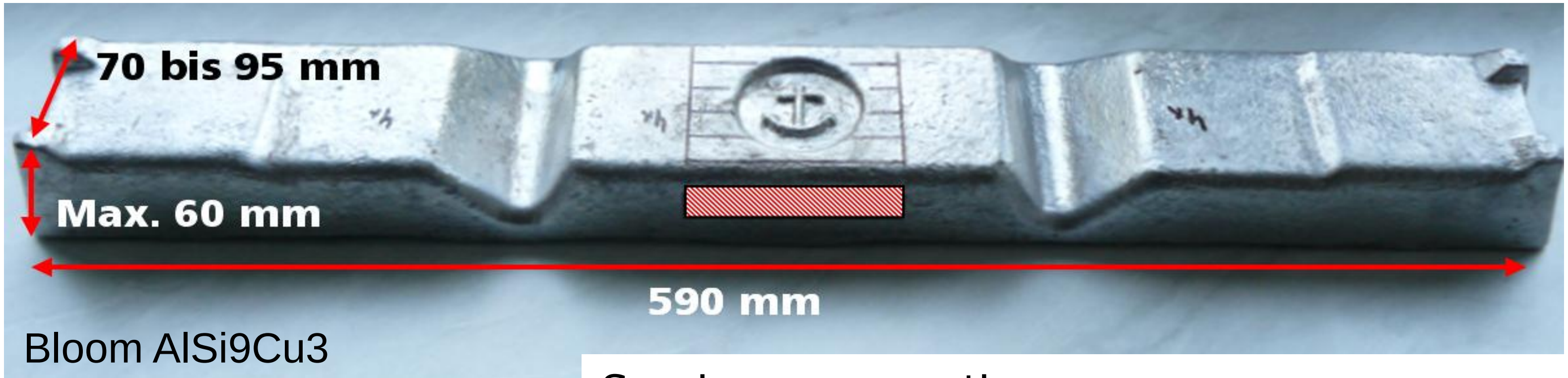
Observations:

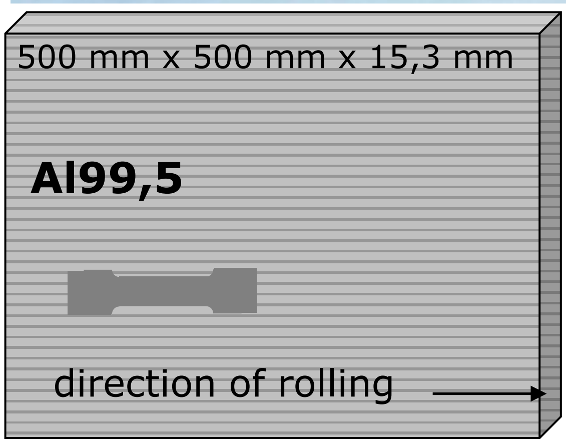
- ⇨ At very high temperatures alcoholate corrosion is shifted towards the vapour phase!
- ⇨ At lower temperatures alcoholate corrosion occurs in the liquid phase due to the lowest boiling point of water-rich EtOH-azeotrope



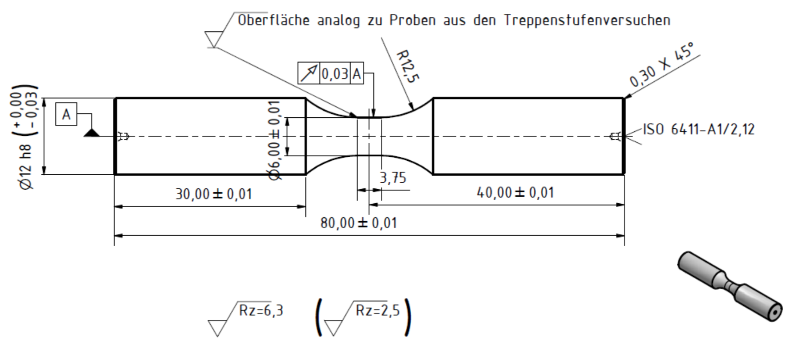
Raw material for corrosion fatigue tests
(Stress ratio R = 0, Fuel: E85)

TECHNISCHE UNIVERSITÄT DARMSTADT





Specimen preparation:
Surface condition comparable to immersion testing



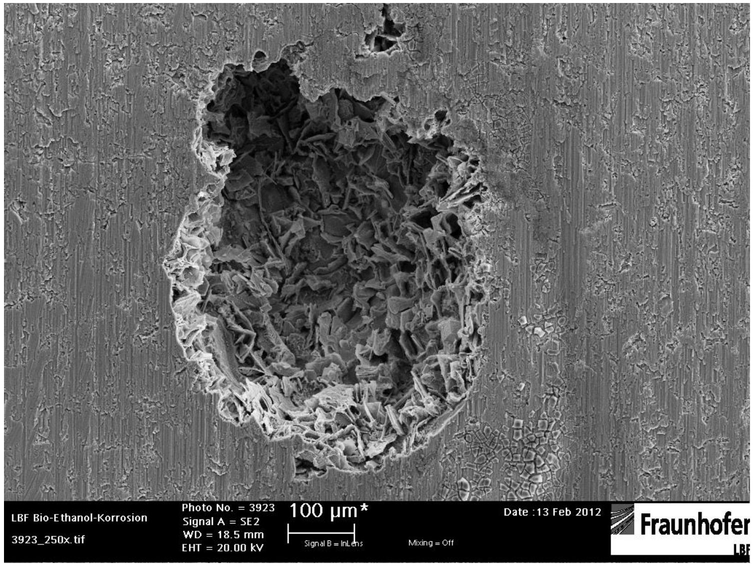
- ⇨ **Test temperature: 10 °C below static (immersion) temperature threshold**
- ⇨ **Load level (R = 0): Stress amplitude lowered by 5 % in relation to the run out level at 1E7 cycles in air**

Corrosion fatigue tests
Observations

Al99,5 in E85 @ 70 °C:
- Fatigue life in E85/70°C reduced by a factor of 10 compared to air
- Signs of initiation of alcoholate corrosion on the fracture surface <u>after</u> rupture

AlSi9Cu3 in E85 @ 50 °C:
- No significant reduction of fatigue life (due to high porosity of the cast material crack initiation still occurs at intrinsic defects), but…

AlSi9Cu3 in E85 @ 50°C - 47,5MPa

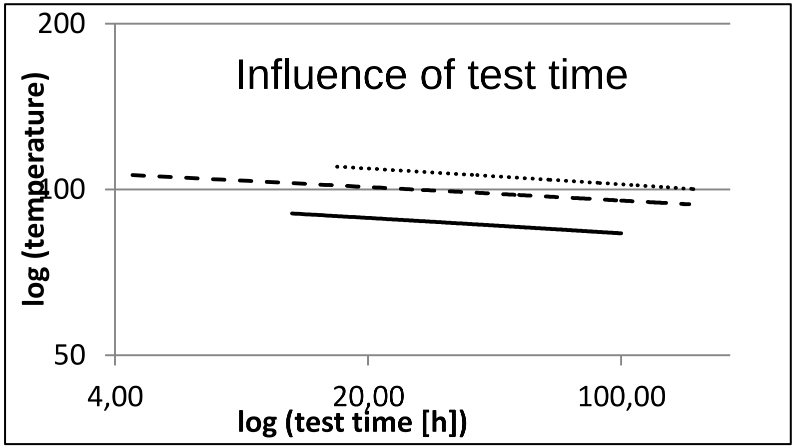


initiation of alcoholate corrosion

Conclusion

Technological temperature threshold as indicator of susceptibility to alcoholate corrosion

- For a given material an fuel, the probability of alcoholate corrosion is strongly influenced by
  - Temperature (T), water content (W), surface area/volume ratio (A), time (t)
  - Order of impact: T >> W > A > t
- The deduction of a technological temperature threshold as an indicator of susceptibility to alcoholate corrosion is suitable to describe further influences like
  - Manufacturing, surface condition, …
  - Mechanical loads
  - Size of sample surface
- Threshold can be used to rank technological influences, but not as a design criterion!



Conclusion

Alcoholate corrosion of aluminium in ethanol blended fuels

- Wrought alloys show higher technological temperature thresholds than cast alloys.
- Inhibiting water content is not only dependent on the ethanol content
- The technological temperature threshold is lowered by superimposed cyclic mechanical loading for the cast alloy AlSi9Cu3 (50 °C fuel temperature)
- Corrosive attacks were observed for Al99,5 at 70 °C but could not clearly be assigned to alcoholate corrosion
- Fatigue life of Al99,5 was considerably decreased by the influence of corrosion
- Fatigue loaded components exposed to ethanol blended fuels should be qualified thoroughly by additional corrosion fatigue tests

Acknowledgment

TECHNISCHE UNIVERSITÄT DARMSTADT

Gefördert durch:

Bundesministerium für Wirtschaft und Technologie

aufgrund eines Beschlusses des Deutschen Bundestages

DFO

The research project „Kraftstoffkorrosion" (15978N) of the Deutsche Forschungsgesellschaft für Oberflächenbehandlung e.V. (DFO) was funded by the AiF as part of the program for »Joint Industrial Research (IGF)« by the German Federal Ministry of Economics (BMWi) by decision of the German Bundestag.

MPA IfW Fraunhofer LBF SzM

Author Contact

TECHNISCHE UNIVERSITÄT DARMSTADT

System Reliability and Machine Acoustics

Dipl.-Ing. Kathrin Bauer

Institute for System Reliability and Machine Acoustics (SzM)

Adress: Magdalenenstraße 4, 64289 Darmstadt, Germany

E-mail: kbauer@szm.tu-darmstadt.de

Internet: http://www.szm.tu-darmstadt.de