Firing of lead free glass enamel colours with high chemical durability

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Lead containing enamel colours traditionally have been used for markings and graduations on volumetric glassware. The enamel has to be fired at ca. 600 °C to ensure a sufficiently high chemical durability against acids and alkaline solutions. At this temperatures decalibration of the volumetric glasses may occur due to softening of the glass. Lead free enamels used for glazing of porcelain or earthenware show superior chemical durability but need firing temperatures of 850 °C and more. This problem is solved by preheating of the volumetric glass up to the transformation temperature by means of IR irradiation and subsequent firing of the enamel by means of a Nd:YAG or diode laser. The radiation of these lasers is absorbed by the colours only and ensures good melting of the enamel where as the underlying glass remains at transformation temperature. The chemical durability of markings and graduations obtained by this procedure is higher than that of conventional lead containing colours.

1. Introduction

The scales and ring marks of volumetric glassware like volumetric flasks, graduated cylinders, burettes and pipettes usually are made of glass enamels. Glass enamels are low melting glasses, consisting of the coloured pigments and the flux. To achieve low melting temperatures, the flux must contain high amounts of lead or bismuth oxide. Since the volumetric glassware is typically used in chemical laboratories the scales and ring marks must show a high durability against acids and alkaline solutions. The required durability is achieved by firing the lead containing enamel in a furnace at a temperature of 600 °C [1].

Lead free glass enamels usually contain bismuth and zinc oxide. The firing at comparable temperatures leads to a chemical durability at high pH's which is similar to that of lead containing enamels. However, the durability against acidic solutions is insufficient. Lead free enamels with high chemical durability do not contain bismuth oxide but require firing temperatures of approximately 850 °C. This is much too high for a furnace firing of glass products, especially for volumetric glasses. The weight of the glass itself already causes at 600 °C a volume change and decalibration of the volumetric glass. The reason is that the transformation temperature T_g of the mainly used borosilicate glass 3.3 is exceeded by 70 K, approximately.

Hence, a new procedure for firing has to be developed by which one can obtain glass enamels with high chemical durability but avoid the decalibration. Additionally, this method should also work with lead free enamels for toxicological and ecological reasons.

2. Solution

In a previous project [2,3] a method was developed to fire conventional lead containing glass enamels as ring marks on volumetric flasks. This was achieved by the method of selective firing. The volumetric flasks were heated conventionally by a hot-air blower up to the transformation temperature. The enamel was fired by irradiation with an Nd:YAG-Laser within a short time. Thus, the temperature of the enamel reaches 800 – 900 °C. This investigation was performed with the mainly blue lead containing material as well as with the lead free one. Blue enamel has in the near infrared an absorption band, the short wave edge of which absorbs the irradiation of the Nd:YAG-Laser (λ = 1064 μm). In contrast the laser irradiation was not absorbed by the borosilicate glass which remains at the transformation temperature. With this procedure the same chemical durability of the ring mark was obtained as that obtained with conventional heating in a furnace. Further mor the decalibration was completely avoided. The chemical durability especially that in acidic solution of the lead free glass enamel, fired in a furnace as well as with laser irradiation, was significantly below the required level.

This first investigation allowed the basic steps to the direction of the further development presented in this paper.

If the glass body of a volumetric glass does not absorb the laser irradiation it should be possible to scan a large surface of the glass with an expanded laser beam. This makes it possible to fire not only single lines like a ring mark but also the complete graduation, e. g. of a burette or a graduated cylinder. This method requires higher laser power due to the fact that the expansion of the laser beam decreases the power density. The recently developed high-power-diode-lasers are characterized by a very compact construction, a line shaped to retangular focus, a long life time as well as a high efficiencly. Thus, such a laser was used in this investigation.

The selective firing allows to reach temperatures of more than 900 °C of the layer to be fired. Hence, materials which cannot to be fired in a conventional furnance process can be used, like lead free enamels used for glazing of porcelain or earthenware.

3. Experimental

3.1 Firing of scales

Glass tubes made of borosilicate 3.3 with an outer diameter of 13 mm were used as representatives for 50 ml burettes. The tubes were fixed in a chamber with a device which allows rotation around the longitudinal axis. The tubes printed with a coloured scale were heated by IR irradiation of long wavelength. The beam of the diode laser (λ = 940 μm, P_{max} = 400 W) was moved along the rotating tubes by means of an additional linear driving gear. The linear movement of the laser beam and the rotation of the tube were synchronized so that the laser beam spot scanned the complete tube surface following the shape of a cochleoid. The optimum firing conditions were adjusted by the variation of the laser power density, linear movement of the laser and rotation of the tube. The temperatures obtained on the enamel surface were determined by an infrared pyrometer.
A schematic sketch of the experimental installation is given in figure 1.

3.2 Testing of decalibration

Decalibration of the tubes was tested with a commercially available AUTOJUST calibration unit for pipettes and burette tubes before and after firing. The volume between two given marks was measured by dispensing water with high precision into the tubes with a high resolution step motor. The matching of the water meniscus with the marks was determined with a magnifying camera in order to avoid imperfect readings. This measurement was repeated 10 times before and after the firing process.

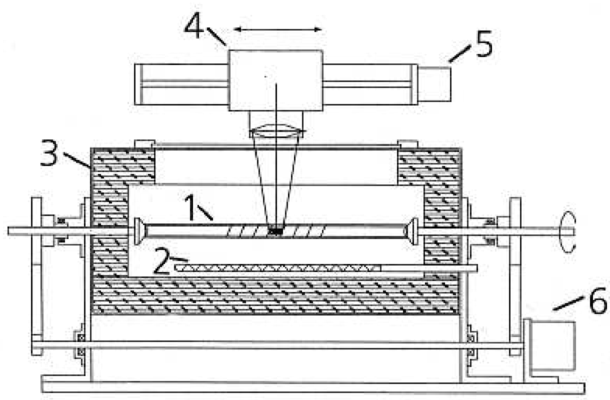

Figure 1: Experimental installation; 1: glass tube; 2: IR heating element; 3: furnace chamber; 4: diode laser; 5: linear driving gear; 6: rotation gear

3.3 Testing of chemical durability

The chemical durability of the fired scales against acids and alkaline solutions was determined in analogy with DIN ISO 4794 [4]. The samples were stored for 1 hour in 2 m HCl at room temperature for testing the resistance against acidic solutions. In the case of alkaline solutions the samples were stored for 2 hours at 80 °C in a mixed caustic solution. After the storage the weight loss was measured to characterise the durability.

4. Results and discussion

The coloured enamels tested in this investigation were of the H56 series form Hereaus, Hanau, Germany, for glazing of bone china and earthenware. The chemical analysis shows, that with the exception of the blue material, the enamels do not contain bismuth or zinc oxides. The blue colours contain zinc spinel. Since the blue and black colours are mainly used for this purposes, they were studied in detail. Other colours like red, yellow, green and white have been tested randomly.

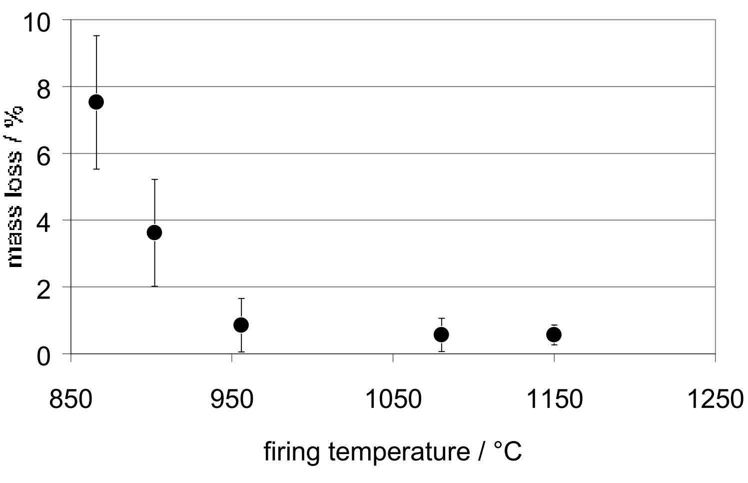

Figure 2: Chemical durability against acidic solution of blue enamel after firing in terms of the firing temperature

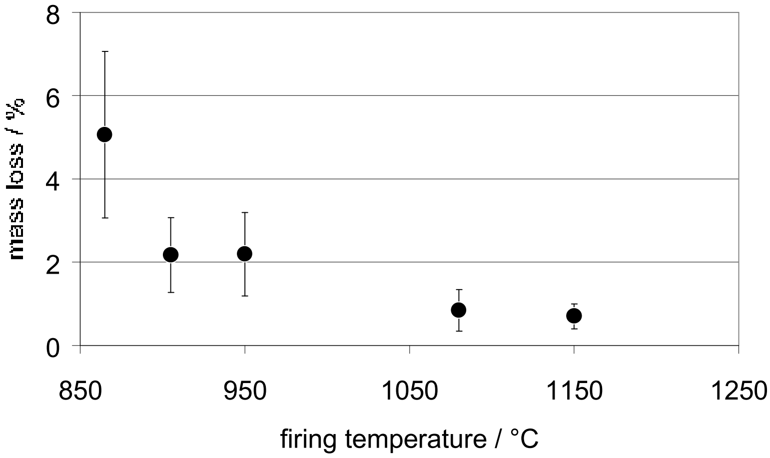

Figure 3: Chemical durability against alkaline solution of blue enamel after firing in terms of the firing temperature

Figures 2 and 3 show the results of the chemical durability tests of the blue colour in terms of the firing temperature. The ordinate gives the relative mass loss of the attack of the acidic and the alkaline solution, respectively. From both figures one can concluded that the firing temperature should reach 950 °C. The minimum firing temperature of the other colours slightly form this value, e. g. that for black is 900 °C, approximately.

The mass loss of the lead containing conventionally fired glass enamels [1] was 1.4 % (acid test) and 9.3 % (alkaline test). The firing with diode laser leads to an increase of the chemical durability against acids by a factor of 2 to 3. The chemical durability against alkaline solutions of enamels fired with this method was approximately 10 times higher than of those obtained by firing in a furnance.

The glass tubes were preheated to the transformation temperature of borosilicate glass, i. e. 530 °C, by means of infrared irradiation. Due to the good absorption of this wavelengths the preheating took only 3 minutes. The following laser firing process depends on the laser power density and the absorption by the enamel as well as on the movement speed which reached values of up to 6 cm/s. During this movement every point of the enamel scales was irradiated by the laser beam spot (area: 0.8 x 8 mm) only for 13 ms. Within this short time a temperature of up to 1200 °C could be reached. For a sufficient quality the firing of a tube (scale) length of 22.5 cm took 20 s.

The scale length and the tube diameter represent the conditions of a 50 ml burette. The scale consists of ring marks with a distance of 1.5 mm. The determined volume changes between the first and the last ring mark (black colour) are given in figure 4. Every value represents a series of 10 measurements, the bars represent the standard deviation. It is clearly shown that only a very small decalibration occurs, compared to the allowed value for a 50 ml burette of + 0.1 %. The order of magnitude of the obtained deviation is very close to the precision of the determination of the volume.

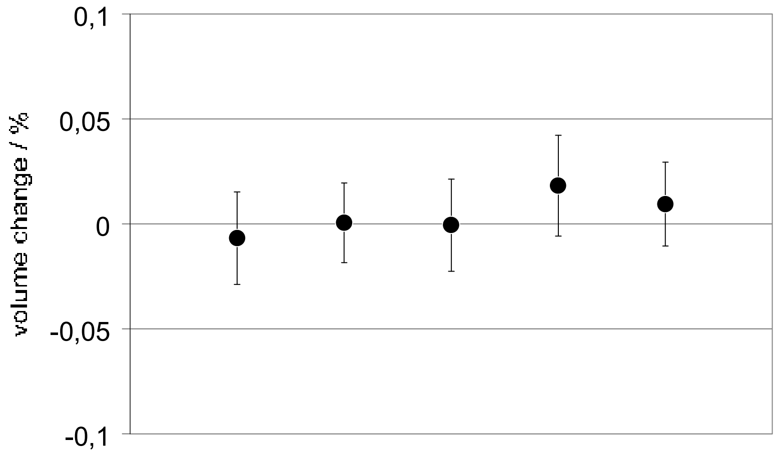

Figure 4: volume change of 5 different tubes after laser firing of black enamel at 930 °C

It can be concluded that the method of selective firing allows to fire scales on glass tubes without noticeable. The use of enamels commonly used for glazing of bone china and earthenware leads to a chemical durability which is significantly higher than that obtained by conventionally fired lead containing enamels.

Acknowledgement

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