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Development of a laser-based glass sealing joining process for the fuel cell manufacturing

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Abstract

In the Central Technology Division of Forschungszentrum Jülich GmbH procedures and manufacturing concepts used in production of stationary and mobile fuel cell stacks on the basis of the material developments of the involved research institutes are developed. From essential meaning is the application of self developed glass sealing materials as joining and isolation medium. The use of glass sealing material is up to now limited on the furnace technology with low heating and cooling rates. The potentials of the laser as adaptable tool for manufacturing and repair of the fuel cell stacks should be evaluated within the scope of this research study.

Keywords: laser; glass sealing; fuel cell

1. Introduction

In the production of the high temperature fuel cells (SOFC) (Fig. 1) joining processes which allow a gas proof and electrically isolating connection of metal components are required.

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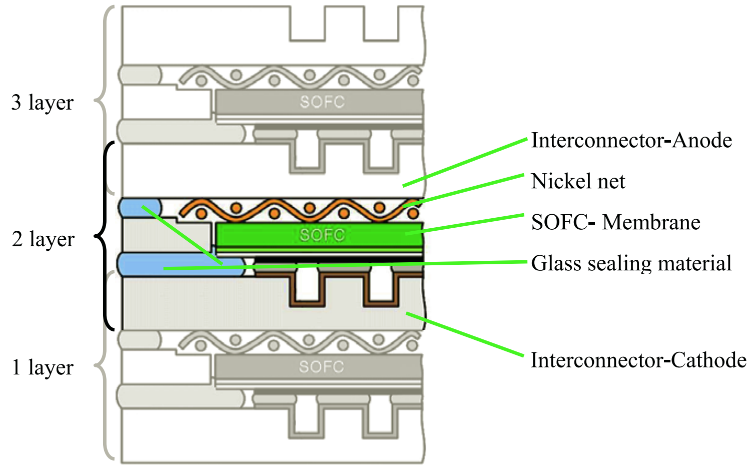

Fig. 1. Schematic diagram of a 3 layer-SOFC stacks

The glass sealing process also belongs to it. Today state of the art is the joining process in a furnace. The layers of the SOFC - stack on which a contour of glass sealing paste with a dispenser was applied (Fig. 2), become stacked on each other and added in the furnace at temperatures between 850 °C and 950 °C.

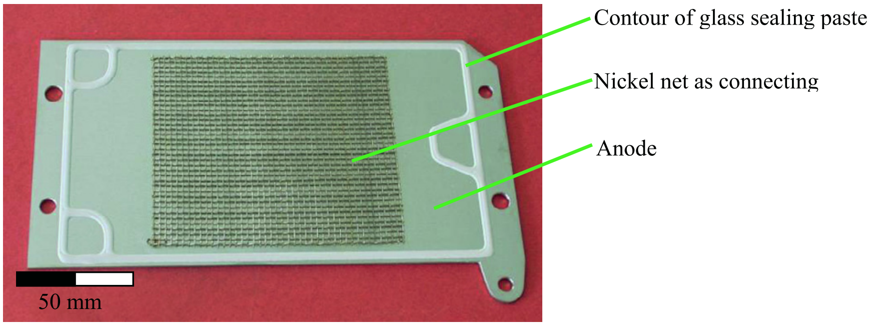

Fig. 2. On the anode applied glass sealing paste

If after joining a layer is leaking, the whole SOFC - stack is useless. The glass sealing material crystallizes by the furnace process to glass-ceramics. To the re-melting of the glass-ceramics more energy and therefore a higher temperature is required than in the pure glass sealing process. Thereby components of the SOFC can be damaged. A process to avoid this complex of problems is laser-based glass sealing joining. In the area of the manufacturing with ceramic components this procedure is already used. However, by the joining of two metal components with a glass sealing the different material properties of the used materials and, especially the Coefficient of Thermal Expansion (CTE) must be particularly considered.

2. Experiments

2.1. Joining of metal components

As opposed to the furnace process the components are not joining simultaneous with the laser-based sealing process. With the laser-based sealing process the laser beam must follow glass sealing contour and melt it continuously. Therefore the laser beam must perform a relative movement to the work piece. This can be realized either with a robot which moves the laser processing head or with a laser scanner whereby only the laser beam is deflected. Alternatively a work piece movement can also occur. The experiments in the following described were performed with different laser-beam facilities (Table 1).

Table 1. Engaged laser- facilities beam

Laser-beam facilities	Wavelength [nm]	Power [W]	Degree of freedom	Mode
Nd:YAG	1064	220	6 (Robot)	pulsed
CO_2	10600	6000	5 (Robot)	cw
Diode	808 + 940	1000	- (static)	cw

The glass sealing materials which were developed in the Forschungszentrum Jülich GmbH/Central Technology Division (CTD) for the SOFC – production were examined. The properties of the glass sealing materials are summarized into the Table 2.

Table 2. The properties of the glass sealing materials [1]

Glass sealing material	BaO [wt-%]	CaO [wt-%]	SiO_2 [wt-%]	Coefficient of Thermal Expansion at 600°C [10^{-6}/K]	Joining temperature [°C]
B	36.72	15.84	46.81	11.9	950
G	34.5	14.87	43.95	10	850
H	48.21	6.05	29.75	9.5	820

The joining experiments were made with metal sheets made of Crofer 22 APU (Table 3). This alloy was developed especially for the application in the SOFC and can minimize on account of its CTE the inducing of strains during the joining process. The metal sheet-thickness amounts to 0.3 mm, 0.5 mm, 1 mm and 2.5 mm.

Table 3. Properties of Crofer 22 APU at 800 °C [2]

Spec. heat [J/kg·K]	Thermal conductivity [W/m·K]	El. resistance [μΩ cm]	Young's modulus [kN/mm^2]	Coefficient of Thermal Expansion [10^{-6}/K]
660	24	115	183 (500 °C)	11.9

For the "couple in" of the laser radiation there are two variations. At the "direct couple in", the laser beam is directly coupled in the glass sealing material, absorbs in it partly and melt it. With the "indirect couple in" the laser beam becomes couple in a metal sheet and the glass sealing material melt by the thermal conductivity in the metal (Fig. 3). By the "direct couple in" the binder contained in the glass sealing paste burns by the effect of the laser radiation with open flame.

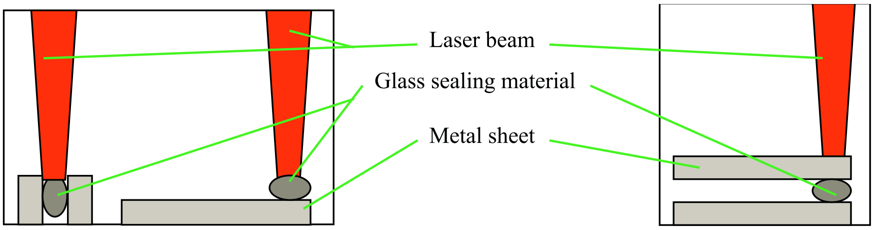

Fig. 3. a) Direct couple in; b) indirect couple in

The binder exists of 95% Terpineol and 5% Ethyl cellulose. α-Terpineol ($C_{10}H_{18}O$) is a clear, colorless liquid of high viscosity, boils at 219 °C and solidifies at 34 °C. The density amounts to 0,935 g / cm^3 (20 °C). The flash point is at 90 °C. α-Terpineol is nearly indissoluble in water. Ethyl cellulose is a hydrocarbon compound and therefore ignitable. The Terpineol evaporates before joining, the Ethyl cellulose is preserved in the glass sealing contour, cannot evaporate completely by the quick heating up and starts to burn.

The metal is higher heated up by the low movement speed of the laser beam and the high energy input per unit length and the binder evaporated by the thermal conductivity in the metal, so that a clean glass sealing contour is formed (Fig. 4). Nevertheless, the binder should be renounced by the laser treatment, because the gaseous binder cannot escape in the short process time from the glass sealing material. This leads to pores in the joint.

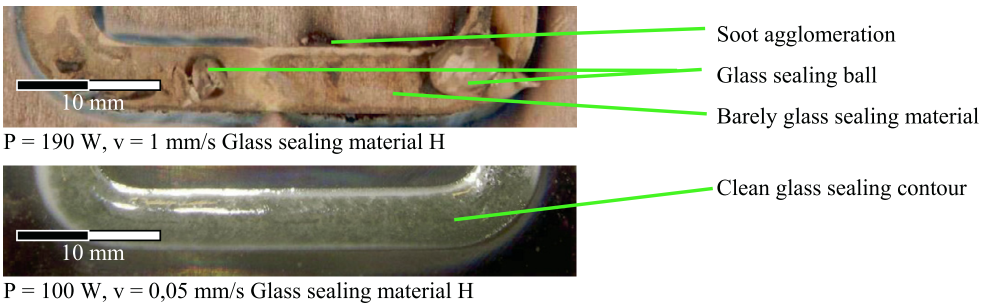

Fig. 4. laser generated glass sealing contour

By the “indirect couple in” the most possible thickness of the metal sheet in which the laser beam becomes couple in must be considered. The difference in temperature ΔT at the top and back of this metal sheet is calculated according the following formula:

$$\Delta T = \frac{\dot{Q} \cdot l}{\lambda \cdot A} \tag{1}$$

$\dot{Q}$: Heat flow [W], l : Thickness of the metal sheet [mm], λ : Thermal conductivity $[\frac{W}{m \cdot K}]$, A: Cross section surface [mm^2]

With P = 800 W, l = 3 mm, λ = 27 W/m·K (Crofer 22 APU) and A = 36mm^2·π (radius of the laser beam spot = 6 mm) a difference results:

$$\Delta T = \frac{800W \cdot 3mm}{27 \frac{W}{m \cdot K} \cdot \pi \cdot 36mm^2} = 786K$$

The joining temperature of glass sealing material G is at 850 °C i.e. on the top of the metal sheet a temperature of 850 °C + 786 °C = 1636 °C must be reached. However, the liquidus temperature of Crofer 22 APU is at 1530 °C, so that the metal will melt before. In any case, the upper metal sheet would be damaged by the high temperature load (Fig. 5). Therefore, the “indirect couple in” makes sense only for thin metal sheets.

Fig. 5. Damaged upper metal sheet a) by spot joining, b) by contour joining

The damage of the upper metal sheet which arises by the "indirect couple in" can be used in a beneficial following described way (pat. pend.). By the joining of two metal sheets the glass sealing material is not applied between both sheets but only on the upper sheet. The glass sealing material becomes melting with a defocused laser beam (r~3 mm), then the laser beam is used highly focused on the metal and drills through the liquid glass sealing material the upper metal sheet. Now the liquid glass sealing material can flow through the accrued hole between both sheets and join them (Fig. 6).

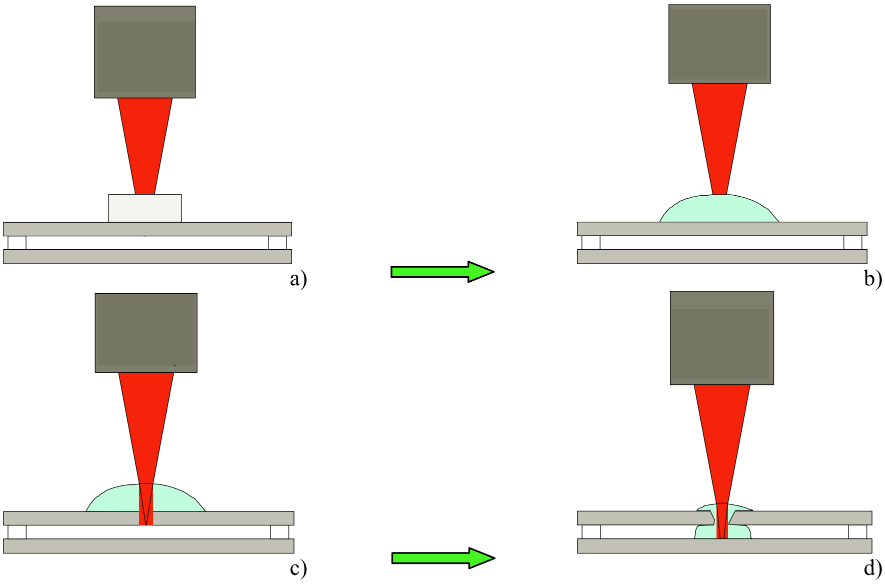

Fig. 6. Schematic diagram of lased-based joining process with a laser-made hole, a) Heating of the glass sealing material, b) Melting of the glass sealing material, c) Drilling of the upper sheet, d) Joining of the both sheets

The experiments show that the upper metal sheet can be drilled with the laser beam through the liquid glass sealing material and the glass sealing material flows through the accrued hole between both sheets (Fig. 7). Tests for a reproducible application are in progress. Actually, the liquid metal flux welds rather both sheets. The application of the ultra short pulse laser could solve the problem of the metal flux however this radiation is also absorbed in the glass.

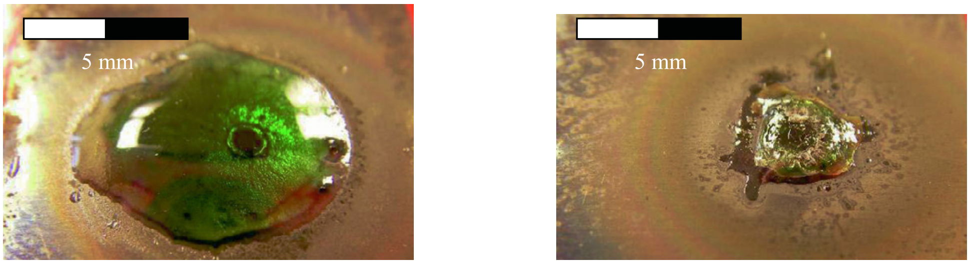

Fig. 7. a) Upper side of the upper sheet, b) Underside of the upper sheet

Another possibility to join two sheets can be performed in such a way that the upper metal sheet is added with a hole before joining and afterwards this is filled with glass sealing material (Fig. 8).

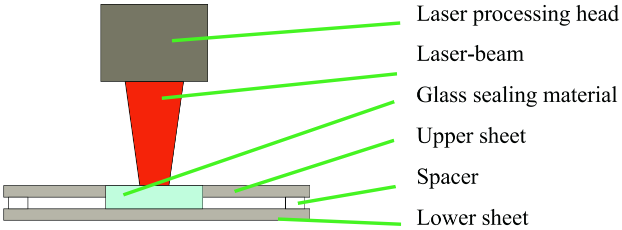

Fig. 8. Schematic diagram of a joining of two metal sheets with a hole in the upper sheet

The metal sheet is destroyed at this point with "indirect couple in" by the laser beam anyway, so it will not come to a firmness decrease by the removal of the material at this area on account of the smaller adhesive surface. Another advantage of this process is the avoidance of an electric short circuit. Because the sheets size is only about 0.5 mm, the volume of the glass sealing material in the hole is not enough to join both sheets reproducible. Two typical joining defects are shown in the Fig. 9. The amount of the glass sealing material often is not enough to bridge the gap between the sheets, so that no joining occurs to the upper metal sheet. If the gap is bridged, the glass sealing material flows on account of the capillary effect between the sheets, the lower metal sheet is thereby highly damaged.

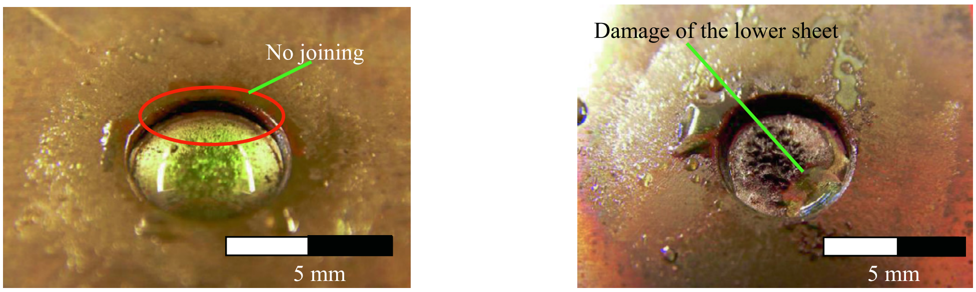

Fig. 9. Joining failure a) no joining with the upper sheet, b) Damage of the lower sheet

A simple additional glass sealing material depot above the hole does not lead to better results. The generating glass sealing ball rolls on the still cold lower metal sheet pulls the glass sealing material from the hole and sticks at the hottest spot of the upper metal sheet, without connection (Fig. 10).

Fig. 10. Glass sealing material depot above the hole a) before, b) after the laser treatment

For a reproducible connection the glass sealing material must be supplied during the process. In addition a powder conveyance with a vibration unit which conveys the glass sealing material powder up to the joining area was developed (Fig. 11).

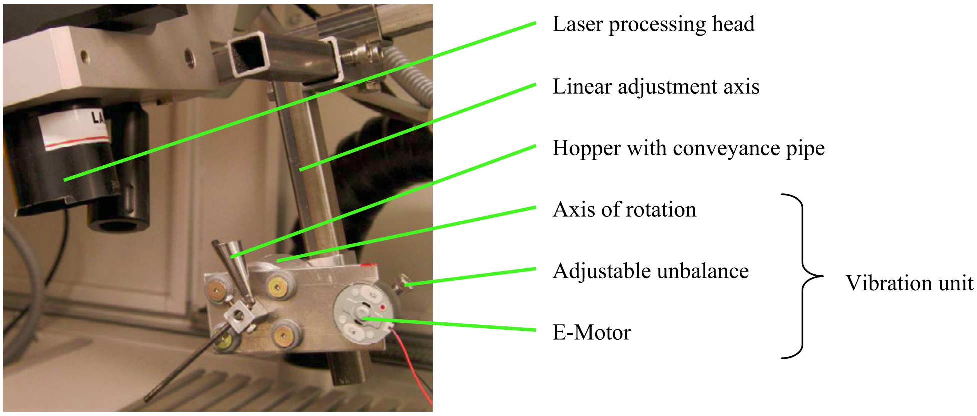

Fig. 11. Powder conveyance

By this powder conveyance several parameters are adjustable like the inclination angle, the electric power and the unbalance radius and in dependence on it the volume stream of the powder for the respective glass sealing material can be adjusted. Because of different grain dimensions of the glass sealing materials, a suitable conveyor process must be determined for every glass sealing material. The first results of the experiments with the powder conveyance show that the joining surface between the sheets has grown around more than the three times what affects directly proportionally the adhesion force (Fig. 12).

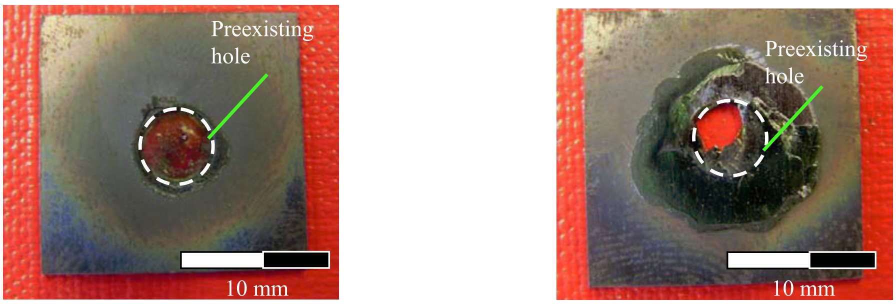

Fig. 12. Glass sealing surface without powder conveyance, b) with powder conveyance

2.2. Repairing of leaky Stacks

The laser as a tool is predestined for the repair of leaky SOFC – stacks. With the laser beam only the leaky area can be warmed up locally and the glass – ceramic becomes melt. The sharp focusing of the laser beam allows even the joining in the gap (h ~ 200 µm) between two sheets. With suitable beam form (big focal length, small angle of aperture) the glass sealing material can be heated up in the depth higher and the sheets are warmed up with the defocused beam (Fig. 13a). The repair experiments became performed with Helium-Leak-Test-Samples (metal sheet measure: 50x50x2,5 mm^3) which can be tested fast and simply for tightness (Fig. 13b).

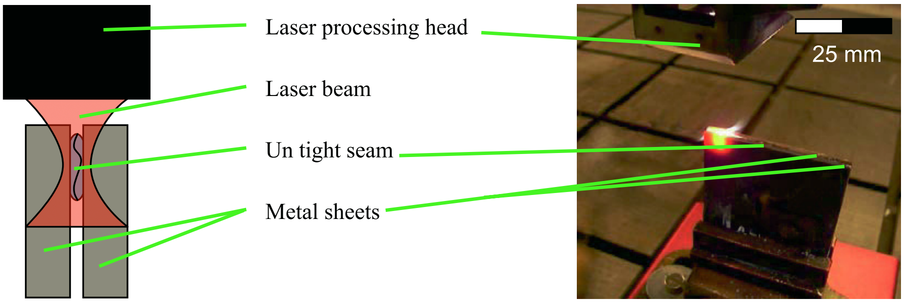

Fig. 13. Repair of SOFC-Stacks a) schematic diagram, b) Helium-Leak-Test-Samples

The first experiments show that it is more favorable to apply additional glass sealing material on the joining area. Both sheets are cooled by this glass sealing material layer and are not damaged and the additional glass sealing material fills the gap between the sheets, so that a connection steel-additional glass sealing material-glass bead occurs (Fig. 14).

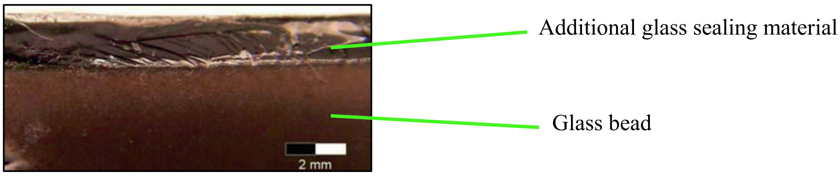

Fig. 14. Opened out Helium-Leak-Test-Sample

Due to the fast cooling down of the components, high thermal strains occur which lead to cracks (Fig. 15a) in the glass sealing material. Especially frequently a laser-generated seam cracks if the laser beam becomes couple in near the seam to join the other side of Helium-Leak-Test-Sample (Fig. 15b).

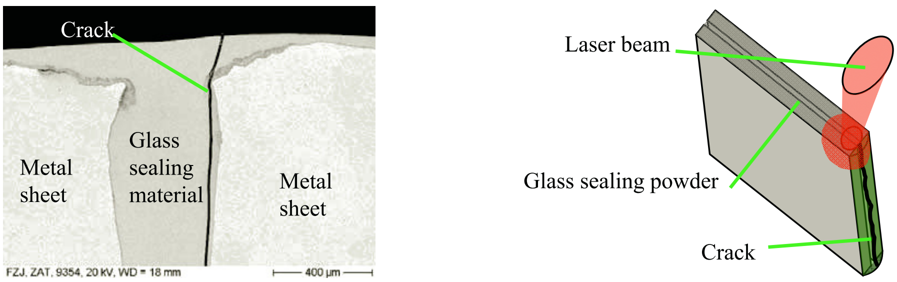

Fig. 15. Cracks in the glass bead a) Crack, b) Inducing of cracks

3. SEM und EDX Verification

To receive knowledge about the structure of the sealed samples, SEM – verifications are performed. The SEM – pictures show another structure of the laser-generated glass sealing materials in comparison to the samples which are soldered in the furnace. The laser-generated samples show an amorphous structure without any crystals. This difference is especially well visible in a sample which became joined and annealed in the furnace, and afterwards became melting with the laser once more (Fig. 16)

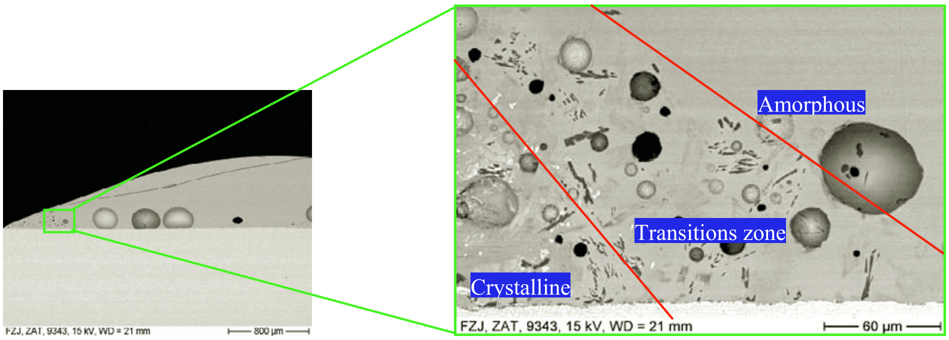

Fig. 16. SEM – picture of furnace joined sample which became afterwards melting with the laser once more

The amorphous structure of the glass sealing material occurs by quick cooling, too fast for crystals growth. By contrast the glass sealing material becomes annealed in the furnace to diminish the thermal strains. This leads to the increase of the firmness of the joining. By this slow cooling ceramic crystals form in the glass sealing material which raise the CTE of the glass sealing material, so that it is adapted to the CTE of the steel. The advantages and disadvantages of the amorphous glass sealing material are summarized in the Table 4.

Table 4. The advantages and disadvantages of the amorphous glass sealing material

Advantage	Disadvantage
Annealing of the micro cracks at high temperatures	Change of properties at glass transition temperature (T_g)
Good wet ability of the metal sheet	High warming up is necessary (with Nd:YAG)
Homogeneous structure without cracks	No mechanism to reduce strains

The reaction zone between steel and glass sealing material was examinated with the EDX – analysis (Fig. 17). It does not differ from the reaction zone of a sample joined in the furnace and amounts about 1 µm. A broader reaction zone was expected on account of the higher temperature by the laser-beam joining.

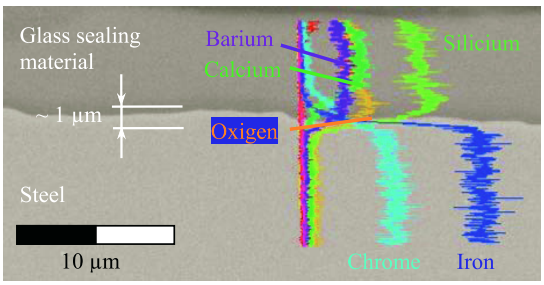

Fig. 17. EDX – Analyse of the reaction zone between steel and glass sealing material

4. Verification of Melt-Dynamics

For the verification of the melt-dynamics high-speed videos were made. The rate amounted to 210 P/s. After the melting of the glass sealing material first a torus forms on account of the surface tension which contracts with rising temperatures to a ball (Fig. 18a, b).

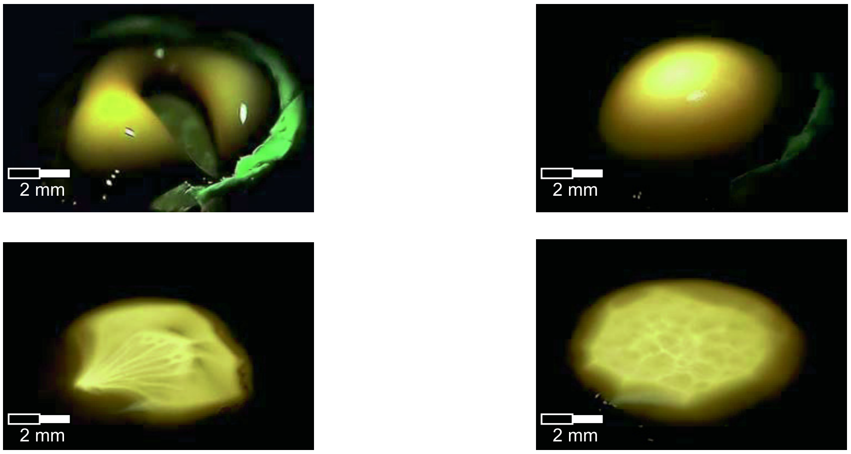

Fig. 18. High speed pictures a) Forming of the torus, b) Glass ball, c) Marangoni- Convection from outside to inside, d) Converse of the convection direction

During the warming up convection flow develops in the glass sealing material. This Marangoni-convection runs first from the outside of the sample to the inside to the laser beam and converse after some time its direction (Fig. 18 c, d). This converse of direction in the glass sealing material should be cleared in continuing investigations.

5. Summary and Outlook

Metal components can be joined by the introduced laser-beam process with glass sealing materials. The laser-beam-joining with glass-ceramic additional materials offers an adaptable alternative to already existing processes. The selective warming with the laser beam allows new process variations which cannot be realized in the furnace. The different wavelengths of the laser radiation have a big influence on their absorption in the glass sealing materials. This can be used by the process optimization, e.g., the CO_2-radiation can be used for melting the glass sealing material and the Nd:YAG-radiation for warming up and oxidizing the metal. The application of a Galvano-scanner would also allow a quasi-simultaneous joining of two components.

The selective processing predestines this procedure for a repair concept for SOFC-components. Besides, only the damaged area can be sealed without stressing the remaining component intensely. This procedure variation cannot be realized by a furnace joining process.

To achieve better process understanding the transmission, the reflection and the absorption should be analyzed at the transformation temperature of the glass sealing material. Additional knowledge about the interaction between glass sealing material and laser radiation during the melting process can be won by this analysis.

References

1. Gross S.M., Koppitz T., Remmel J., Reisgen U., Glass-ceramic materials of the system BaO-CaO-SiO2 as sealants for SOFC applications. Ceram. Eng. Sci. Proc. 26 (2005), 239-245
2. Crofer 22 APU Werkstoffdatenblatt Nr. 4146 Ausgabe Juni 2008