DEVELOPMENT AND PROPERTIES OF FOAM ENAMELS

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Development and Properties of Foam Enamels

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1. Abstract

It turned out to be possible to develop foam enamels from foaming enamel slurries using inorganic substances which release gases at the typical annealing temperature of enamels. To get a general idea of potential foaming agents able to produce gases, a catalogue was provided of all relevant compounds. In doing so, toxic, radioactive or extremely expensive materials were excluded. In general high temperature resistant carbides, carbonates and inorganic water containing compounds as well as mixtures were suitable as foaming agents for the preparation of foam enamels.

From this catalogue some substances suitable from technical aspects of glass and enamel production were chosen and experiments were performed to foam three slurries. Substrates, ways of preparation, annealing temperatures and firing times as well as the water contents of the slurries were varied. Slurry compositions were modified as well as the process engineering (preparation, layer thickness of the coat, drying time, baking regime) had to be adapted to the special needs of these enamels as thick layers. Thus a special cooling procedure had to be applied dependent on the thickness of the coatings. The common additives of conventional enamels, e. g. quartz and zircon, degrading generally the porosity of enamels, were omitted. The water content was chosen as low as possible. In addition, the viscosity of the slurry was adjusted with potash (K_2CO_3) to obtain a paste-like coating on the steel plates.

Pore volumes of about 87 Vol.-% resulted with an addition of 2.5 % SiC to a ground coat, in contrast to a pore volume of only 78 Vol.-% with 2.5 % SiC added to a cover coat. The origin of the low porosity of the cover coat enamel and of the lower maximum content of foaming agents to be mixed is due to the chemical composition of the cover coat enamels. These cover coats use to melt earlier forming a plane surface.

It has been proved that the melt viscosity of the enamel and the temperature-viscosity-behaviour of the foaming agent, which depends on the chemical composition, have a strong influence on the formation of foamed enamels.

The best foaming agent for conventional enamels is SiC as an additive to the slurry with contents of 2.5 - 5 %. It increases the viscosity of the enamels and therefore the stability of the foam.

Other foaming agents, e. g. potash and limestone, decrease the viscosity of the enamel melts making them less suitable at usual annealing temperatures. Alkali and alkaline earth carbonates form gases at the annealing temperature of the enamels. This probably makes them applicable for slurries that melt at higher annealing temperatures, e. g. for enamels for the production of chemical apparatuses. Soda (Na_2CO_3) is unsuitable as a foaming agent, for it results in a “short glass” with a narrow temperature range of melting.

Special procedures to investigate the chemical and the thermal resistance of foam enamels were developed and modified, respectively.

It was verified that the chemical resistance of foam enamels is similar to that of conventional enamels if appropriate foaming agents and a suitable baking regime were used.

The coefficients of the thermal conductivity specific for the material proved to be suitable, i. e. the U-coefficient (coefficient of the thermal conductivity independent of the layer thickness) of the foamed ground coat was 5.7 % of that of the conventional enamel with the same layer thickness.

Thus foam enamels are best qualified to protect other sensible parts in buildings, e. g. in tunnels, tubes and airports. This is due to the non-toxic, inflammable properties of enamels.

2. Introduction and objectives

Since the enamel and steel industries are keen to explore new areas of application, it makes sense to develop alternatives to organic insulating materials for structural engineering. This is due to their higher durability, resistance against fire and humidity as well as the environmental sustainability of enamels [1]. The required properties (thermal, acoustic, vibrational insulation) can be obtained by thick-layer (10 - 20 mm) foamed enamels containing a high percentage of enclosed pores. Therefore the purpose of this study was the development of novel inorganic enamels on steel substrates, with coatings executed as foam enamels like foamed glass. Organic insulating materials and adhesives, on the other hand, are flammable and are able to emit toxic vapours while burning.

The most important property parameter of these new foam coats is its porosity. It should be by 80 - 95 Vol.-% of the volume of the coating to ensure a low thermal conductivity and a respective high thermal insulation. Despite this high porosity a sufficient compressive strength and a good adhesion were to be assured. These foam enamels are provided to be used for panels of architecture in the construction industry, where the rear side is executed as a foamy insulating coat and the front side as an aesthetic thin layer of enamel. Further technical applications should be possible in energy, environmental, chemistry, automotive and traffic engineering and for fire protection.

3. Literature overview

3.1 *Porosity of enamels*

One publication has been found only concerning the preparation of foam enamels [2]. Fig. 1 shows the results obtained using 15 % SiC of two grain sizes added to common enamel slurries. However, this foam enamels contained pores up to 10 mm, which make the surface of those enamels unsuitably uneven when fired at the common baking temperatures of enamels [2]

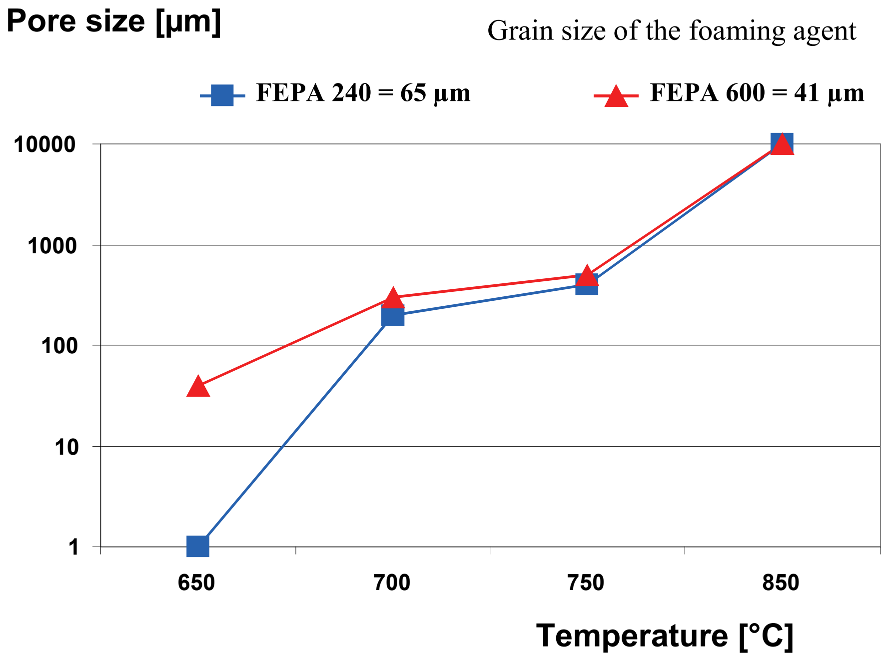


Fig. 1 Foam enamel with 15 % SiC as foaming agent [2]

Pores in unfoamed enamels display a defined distribution of bubbles, being desired for compensation of the different thermal expansion coefficients and as space for storage of the gases (H_2, H_2O, CO_2), emitted during the production of the enamels. The addition of quartz (SiO_2) and zircon ($SiO_2 \cdot ZrO_2$) to the mill reduces this porosity of enamels to ≈ 15 Vol.-% [3][4][5].

3.2 *Foaming agents to manufacture foam enamels*

To find suitable foaming agents for the preparation of foam enamels, potential foaming compounds were inspected. Radioactive or extremely expensive substances were excluded. Well-known fining agents for glass production (e. g. sulfates, nitrates, sulfides) were not considered since they emit toxic gases at high temperatures. On the other hand compounds like hydrates (borates, aluminates, silicates, to some extent also phosphates), carbonates, carbides and manganese dioxide seemed to be potential foaming agents, particularly also because cations like Si^{4+}, Na^{+}, K^{+}, Ca^{2+}... are suitable compounds both in glasses and enamels [6].

4. Preparation of foam glass and foam enamels

From these groups of compounds substances like SiC, Na_2CO_3, K_2CO_3 and $CaCO_3$ were chosen for the experiments. The criteria of choice were availability, prize and especially the behaviour as raw material with respect to viscosity and chemical resistance.

The structure of the experiments is illustrated in Fig. 2. According to this we tested the possibility to prepare foam enamels as well as foam glass (for comparison) and the addition of porous aggregates. For preliminary tests we used dry enamel powder mixed with foaming agents in a muffle furnace. The final tests we carried out with steel sheets and enamel slurries mixed with the powders of the foaming agents in chamber kilns.

Further the temperature regime of the blowing process was examined in a tube furnace heated at a rate of 20 K/min. After foaming properties like adhesion, chemical stability and thermal conductivity were checked. All these tests had to be adjusted appropriately to the needs of the foam enamels with regard to their high porosities.

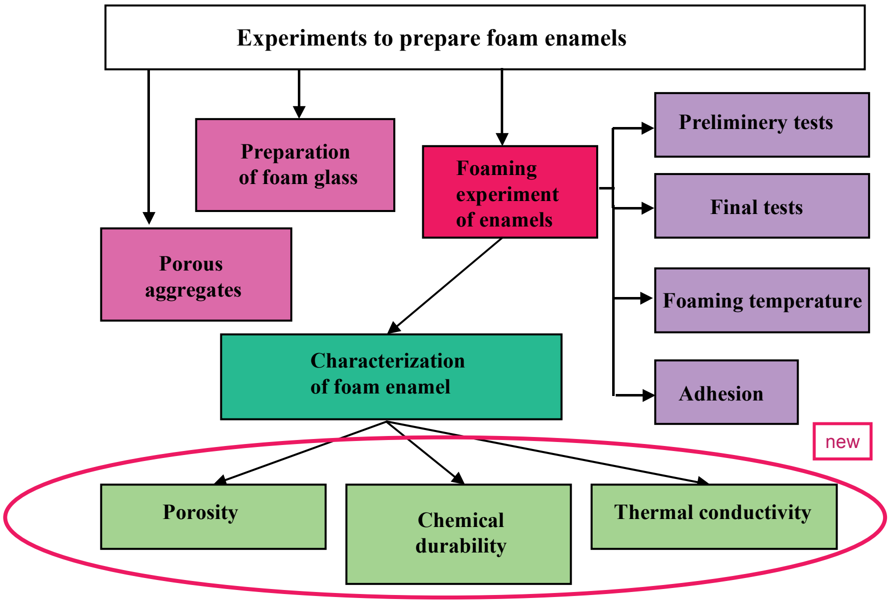


Fig. 2 Structure of the experiments

A usual enamel firing regime with 2 firing times (2 and 4 min) and 2 firing temperatures (800 and 820 °C) was used. Due to the high thicknesses of the raw coatings (4 mm) and of the foamed enamel coatings (up to 20 mm) a cooling process like that for a standard glass had to be introduced.

As samples two ground coats (1 Premix of commercial recipe, 1 with a modified recipe) and 1 cover coat with a modified recipe were applied. The modifications of the recipes of the slurries were:

- elimination of any crystalline addition to the mill (quartz and zircon)
- decrease of the water content (47 ⇒ 42 %) of the slurry
- increase of the content of the set-up agent potash of 10 %

in order to get a stable layer while coating. The chemical compositions of the samples used is shown in Fig. 3, demonstrating that the network forming components being high in the cover coats like in foam glass but are relatively low in the ground coat. In contrast the contents of the alkali oxides and the intermediate oxides are relatively high in the ground coats. As shown later this is important for the formation of a melt of high viscosity and therefore also for the formation of a stable foam.

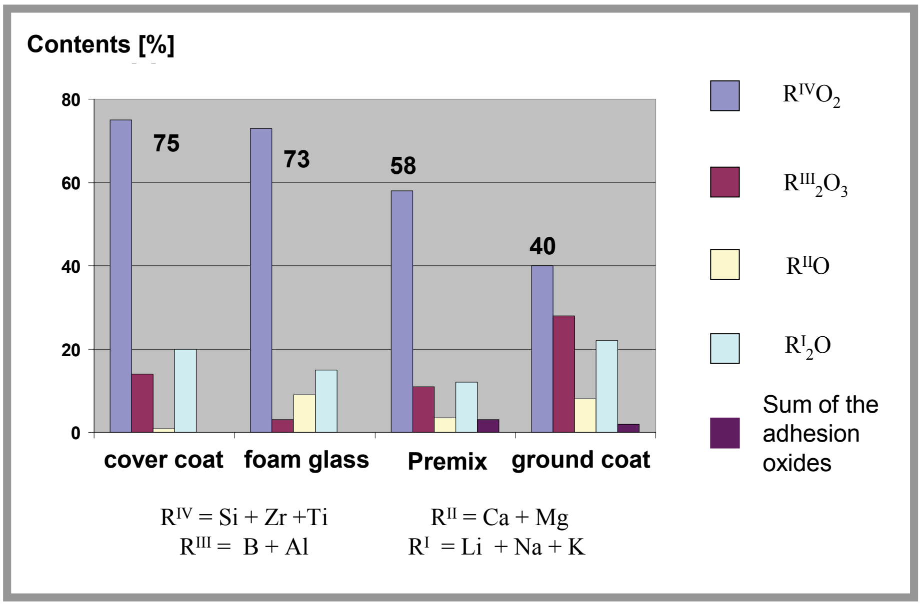


Fig. 3 Chemical composition of enamels and foam glass

5. Results

5.1 Experiments to prepare foam glass and foam enamel

5.1.1 *Porosity of foam glass and foam enamels*

5.1.1.1 Foaming experiments with dry enamel powder

By means of preliminary tests with dry enamel powder (Fig. 4) foam enamels were made from Premix with 10 % SiC. It will be shown later that using the modified enamel recipes (slurries) less foaming agent is required. These preliminary tests proved that organic materials like different kinds of wood, sugar, flour or cream of tartar were not suitable due to their low temperatures of firing. Inorganic agents like gypsum, $CaSO_4$, borax or $MgCO_3$ reduced the viscosity of the enamels, being unable to result in a stable foam, had to be eliminated. Thus only potash and SiC turned out to be suitable foaming agents in dry enamel powders with a concentration of 10 %.

Water insoluble SiC with a melting point of 2700 °C is being corroded by the enamel melt while the carbon is oxidised to CO and CO_2 [6]. The silicon is integrated into the matrix of the enamel increasing the viscosity. The water soluble potash (m. p. 891 °C) also reacts and pyrolises in the melting range of the enamel ($K_2CO_3 \rightarrow K_2O + CO_2\uparrow$) [6]. The formed K_2O is introduced into the enamel matrix being there the decisive component of “long glasses”, extending the melting range of the enamels where the highly viscous melt is able to keep the CO/CO_2 gases in the foam.

As will be shown later, the mechanism of potash introduction is different in dry enamel powder to that in hydrous slurries. This is due to the solubility of potash in the hydrous slurry caused by the formation of hydrogen carbonate bonds.

Fig. 4 shows an image of a foam enamel prepared from Premix and SiC. There the filling degree of the enamel powder is marked, thus the increase of the volume caused by the foaming is recognisable.

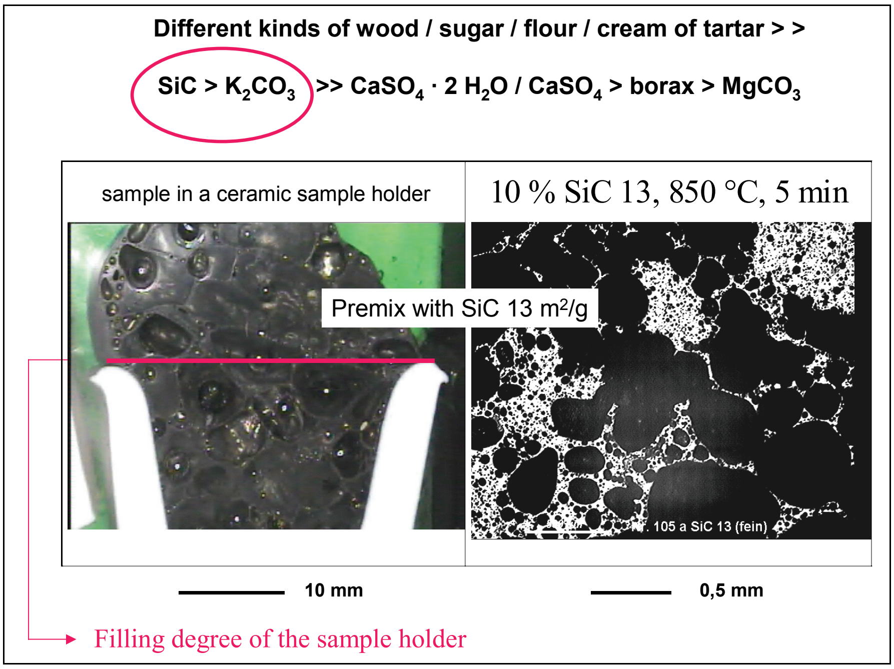


Fig. 4 Foam enamel prepared with dry powder

5.1.1.2 Foaming experiments with glass

In comparison to foam enamel experiments with recycling glass were carried out, using SiC as a foaming agent. It could be shown that there is an optimized concentration of foaming agent (2.5 - 5 %). Above this range of concentration too many bubbles were formed, which coalesced with other bubbles becoming big ones. These bubbles are able to ascend to the surface, then leave the sample (degasification) and decrease its volume. This is the reason why the previous study [2], where too much foaming agent was applied, failed. Fig. shows the dependence of the increase of the volume caused by the addition of SiC. Thus concentrations of 2.5 - 5 % SiC were used for the final tests, elucidating the independence of temperature, concentration of the agent, kind of agent selected and enamel slurries. In a test Fig. 6 confirms that the microstructure of the foam glass consists of enclosed pores of approximately same size.

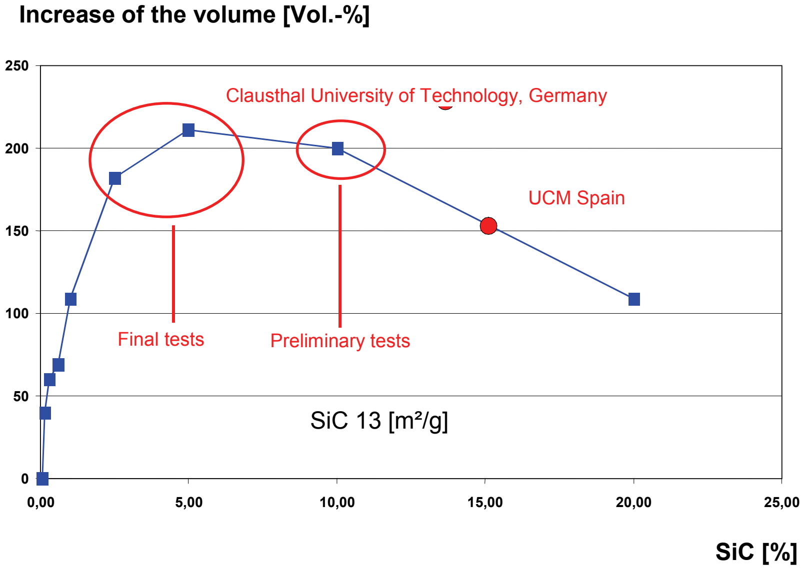


Fig. 5 Foaming tests with recycled glass

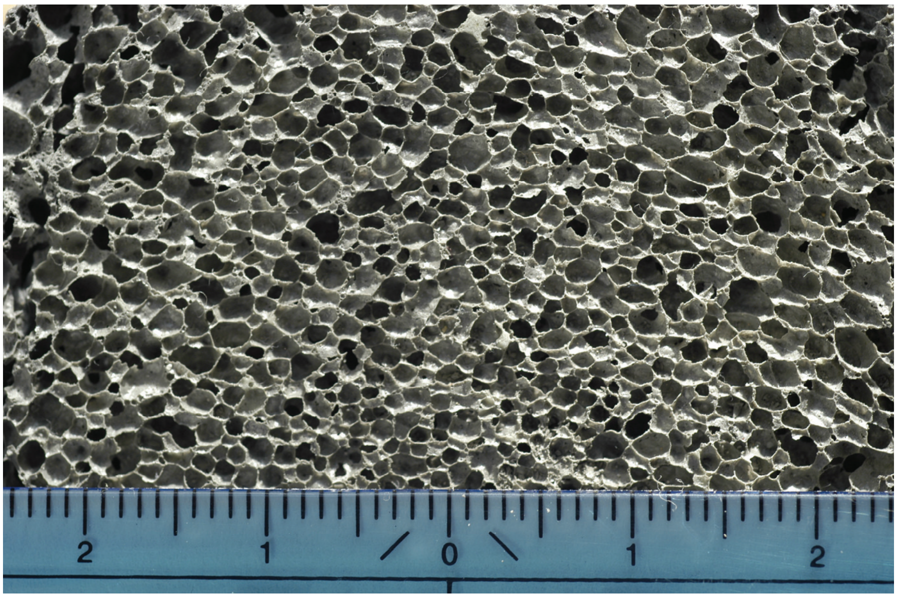


Fig. 6 Foamed recycled glass with 5 % SiC

5.1.1.3 Foaming experiments with enamel slurries

Fig. displays that the optimised amount of 2.5 - 5 % SiC does not only hold for foam glass but also for enamels. However, a semi-quantitative inspection shows that besides the high porosity also a smooth surface is important. This is evidenced by the standard deviation of the porosity which is deduced by measuring the coat thickness of the foam enamels. Furthermore it may be seen from figure 7 that in contrast to Premix (commercial recipe) the enamel slurries (modified recipes for ground and cover coats) result in higher porosities and lower standard deviations. Therefore a standard deviation > 1 Vol.-% already is an indicator that degassing causes lower porosities and a lower smoothness of the foam enamel surfaces. This is only avoidable by a decrease of the concentration of the foaming agent and/or a lowering of the firing temperature. However, high firing temperatures are inevitably necessary to guarantee a sufficient adhesion between the enamel coating and the steel sheet.

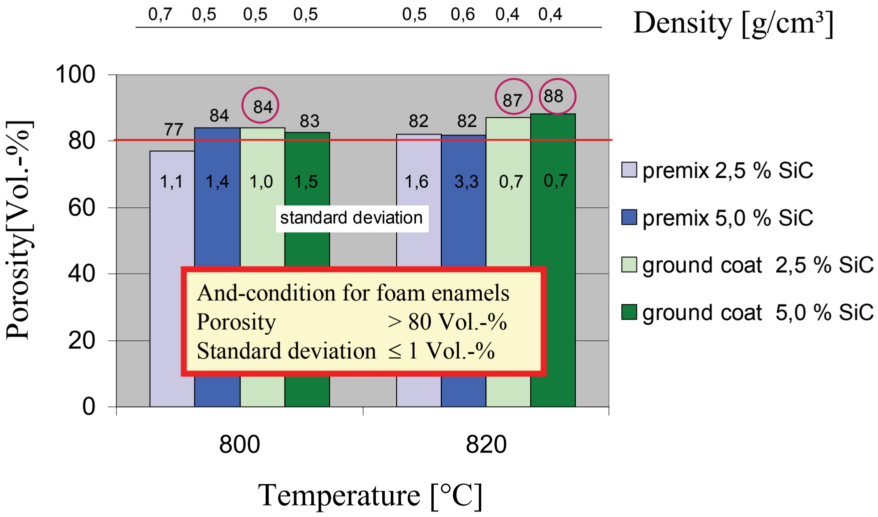


Fig. 7 Ground coats with porosities > 80 Vol.-%

Fig. 8 shows the porosities as a function of different agents (B_4C, MnO_2, SiC + $CaCO_3$, SiC + K_2CO_3, citric acid, baking powder and foam glass) and different enamels (Premix, ground and cover coat with modified recipes). This evidences the efficiency of the foaming agent SiC. Any addition to SiC even decreases the porosity and/or increases the standard deviation i. e. the roughness of the surface. Salts like potash or baking powder which result in high porosities in the dry powder are less efficient (porosities and standard deviations) in the case of foam enamels made from water slurries. These salts are dissolved in water, forming carbonic acid, decomposing already at low temperatures. Agents containing cations like B^{3+} or Mn^{4+}, which are important components of enamels, decrease the viscosity of the melt, thus a stable foam formation is impossible (easy degassing).

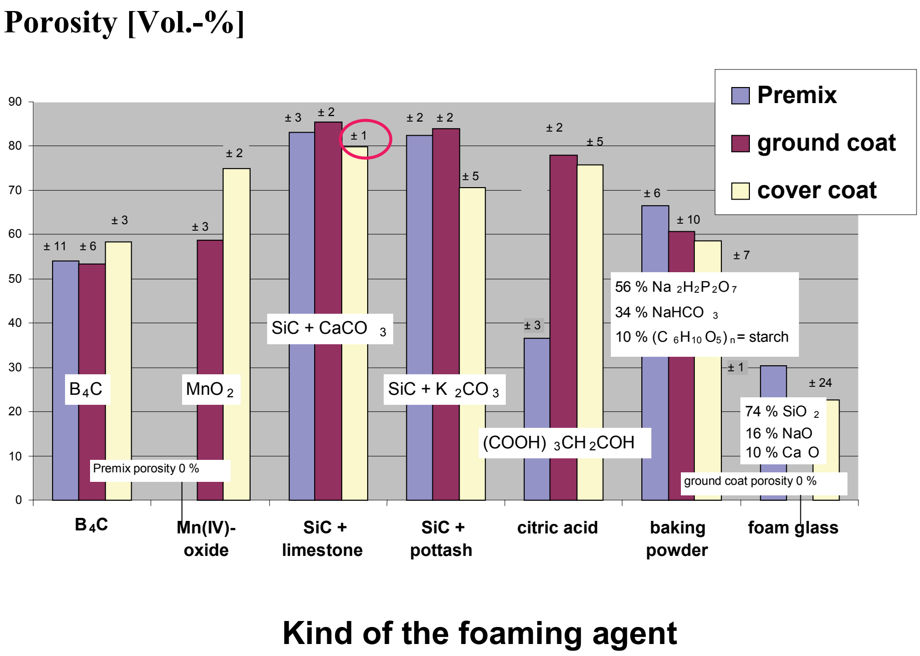


Fig. 8 Porosities of different foam enamels

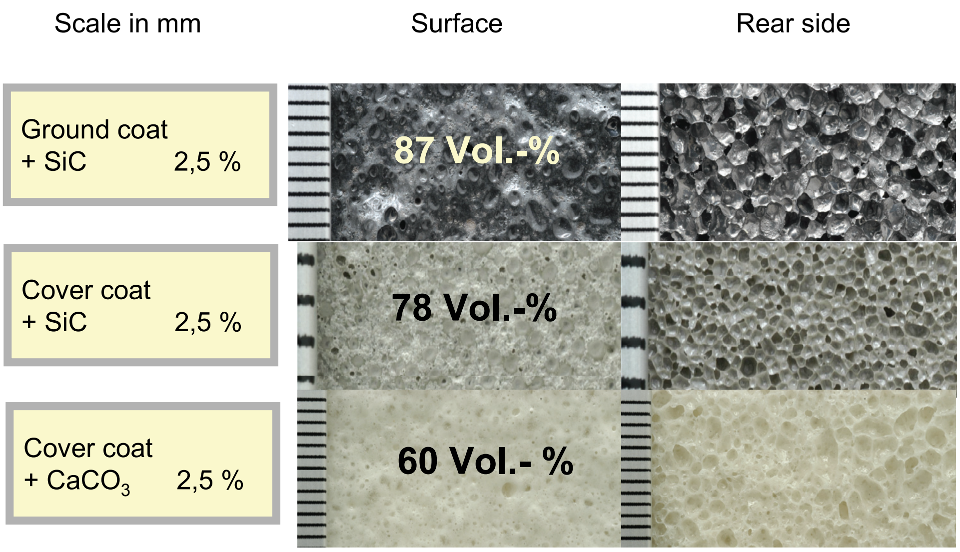


Fig. 9 Typical foam enamels with high porosities

Fig. exhibits successfully prepared foam enamels made from enamel slurries. Thus it is proved that the best foam enamels can be made using modified enamel slurries with SiC. Due to its easily obtainable smooth surface the cover coat does not show such a high porosity compared to a ground coat. Advantageous for the formation of foam enamels is that the enamel melt shows a wide range of melting temperature with a high viscosity ("long glass"), with particles of the slurry of approximately the same size [7].

5.2 *Properties of foam enamels*

5.2.1 *Chemical resistance*

With regard to conventional enamels the testing procedure for the chemical resistance of foam enamels had to be modified since it turned out to be impossible to use plates of foam enamels which are able to close the testing cylinder according to EN 14483. Instead DIN 719 was applied accordingly. Coatings of the foam enamel were removed from the steel substrates, hammered to sizes of 125 – 250 µm and cooked in boiling water for 2 h. The loss of mass after boiling served as an indicator for the chemical resistance.

An important result was that the chemical resistance of the foam enamels is lying in the same range as that of unfoamed enamels. According to Fig. 10 the resistances seem to be dependent on porosity. The reason for that is that apparently the fraction of pores < 125 µm is very high. Thus the real surface is much higher than the calculated one. Future investigations should apply e. g. adsorption methods to determine the porosity in order to obtain the specific surface of the foam enamel powder. However, it has to be borne in mind that while using foam enamels their surfaces have to be as smooth as possible (standard deviation of the porosity < 1 Vol.-%). Therefore in reality not the closed pores but only the surface of the foam enamels is of importance for the chemical resistance.

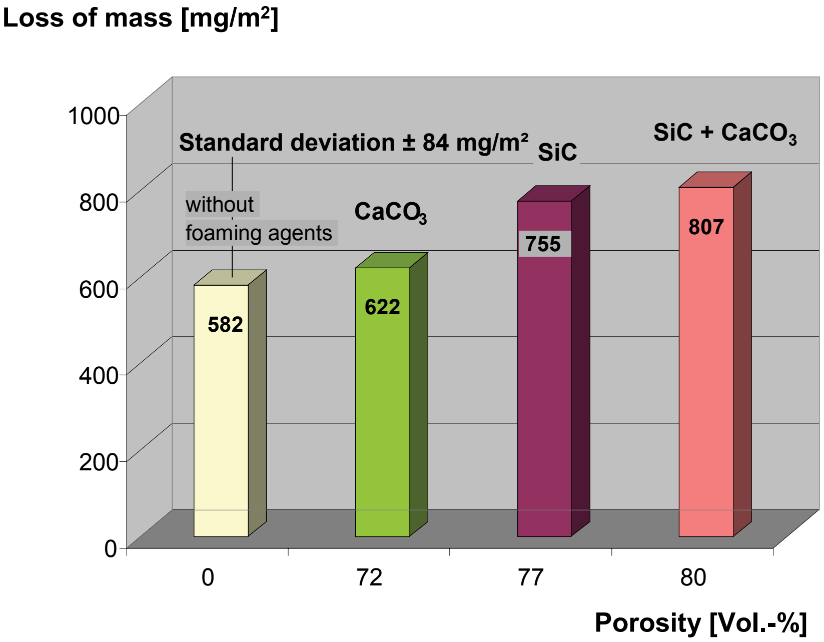
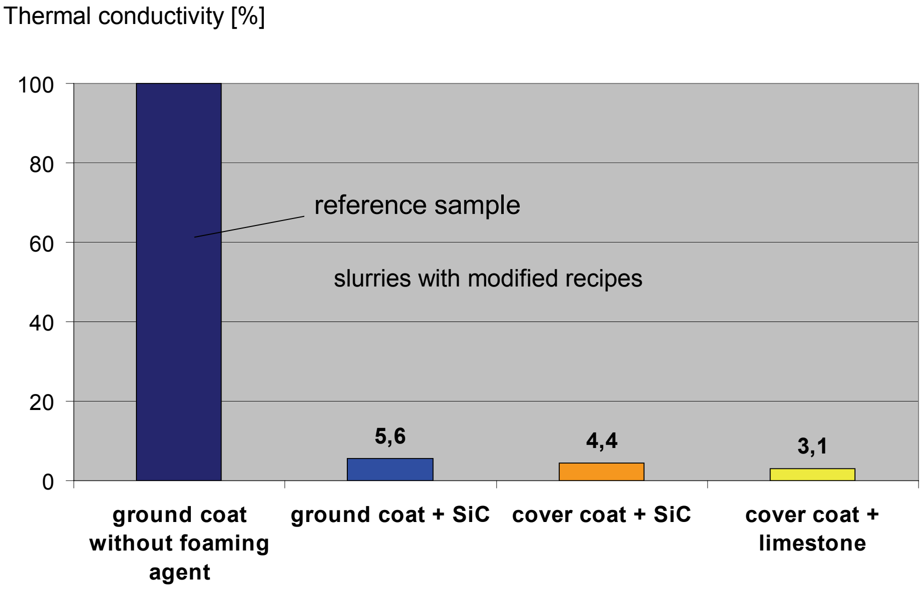


Fig. 10 Chemical resistances of foam enamels

5.2.2 *Thermal conductivity of foam enamels*

The preliminary thermal conductivity of the foam enamels was estimated by a - not yet fully developed - laser method. However, Fig. 11 indicates that the foaming effect considerably decreases the thermal conductivity [8].



Foam enamels with different foaming agents

Fig. 11 Thermal conductivities of foam enamels

6. Conclusions

It was proved by this investigation that both a systematic development and preparation of foam enamel is possible, especially if the recipe is modified. Further a very fine grain size of the foaming agent and a very good homogenisation of the raw materials is necessary. Already low concentrations (2.5 – 5 %) of the foaming agent give satisfying performances. A high viscosity of the slurry as well as of the melt is important. Firing temperature and time are nearly independent of the foaming agents. However, both special firing and cooling routines are necessary. The chemical resistance is approximately the same as in the case of unfoamed enamels.

7. Acknowledgement

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