

Enamelling of glass by CO₂ laser treatment

Claudia Buerhop and Rudolf Weißmann

Institut für Werkstoffwissenschaften III (Glas und Keramik), Universität Erlangen-Nürnberg, Erlangen (Germany)

Dedicated to Prof. Dr. Heribert J. Oel on the occasion of his 70th birthday

Decoration of glass using enamel is interesting for hollow glassware as well as for flat glass sheets. Laser radiation can be used advantageously to increase the temperature of the product locally. The reactions which take place during CO₂ laser heat treatment of a conventional PbO-containing frit are discussed intensely. Pyrometrical temperature measurements accompany the experiments to investigate the temperature development during CO₂ laser irradiation. At temperatures above T_g optimal results concerning low surface roughness, high brightness and intensive colouration are obtained without deformation of the shape of the product. Very promising results show that higher temperatures can be achieved by laser application and therefore PbO-free frits can be used.

Emaillieren von Glas mit CO₂-Lasern

Das Dekorieren von Glas mit Emails ist sowohl für Hohlglas als auch für Flachglas interessant. Die Laserstrahlung kann hier vorteilhaft zur lokalen Temperaturerhöhung von Produkten eingesetzt werden. Die Reaktionen, die während der CO₂-Laser-Wärmebehandlung von konventionellen PbO-haltigen Fritten stattfinden, werden ausführlich diskutiert. Pyrometrische Temperaturmessungen begleiten die Versuche, um die Temperaturentwicklung während der CO₂-Laser-Bestrahlung zu untersuchen. Bei Temperaturen oberhalb von T_g werden optimale Ergebnisse bezüglich niedriger Oberflächenrauigkeit, hohen Glanzes und intensiver Farbwirkung erzielt, ohne daß das Produkt seine Form verliert. Die vielversprechenden Ergebnisse zeigen, daß höhere Temperaturen durch den Lasereinsatz erreicht werden und daher PbO-freie Fritten verwendet werden können.

1. Introduction

The significance of glass enamels for decorating purposes in the glass industry grows [1 and 2]. A glass enamel consists generally of a transparent frit and the staining-colour constituents. Normally, the enamelling process is performed by heating the entire product in a furnace at temperatures below T_g [3 and 4]. This makes sure that the glass does not lose its shape but requires on the other hand high amounts of PbO in the frit. For this reason, the conventional decorative enamels flow easily at rather moderate working temperatures.

Recent investigations demonstrated that CO₂ lasers can be used advantageously for glass surface treatment, like polishing of lead crystal glass [5]. Here, the ground facets of crystal glassware are smoothed due to the viscoelastic flow of the material after the strong heating of the irradiated area.

This effect can also be used for decorating glass products covering the surface partially or totally with glass enamel [6]. Figure 1 demonstrates schematically the enamelling process using laser radiation. A glass is covered loosely with the enamel which consists of frit and colour particles. When the laser beam passes the surface, the particles under the beam are heated, they move

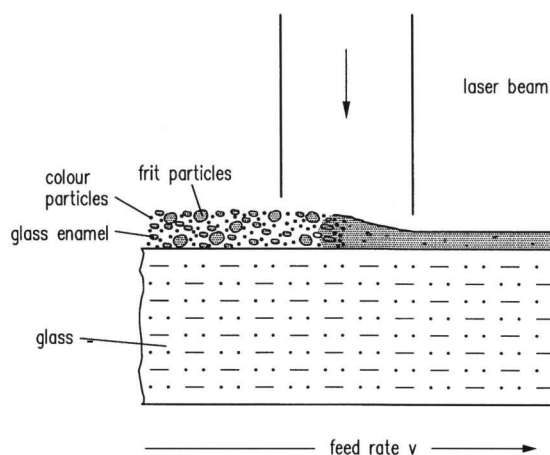


Figure 1. Enamelling using laser radiation.

closer and melt together. The result is a smooth coloured surface layer on the transparent glass.

There are a lot of advantages of CO₂ laser application compared to traditional heat treatment in a furnace. Different and more resistant colour pigments (like in the porcelain industry) might be applied to improve the dishwasher stability [7]. It also might be possible to decorate glasses, which are normally difficult to handle due to missing frits and colours. Another advantage may be the combination of various fabrication steps, i.e. bending and enamelling of windshields.

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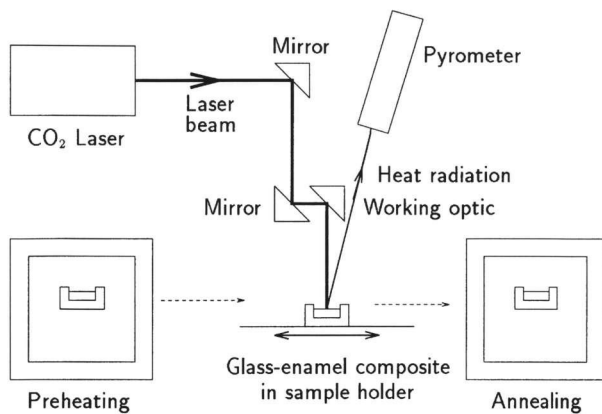


Figure 2. Experimental set-up.

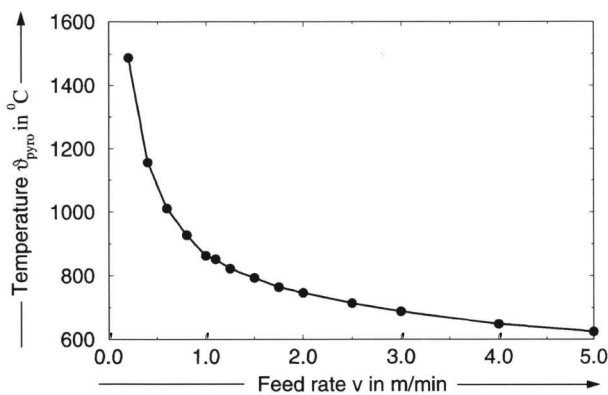
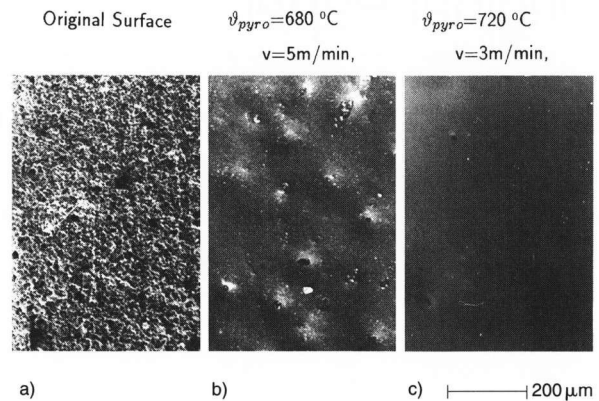


Figure 3. Measured temperature development at the glass surface during CO_2 laser irradiation.

The fundamentals of the interaction between CO_2 laser radiation, $\lambda = 10.6 \mu\text{m}$, and glass are discussed extensively in [8]. The infrared laser radiation is absorbed strongly in silicate glasses due to the Si=O vibrational band. Within a narrow surface region the energy is converted to heat and is distributed in the material by heat conduction and heat radiation. Glass is a material with a very low heat conductivity which, on one hand, enables local heat treatment but, on the other hand, leads to steep temperature gradients and therefore to thermal stresses. These stresses have to be minimized to guarantee a successful laser treatment of glass. Preheating at temperatures about T_g reduces the temperature gradient. The viscoelastic state is reached almost immediately, when the additional energy of the laser beam is deposited, and stresses are destroyed.

The aim of this work are fundamental investigations of the enamelling of glass by CO_2 laser radiation. The reactions of commercially available frits (containing high amounts of PbO) and pigments under laser irradiation are studied. On the basis of these studies, new frits and colours should be developed which are more suitable for a laser treatment.



Figures 4a to c. Melting behaviour of a lead-containing frit with CO_2 laser, $I = 180 \text{ W/cm}^2$.

2. Principle of the experimental procedure

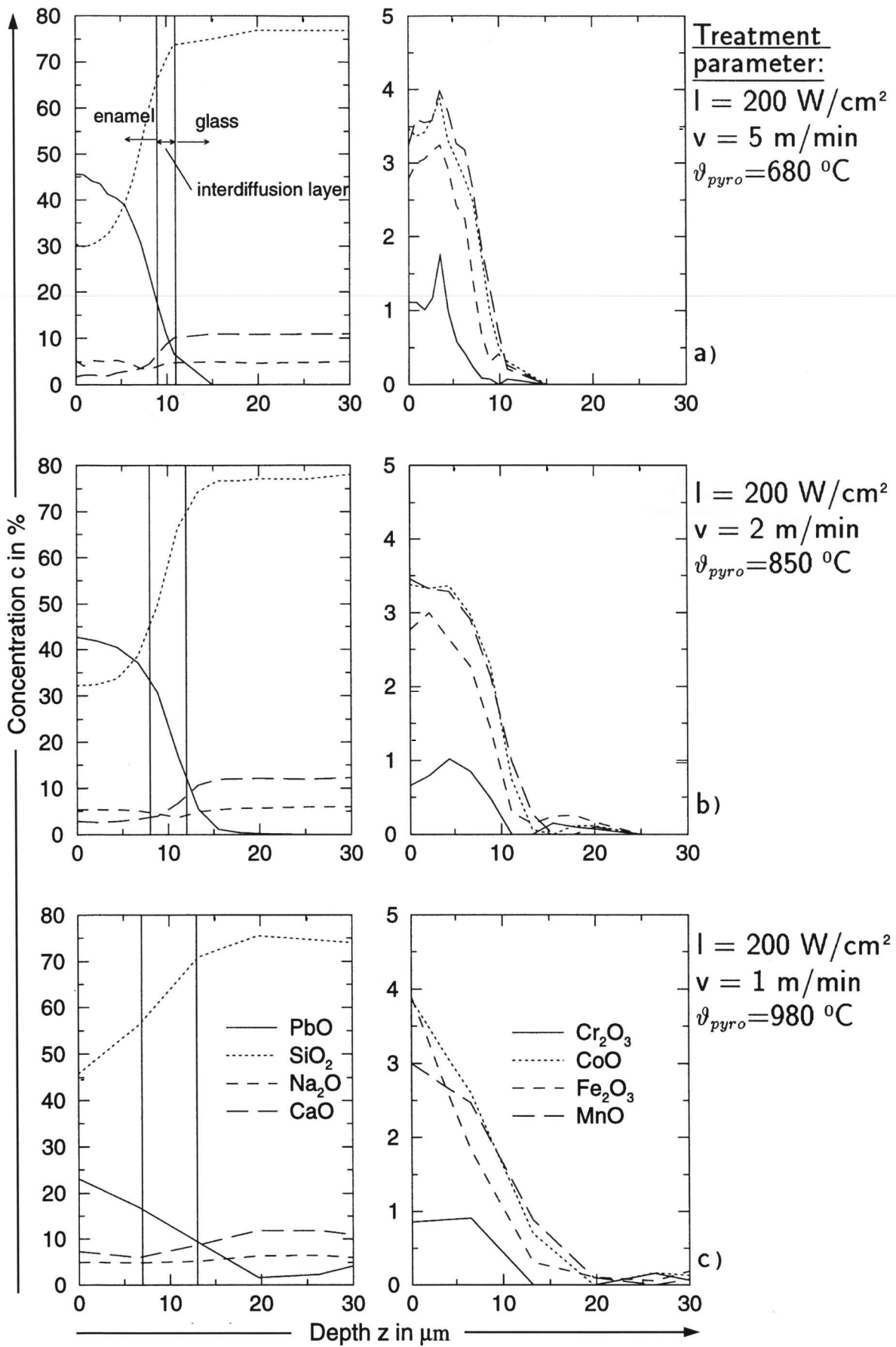
For the enamel preparation commercially available frits (containing 40 to 60 wt% PbO) were ground to a particle size distribution with $d_{50} = 10 \mu\text{m}$. For colouring effects the transparent frit was mixed with different colouring agents (Fe_2O_3 , Cr_2O_3 , MnO , CoO) to get colours like black with a mixing ratio of frit to colour pigment $\approx 70 : 30$. Then, an organic solution was added to the homogenized powder to enable screen printing. Depending on the particle size distribution, generally, the ratio powder : organic solution $\approx 70 : 30$ was used for the experiments. After a direct or indirect printing process of the enamel onto flat glass samples, the glass-enamel composite was dried at moderate temperatures to get rid off the organic which would burn out lightly during the CO_2 laser irradiation.

The experiments were performed using a 4 kW CO_2 laser (Eurolas 4000). Figure 2 shows the experimental set-up. The laser radiation was directed onto the sample using water-cooled copper mirrors. The working optics produced a rectangular beam cross-section. The intensity distribution was almost homogeneous to realize a uniform treatment of the sample.

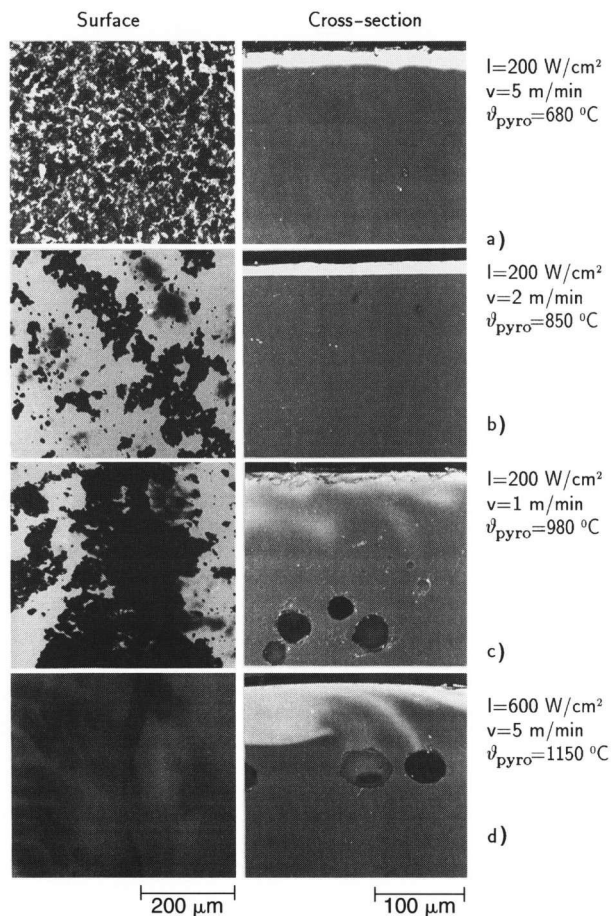
The samples were preheated in a furnace at temperatures in the range of T_g . For the experiments the power density I , the feed rate v and the size of the irradiated area A were varied. After irradiation the samples were cooled down slowly to room temperature.

During the laser treatment the temperature of the sample was registered using an infrared pyrometer (Firma Kleiber, Erlangen (Germany), type 0247/5) with a spectral range of 4.8 to 5.2 μm and measuring temperatures of 400 to 1600 $^{\circ}\text{C}$. The emissivity ϵ was taken as constant, $\epsilon = 0.8$. The measuring spot of the pyrometer was much smaller than the irradiated area.

The samples were characterized in terms of surface morphology, surface roughness, brightness, colour using an SEM, Perthometer, reflectometer (Dr. Lange, Berlin (Germany)), and an CIELAB analyzer (Elrepho 2000, Datacolor AG, Zürich (Switzerland)) [9], respectively.



Figures 5a to c. EDS analysis, change of component concentration of a laser-treated enamel on glass as a function of depth.



Figures 6a to d. Backscattering pictures of the surface and the cross-section of an enamel.

3. Results

3.1. Material behaviour under laser irradiation

Due to the absorption of the CO₂ laser radiation, the glass is locally heated. The measured temperature ϑ_{pyro} as a function of feed rate is shown in figure 3. Higher temperatures are measured for lower feed rates, because the interaction time is longer. Note that the measured temperature is not the real temperature of the glass surface, but the mean temperature of a surface layer of approximately 200 μm thickness, which is intensely discussed in [8]. The actual temperatures can be up to 150 K higher than the measured temperature, depending on the power density of the laser radiation.

Depending on the temperature and the interaction time the glass reacts differently in respect of:

- heating,
- stress generation,
- wetting,
- softening, melting,
- diffusion,
- gas development, bubble growth,
- decomposition.

First, the glass is heated up. If the temperature gradients become too large, induced tensile stresses may lead

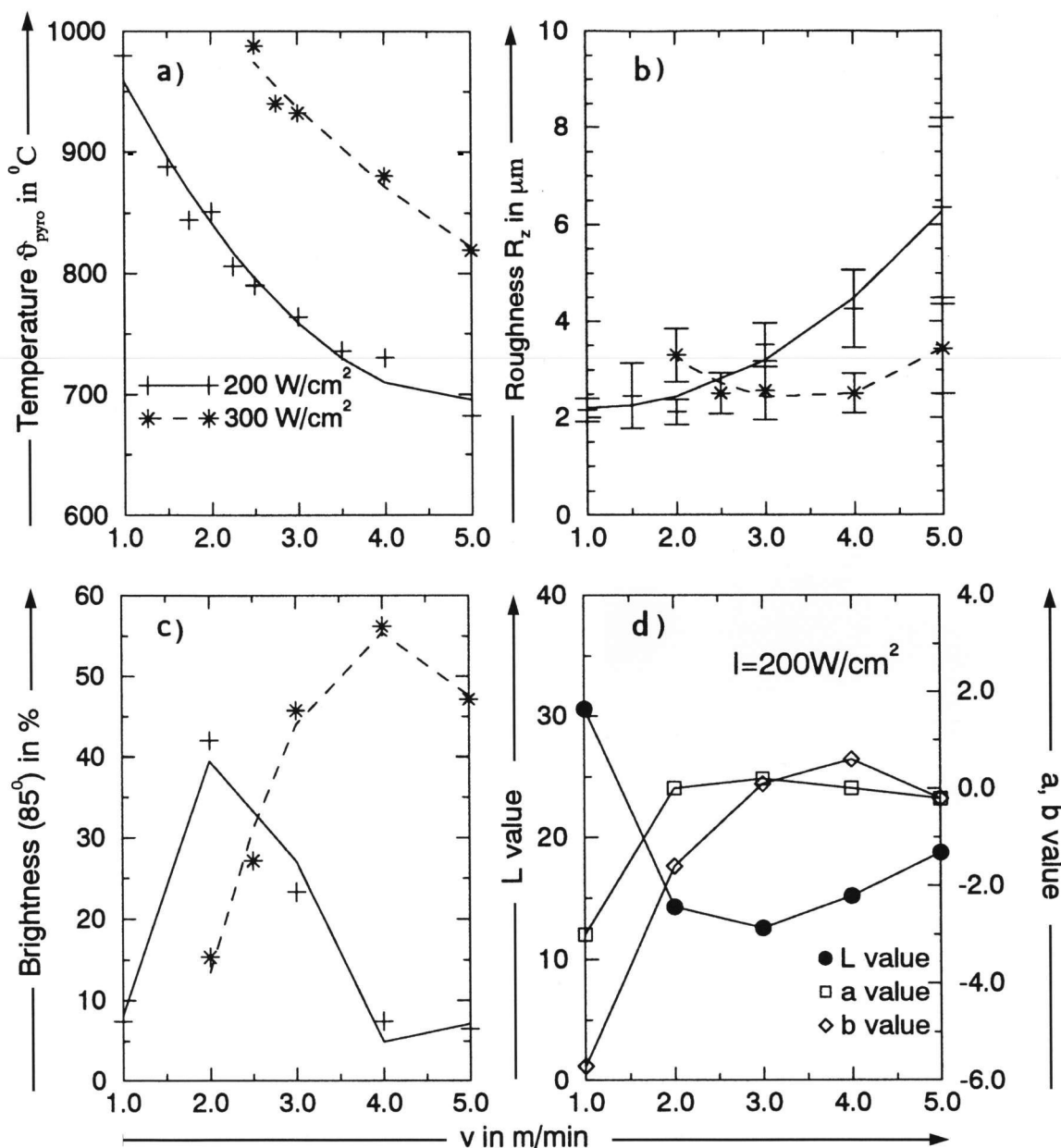
to cracks and failure of the product. By preheating to temperatures just below T_g these critical stresses can be avoided. At higher temperatures the frit particles start to melt and wet the glass surface. Increasing the temperature, the viscosity of the frit is reduced so that the glass is covered completely with the coating. At very high temperatures gases are released and bubbles grow. Additionally, diffusion between the coating and the substrate glass takes place and some constituents may decompose.

Figures 4a to c show the important steps of the laser enamelling process for a variation of the feed rate. The original surface of the coating appears rough and porous (figure 4a). At high feed rate, and correspondingly relative low temperatures (figure 4b), the frit begins to flow and wet the substrate glass due to the surface tension of the PbO-containing frit. For lower feed rates and higher temperatures (figure 4c), the frit covers the substrate completely. This was demonstrated by Energy Dispersive Spectrometry (EDS) analysis. The previously loose layer of 40 μm thickness is transformed to a homogeneous layer of 10 μm thickness due to the heat treatment.

Due to the strong heating some components of the enamel diffuse into the glass and components of the glass diffuse into the enamel. EDS analyses show that predominately, PbO and the colouring components, like Cr₂O₃, CoO, Fe₂O₃ and MnO tend to move into the glass, whereas Na₂O and CaO diffuse into the enamel (figures 5a to c). The interdiffusion layer between the enamel at the surface and the glass is outlined. This mixing effect is more pronounced at higher temperatures (figures 5b and c). Melting and decomposition followed by a destruction of the colouring layer was demonstrated by backscattering SEM analysis (figures 6a to d). At elevated temperatures ($\vartheta_{\text{pyro}} \approx 850^\circ\text{C}$) the interdiffusion layer causes a good adhesion between the enamel and the glass (figure 6b). When the temperature rises further, the black pigment is destroyed (figures 6c and d). The colour changes from black to green or blue depending on the components of the enamel, similar to the production of enamel by conventional heating techniques [10]. Now, the constituents solved in the enamel increase the thickness of the coloured surface layer. When additionally convection and bubble rise occur, the homogeneous layer is disturbed according to the flow (figures 6c and d).

3.2. Characterization of the enamelled glass

The glass enamels after the CO₂ laser heat treatment are evaluated in terms of temperature, surface roughness, brightness, and colouration (figures 7a to d). Increasing the interaction time, i.e. reducing the feed rate rises the temperature (figure 7a). At temperatures well above T_g the viscosity becomes rather low, so that the upper glass layers begin to flow. The resulting surface can be characterized in terms of surface roughness R_z (figure 7b). Decreasing the feed rate, very low roughness values in the range of $R_z < 2.5 \mu\text{m}$ can be obtained. The surface



Figures 7a to d. Characterization of CO₂-laser-molten enamels (enamel of lead-containing frit with black pigments). As a function of feed rate are shown: a) temperature, b) roughness, c) brightness, d) L, a, b values.

roughness increases again, when the feed rates are decreased further. This effect is due to the gas generation of the decomposed components which causes bubble growth. According to the decrease in roughness, the brightness increases (figure 7c).

The colour and its intensity are illustrated by the L, a, b values (shown only for $I = 200 \text{ W/cm}^2$) (figure 7d). The L value describes the colour intensity. Low L values are equivalent to dark colour. The a and b values show the position on the red-green axis and the blue-yellow axis, respectively, in the colour coordination system. The colour black is therefore described by a and b close to zero and a low L value. Black enamels are obtained at moderate temperatures. At low feed rate, i.e.

high temperature, the glass becomes transparent and appears blue due to dissolved CoO in the glass matrix.

3.3. Comparison of normal and lead-free frits

“Laser enamelling” with good results in terms of low surface roughness, high brightness and black colour is possible within a rather large parameter range considering power density and feed rate (figure 8). At low power density and high feed rate the temperature is too low, the enamel does not melt satisfactory. On the other hand, if the temperature is too high, the enamel is destroyed by bubble generation, destruction of the colour pigments and evaporation of singular constituents. Therefore, the best results

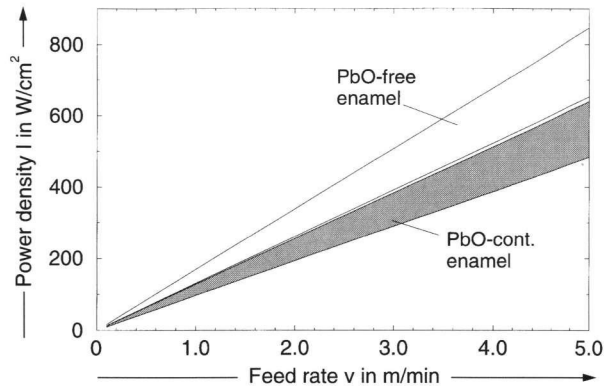
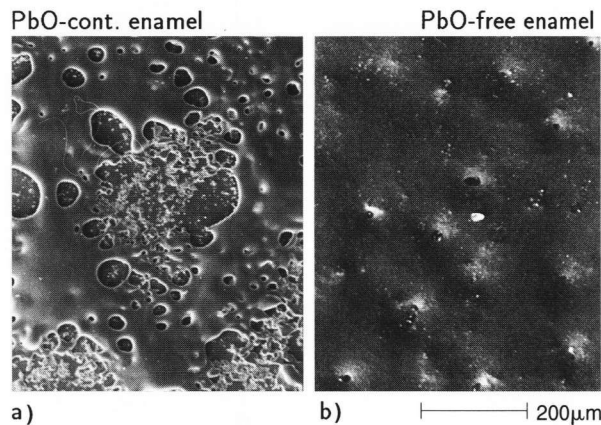


Figure 8. Optimal treatment regions for black enamels.



Figures 9a and b. Comparison of the melting behaviour of lead-containing (figure a) and lead-free (figure b) frits, $I = 180 \text{ W/cm}^2$, $v = 5 \text{ m/min}$.

are obtained at moderate temperatures. High feed rates require high power density of the laser radiation.

Figure 8 also shows first results for a lead-free frit. The composition of the frit is adjusted to the glass. Due to the missing PbO content, which normally lowers the melting temperature, the temperatures necessary for enamelling are higher. For this reason lower feed rates are possible for a given power density compared to the PbO-containing enamel. The differing surface appearances for these two frits after irradiation using the same parameters are shown in figures 9a and b. Whereas the conventional frit (figure 9a) is molten almost completely, the new frit (figure 9b) does not cover the ground glass. Further investigations will be carried out to optimize the laser parameters to improve the appearance of the PbO-free frit.

4. Conclusion

It is shown that glass can be decorated using CO₂ laser radiation. Enamels, consisting of PbO-containing frits and staining pigments, were molten during laser ir-

radiation. At temperatures, which are well above those of the conventional heating process in a furnace, the surface appears smooth and brilliant without losing the shape of the product. This is a result of the local deposition of energy and steep temperature gradients. Optimal results are obtained over a wide range of parameters.

The enamelling of a new developed PbO-free and accordingly high-melting frit was successfully accomplished, due to the high temperatures at the surface. This frit is more resistant against chemical attack, like in dishwashers.

Also enamelling using a Nd:YAG-laser ($1.06 \mu\text{m}$) may be advantageous. The radiation is absorbed by the rough surface and the pigments in the frit. A similar performance as for the CO₂ laser is expected. Additionally, the treatment can be carried out in a furnace because the laser beam can pass into the furnace easily through normal window glass.

Nevertheless, the laser treatment cannot substitute the conventional heating in a furnace completely, because for heating large areas (several square centimetres) very high-power lasers are necessary which make the process uneconomical. It will be a good alternative for enamelling small areas and for special applications.

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