TECHNISCHE UNIVERSITÄT ILMENAU

Ernst-Abbe-Hochschule Jena
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Investigations on the layer-by-layer solidification of liquid alkali silicates using CO_2 laser radiation

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Outline

Introduction

Aim

Additive Manufacturing of complex structures based on waterglass

(based of European patent EP3 566 868 B1 ; EAH Jena)

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European Patent Office
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(11) **EP 3 566 868 B1**

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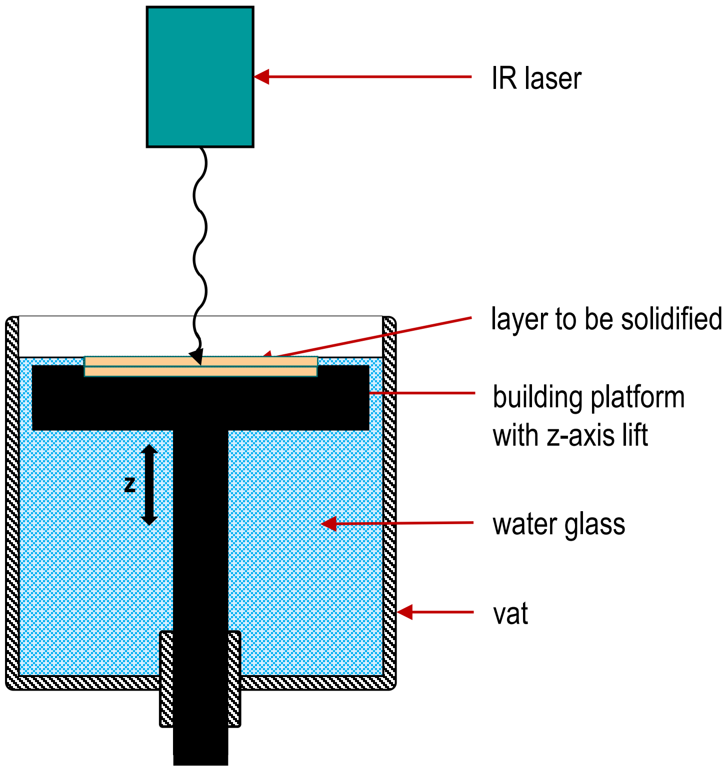
(22) Anmeldetag: **07.05.2019**

(54) **VERFAHREN ZUM DREIDIMENSIONALEN ADDITIVEN AUFBAU EINES FORMKÖRPERS AUS WASSERGLAS**

METHOD FOR THREE-DIMENSIONAL ADDITIVE MANUFACTURING OF A WATER GLASS ARTICLE

PROCÉDÉ DE FABRICATION ADDITIVE TRIDIMENSIONNELLE D'UN OBJET EN VERRE SOLUBLE



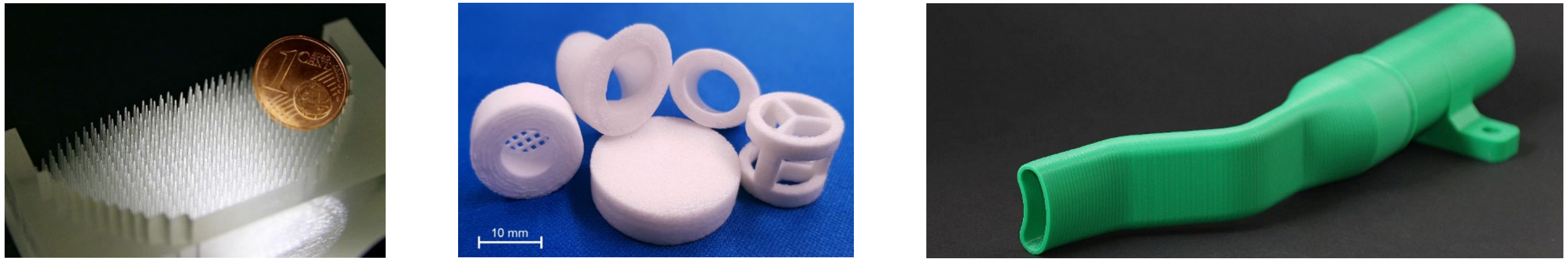
Approach: *targeted water dehydratation using IR radiation*

→ Solidification due to polycondensation

Introduction

State of the art – additive manufacturing

Flexible production of complex and individual components using numerous process approaches (SL, L-PBF, FLM, …)



Demonstrators of the additive processes SLA, L-PBF and FLM (Reference: AG Bliedtner / EAH Jena)

Disadvantages in 3D printing:

(1) partially high costs of the previously available feedstocks

(e.g. Stereolithography (SL) polymers > 150 €/kg)

(2) applications for glass materials mostly on a laboratory scale

(poor (contour) accuracies, inhomogeneities, post-processing steps, …)

Introduction

State of the art – additive manufacturing (glass)

Possible disadvantages:

- Insufficient resolutions and accuracies

  → *especially Fused layer modeling (FLM)*

- Insufficient surface qualities

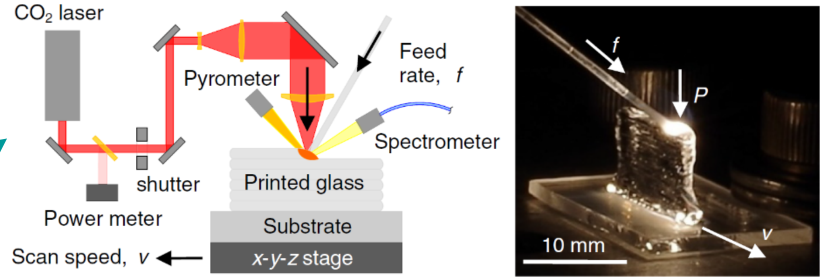
  → *especially for powder-based processes*

- Multi-stage postprocessing

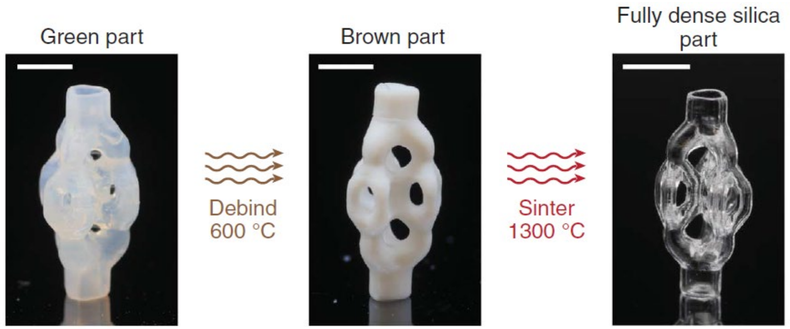
  → *especially debinding and sintering*

- High system requirements

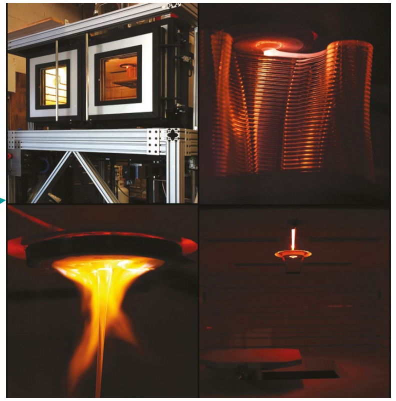
  → *especially high-temperature FLM*



Filament based 3D printing of glass [Luo18]



Post-processing steps of the micro-CAL-process [Too22]


Setup and process technology of the material extrusion of glass [Ina18]

Introduction

Motivation

Additive Manufacturing based on Waterglass:

Combine advantages of previous 3D printing approaches!

- **High resolution of Stereolithography-parts**

+

- **Resistance of silicate components**

→

inorganic 3D components of flexible geometry

- High resolution + high resistance
- Properties specifically adjustable using additives
- inexpensive (waterglass ≈ 10 €/kg)
- eco-friendly and sustainable

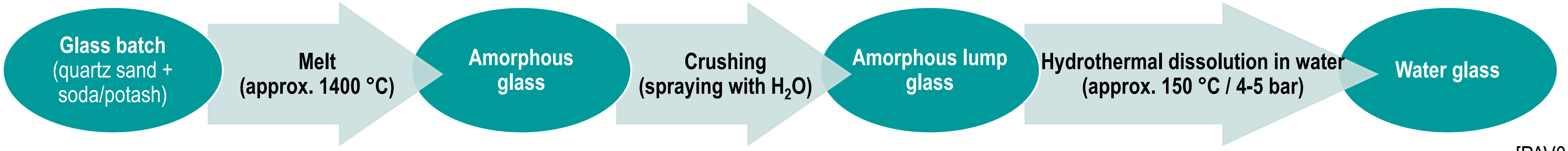
→ Substitution of conventional processes and of plastics by establishing a new additive manufacturing process based on water glass

Liquid alkali silicate (water glass)

definition

- alkali silicates = solid (amorphous) alkali silicates and their (aqueous) solutions **(→ „water glasses“)**
- in generell: **x SiO_2 · y Me_2O** (· z H_2O) Me = alkali metal (Na, K, Li)

Production



[PAV05]

Liquid alkali silicate (water glass)

Key values

- Alkali module M: $SiO_2 : Me_2O$

(molar ratio) $$MVZ = \frac{n\ SiO_2}{n\ Me_2O}$$ (weigh ratio) $$GVZ = MVZ \cdot \frac{M\ SiO_2}{M\ Me_2O}$$ usually between 1.6 and 4

Alkali module ↑ → pH value ↓ / density ↓ / viscosity ↑

Alkaline / low modulus water glasses:	MVZ < 2.5	→ higher strengths / slower condensation
Neutral / medium modulus water glasses:	MVZ = 2.5 – 3.4	
High silica acid / high modulus water glasses:	MVZ > 3.4	→ higher chemical resistance

- Solids content: adjustable by the addition of water usually between 30 und 50 wt.%

solids content ↑ → density ↑ / viscosity ↑

Liquid alkali silicate (water glass)

Previous applications of "water glass"


Application in the construction industry for sealing (Sailer Markus GmbH, 2022)


Application in agriculture as a tonic against grape rot (LVWO Weinsberg, 2007)


Application as a sealant against radioactive radiation at the Fukushima nuclear power plant (Deutschlandfunk, 2011)

→ chemical-, temperature- and weather-resistant, durable, high-strength, sealing ...

Application in 3D printing

- offers for the first time the possibility to produce inorganic 3D components directly from the liquid phase
- Physical solidification by thermal removal of water → **Condensation and gel formation**

[Pav05] [Rog09] [Pol12]

Single layer experiments

Aims

→ Functional proof of process on single layers

→ Investigation of fundamental interactions between laser radiation & material

- cure time and depth as a function of laser parameters (P, v_s, d_f, …)
- achievable properties (layer thickness, homogeneity, stability, etc.)

Surface energie (exposure):

$$E_{max} = \frac{P_L}{v_s \cdot h_s}$$

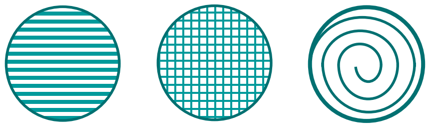
[Geb16]

Cure depth:

$$C_d = D_p \cdot \ln\left(\frac{P_L}{v_s \cdot h_s \cdot E_c}\right)$$

?

→ Evaluation of suitable scanning strategies for homogeneous layer curing



meander / cross / spiral
(with or without contour line)

Single layer experiments

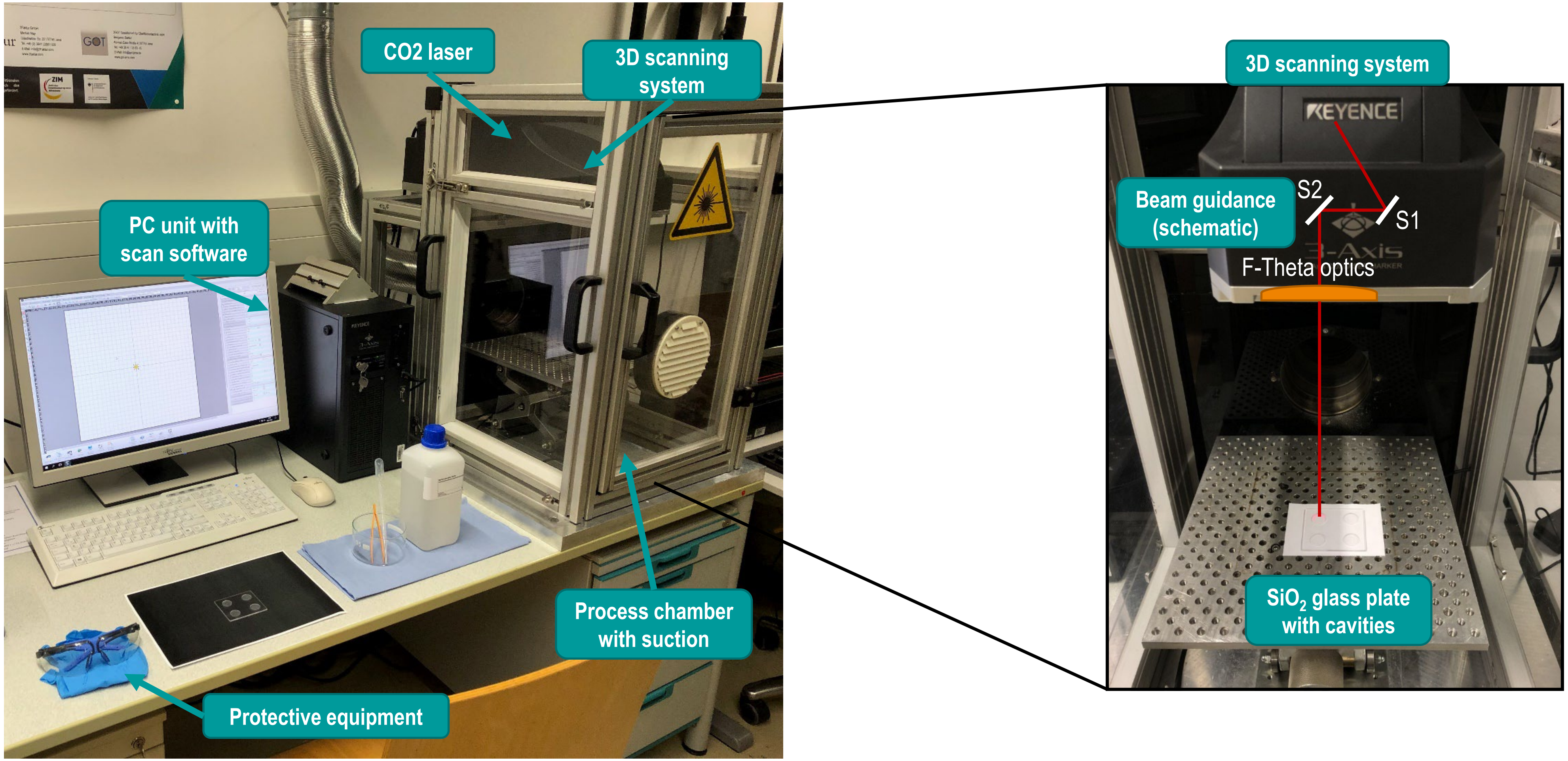
Material selection

* provided by IGP Chemie GmbH

	Sodium silicate		Potassium silicate	
	NaWg 40/42	NaWg 44	KWg 28/30	KWG 35
Molar ratio	3.21	2.77	4.00	3.34
Weigh Ratio	3.11	2.69	2.55	2.13
Solids [%]	36.86	44.33	29.27	34.74
Viscosity dyn. [mPa·s]	150 - 400	2670	130	?
pH value	11 - 12	11 - 12	11,5	11,4

Single layer experiments

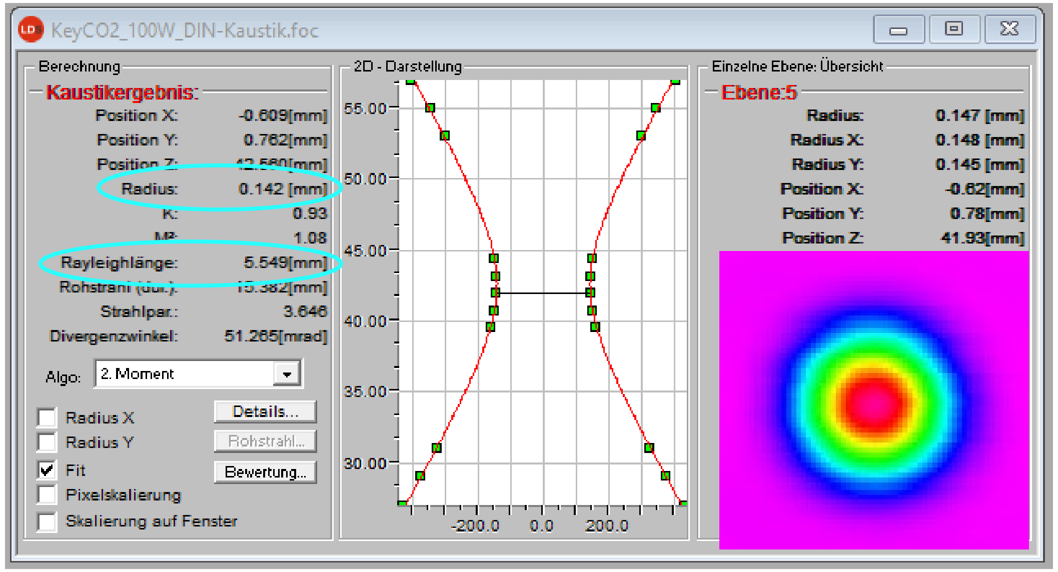
Experimental setup



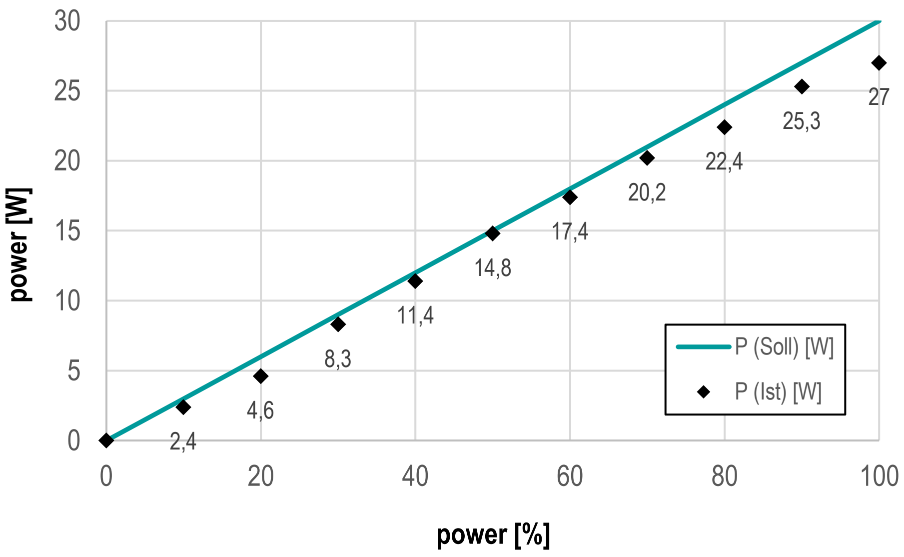
Single layer experiments

Characterisation - Setup

Laser beam caustic



laser power



parameters

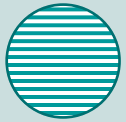
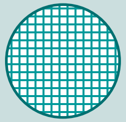
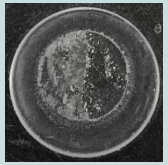
wavelength	focal length (optic)	focus diameter	power P_{max}	beam velocity v_s
10.6 µm	300 mm	284 µm	30 W	6 m/s

Single layer experiments

Scan concept

options:

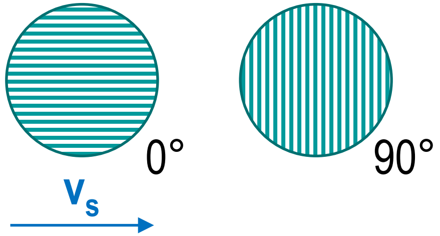
(with or without contour line)

meander / lines	cross	spiral
		
- directionality - „cross-linking“ only in one direction - shape accuracy insufficient	- generally suitable - less directional - better cross-linking / homogeneity	- Not suitable - energy accumulation in the middle - defects / adhesions to platform
		

Single layer experiments

process window

- circle contour (d = 10 mm)



P = 27 W (100%)
LA = 100 µm
n = 6 (3 scans per direction)

v_s variable
(1700 - 4100 mm/s)

(1) Removal of solidified layer

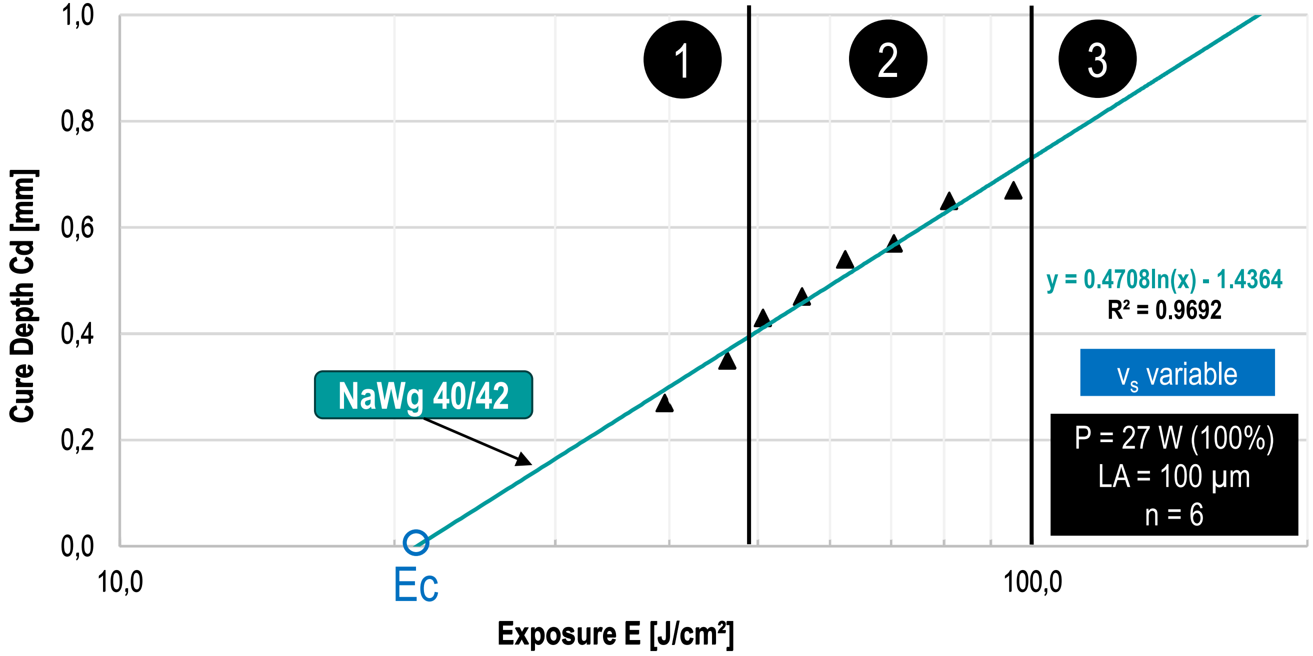
(2) Layer thickness measurement

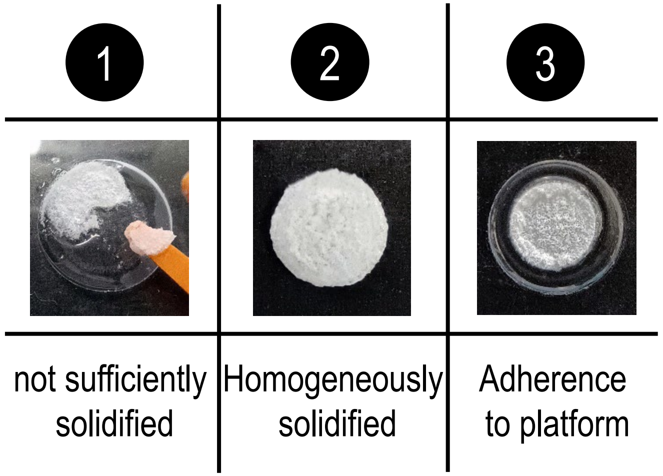
→ Cure depth as a function of the energy input ("working curve") to determine possible resolutions (layer thicknesses)

Single layer experiments

process window

Depth of cure as a function of energy exposure





$$C_d = l_\alpha \cdot \ln\left[\frac{P}{v \cdot h_s \cdot E_c}\right]$$

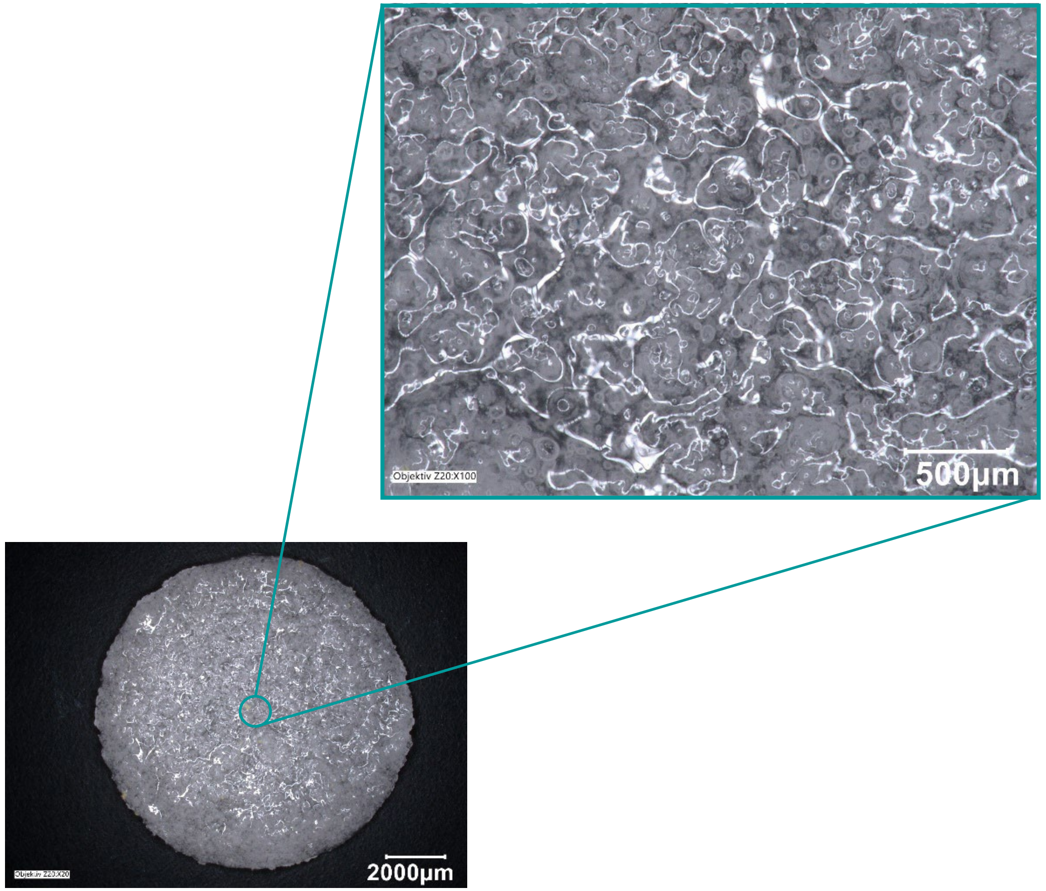
l_α ~ 500 µm
(accumulated)

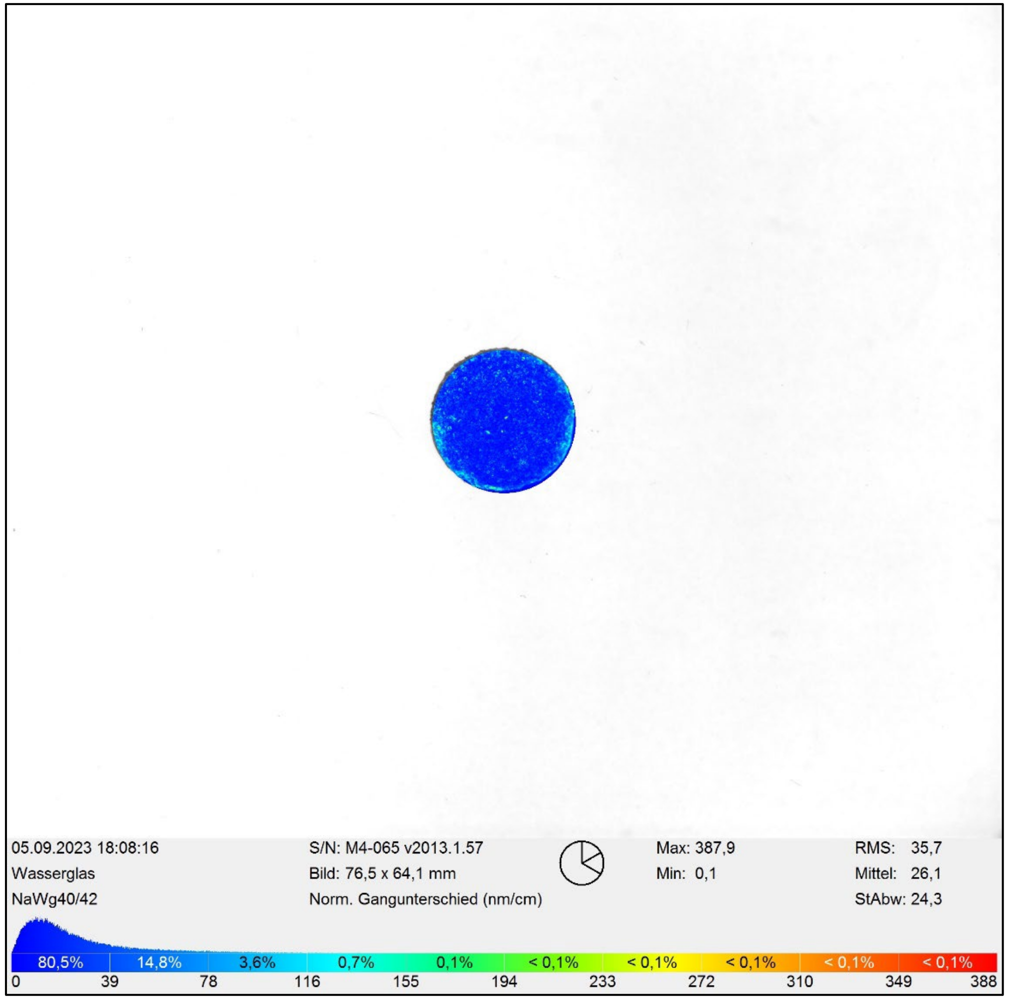
C_d Cure Depth, E_c Critical Exposure, l_α Penetration Depth

Single layer experiments

Residual stresses

- NaWg 40/42 with partly glazed structures



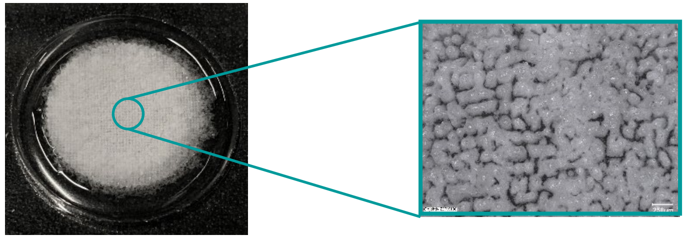


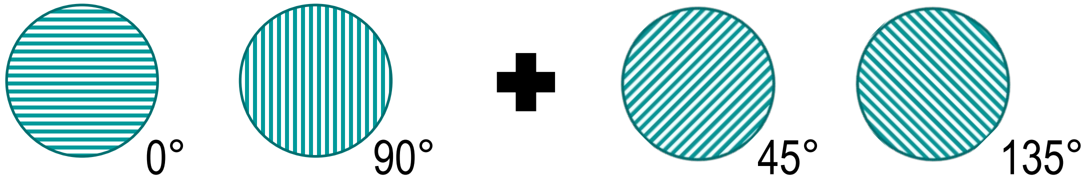
→ Normalized Retardation – mean value ~ 26,1 nm/cm

Single layer experiments

problems and approaches to solving them

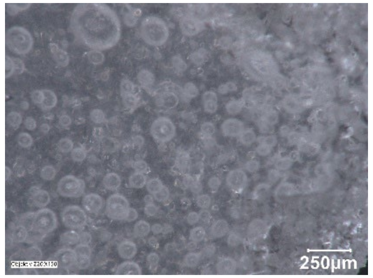
- **Cross pattern** visible from laser scanning → adjust scan concept (also under 45° direction)





- **Damaged layers** due to too much energy input per time→ more repetitions (number of scans) / v_s and LA ↑

- **bubbles** in the layer → careful filling of the material, but with some parameters unavoidable



Conclusion

- Layer-by-layer solidification of alkali silicate solutions by means of CO_2 laser radiation is generally possible

- Equations of stereolithography are generally applicable to the new material

    → *Layer thickness can be adjusted specifically*

- Energy input should not be too fast (layer defects/heat build-up)

- Current experimental setup only suitable to a limited extent

    → *beam properties* ↔ *insufficient resolution*

    → *Adaptations necessary for 3D components*

Outlook

Further experiments:

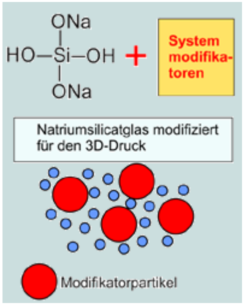
- Comparison of different material systems (WG suspensions, additive addition) and investigation of the resulting layer & component properties

→ *Addition of Li- to Na- water glass increases e.g. chemical resistance* [Rog21]

→ *Addition of K- to Na- water glass increases e.g. the strength* [Rog21]

→ *Addition of additives to increase strength (metal oxides e.g. Fe, Ti) or colouring (e.g. Fe_2O_3)*

→ Additives max. 60 wt.% → too high content increases viscosity too much (handling!) [Pol12]



Addition of additives for modification

- Transfer to 3D parts (layer bonding, resolution, contour fidelity, strength)
- Investigation of the sample structure (crystalline/amorphous fractions) by means of X-ray spectroscopy
- Sintering tests for the production of (partially) transparent components

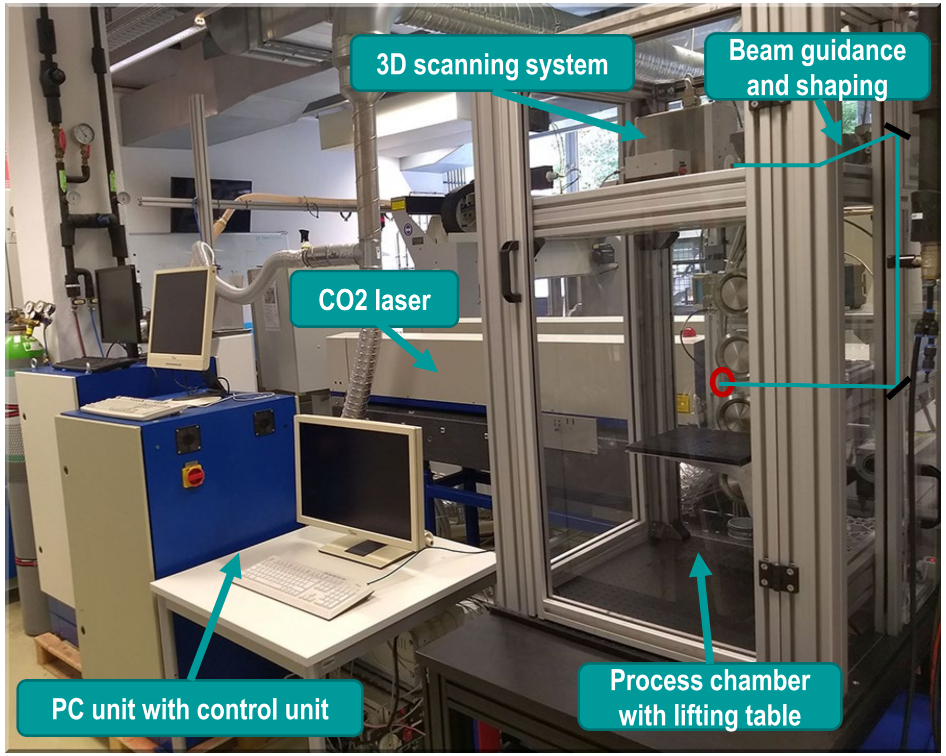
Applications:

- Highly resistant prototypes, precision mechanics (e.g. housings for opt. sensors), microlens arrays (optical separation of channels), coating on LTCC ceramics

Outlook

System Setup:

- Development of a system with wide parameter range (P, v_s, d_f) due to suitable beam guidance and shaping



New experimental setup under construction (600W-CO_2 laser with 3D scanning system)

To Do‘s:

- Interconnection of laser and scanner control
- Protection of the optics (crossjet, protective window)
- suitable material container (alkaline solution!)
- Material delivery system (wiper/squeegee)
- Extraction device (for any vapours that may occur)
- Sensors (temperature, air humidity)

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Thank you for your attention!

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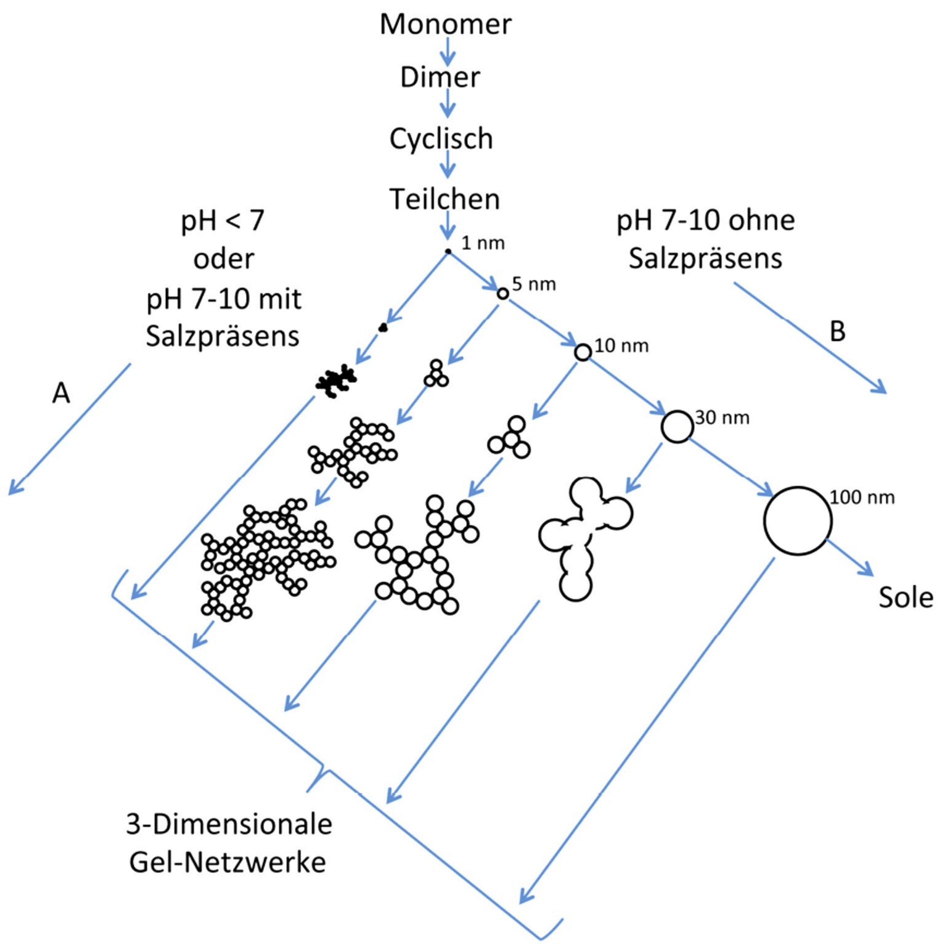
Anhang

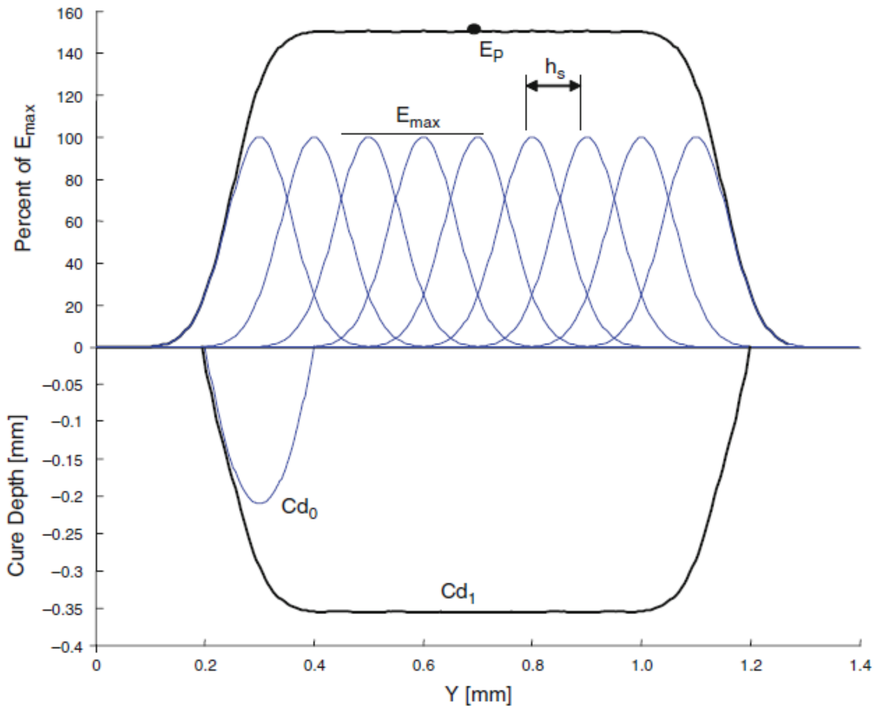
Lithiumsilikat	MVZ = GVZ x 0,497
Natriumsilikat	MVZ = GVZ x 1,032
Kaliumsilikat	MVZ = GVZ x 1,566

Umrechnung MVZ <-> GVZ



Theorie zur Aushärtung der Wassergläser durch Polymerisation nach Iler [Ile79]

Akkumulation der Flächenenergie



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Externe

Promotion

EAH Jena
Prof. J. Bliedtner

TU Ilmenau
Univ.-Prof. E. Rädlein

3Faktur

SCHOTT
glass made of ideas

IGP
CHEMIE

peako

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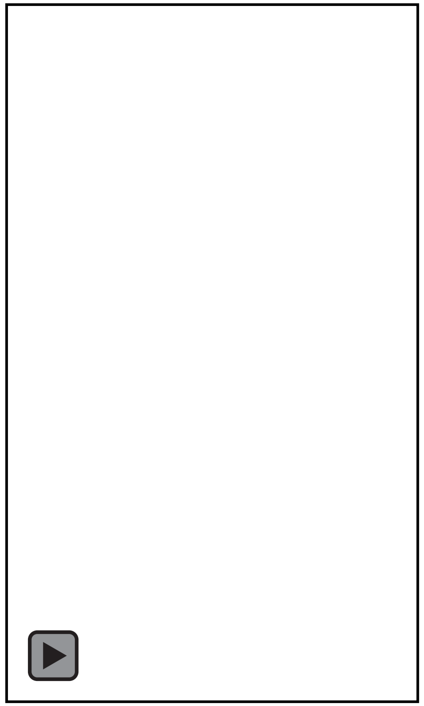
Experiment 3D-Formkörper

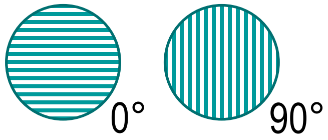
Einfacher Vorversuch

an einem CO_2-Laser (Fa. Keyence)

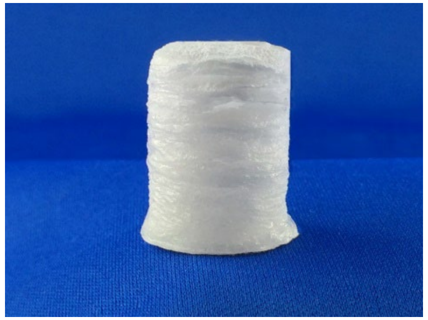


Material:
- Natronwasserglas

Parameter:
- Kreis 20 mm Ø
- Kreuzmuster



- d = 300 µm
- P = 100 % (30W)
- v_s = 3500 mm/s
- n = 2



- zylindrischer Formkörper aus ca. 100 Schichten
- Durchmesser = 10 mm und Höhe = 50 mm