Enamels for Use in High-Temperature-Applications

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Introduction

Technical porcelain enamels are high-performance materials and assert themselves on the market. There is still a lack of enamelled materials which are stable at operating temperatures above 500 °C [1-5]. Metals are protected from corrosion at high temperatures by different methods: thermal spraying in different variations, physical or chemical vapour deposition processes (PVD or CVD), complex multi-step processes (e.g. for thermal barrier coating - TBC, environmental barrier coating - EBCO). The use of high alloy materials may also be seen as a corrosion protection. The major disadvantage of thermal spraying is the porosity of the coated layer. Sputtering or vapor deposition systems are technically very complex and work on limited geometry. Resources for alloy metals such as Cr, Ni, Mo and W are rare. So all described methods have disadvantages and high temperature vitreous enamels might be beneficial. In oxidation protection, enamel is even superior to very dense ceramic layers due to the lower diffusion rate of oxygen in glassy phases.

High temperature enamels are developed and applied since the 1950s. They have been replaced by other coating methods and super alloys. Due to changes in the raw material situation and increasing requirements on durability of materials, it is appropriate to develop high temperature enamels that meet today's requirements using the present state of knowledge.

Applications can be entire furnace and firing constructions (kilns and furnaces, heat exchangers, gas pre-heater, exhaust systems, parts of incinerators, fuel racks and hangers) but also the chemical reactor construction or certain tools for metal forming.

Metals which are used at high temperatures must be both corrosion resistant and solid at operating temperatures. Depending on the atmosphere, oxidation, carburization or nitriding can lead to embrittlement and so diminish strength. An overview of possible materials is given in table 1.

Table 1: properties of some steels
It can be seen that the coefficients of thermally expansion (CTE) of some steels are even higher than the CTE of ordinary steel for enamelling. The CTEs of usual enamels (for temperature range 20 ... 300 °C) are (80 ... 120)-10⁻⁷/K. High temperature enamels have a higher SiO₂ and lower alkali content resulting in lower CTE. The physical requirements of a high-temperature enamel (high softening temperature combined with high CTE) cannot be meet by adjustment of the chemical composition of the glass phase because they are self-contradictory. The often required high thermal shock resistance, in turn, cannot be achieved with a high CTE. After all, enamels with high softening temperature show good chemical resistance due to low alkali content.

Known high temperature enamel frits are mostly alkali-free and have relatively low CTE of 80 to 95·10⁻⁷/K. Cr₂O₃ or corundum were used as mill additions, having a similar or lower CTE. One way of enamelling with very different CTE, is to apply a thin layer of about 40 microns, so that resulting stress remains within limits [2]. The feasibility of this way was shown in [6] with a modified frit A418 on a CrAlFe-type alloy Kanthal A1.

However it is better to work with usual layer thicknesses of about 150 microns, because the oxidation protection is increased. Therefore crystalline inert materials with high CTE should be added to the high-temperature frits. Such substances are e.g. cristobalite, wollastonite or enstatite. The principle of addition of inert materials for setting the CTE is known from solder glasses in electronics technology [7]. There the firing temperatures are generally low and the inert substance is really inert. Given the anticipated high firing temperatures for high temperature enamels, part of the additives is expected to be dissolves in the glassy phase [8, 9].

Crystalline phase can also be achieved by crystallization from the glassy phase. There have been many studies of glass-crystalline materials in recent years, so that new ideas from this side can be included [10-13]. So glass-ceramics with cristobalite as main phase are known which causes high CTE [12], [14].

The advantage of using glass-crystalline enamels is relatively low firing temperatures which are common in enamelling industry. High softening temperatures are achieved by obtaining defined crystalline phase content by defined annealing. The glassy phase is limiting the application temperature. It should have a good corrosion resistance to the ambient conditions.

Glass ceramics might have much higher softening points than the parent glass, like shown in [11], p.299: softening points of parent glasses in the system SiO₂ – Al₂O₃ – ZnO – MgO – Li₂O are in the range of 500 °C und 575 °C and temperatures for corresponding class-ceramics lie between 850 °C and 1000 °C.

Examples for very high application temperatures (> 1450 °C) are indialite- and mullite-based glass ceramics of the system alkaline earth oxide - Al₂O₃-SiO₂-TiO₂ [14]. Nevertheless those have quite low CTEs.
Properties and technological conditions of moulded glass-ceramics are not directly transferable to crystalline glass enamels, so that appropriate adjustments must be made. Also from literature, no experiences are known.

**Methods**

The aim of the present work is to show an example of possible enamelling austenitic steel with high CTE and therefore good oxidation protection.

As a stainless steel, 1.4404 (V4A type, thickness 1 mm) and as a high-temperature steel, 1.4841 (sheet thickness 1.5 mm) were chosen. The linear thermal expansion coefficients are given in table 2. For pre-treatment the sheets (70 mm x 70 mm) were grit-blasted and then purified in an ultrasonic bath.

**Table 2: linear coefficient of thermal expansion of some substances**

<table>
<thead>
<tr>
<th>Substances</th>
<th>Description</th>
<th>CET&lt;sub&gt;20...400 °C&lt;/sub&gt;</th>
<th>CET&lt;sub&gt;20...500 °C&lt;/sub&gt;</th>
<th>CET&lt;sub&gt;20...600 °C&lt;/sub&gt;</th>
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</thead>
<tbody>
<tr>
<td>1.4404</td>
<td>V4A-grade steel</td>
<td>175·10&lt;sup&gt;-7&lt;/sup&gt;/K</td>
<td>180·10&lt;sup&gt;-7&lt;/sup&gt;/K</td>
<td></td>
</tr>
<tr>
<td>1.4841</td>
<td>highly heat resisting steel</td>
<td>170·10&lt;sup&gt;-7&lt;/sup&gt;/K</td>
<td></td>
<td>180·10&lt;sup&gt;-7&lt;/sup&gt;/K</td>
</tr>
<tr>
<td>A418</td>
<td>frit</td>
<td>82·10&lt;sup&gt;-7&lt;/sup&gt;/K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td>80·10&lt;sup&gt;-7&lt;/sup&gt;/K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cristobalite</td>
<td></td>
<td>270·10&lt;sup&gt;-7&lt;/sup&gt;/K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S7/3-5</td>
<td>enamel</td>
<td>125·10&lt;sup&gt;-7&lt;/sup&gt;/K</td>
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</tbody>
</table>

As a high temperature enamel frit, A418 [1, p.108] is selected and slightly modified. Melting was carried out in corundum crucibles at 1400 °C for two hours. The mill batch, hereinafter referred as AS5, consists of frit A418, Cr<sub>2</sub>O<sub>3</sub>, cristobalite, clay and set-up agents. The slip was applied by spraying. The samples were fired in a muffle furnace at 1100 °C for 5 or 6 minutes. The coat thicknesses were 130-220 µm.

For a specific application, slip S7/3-5 was developed and tested. It has a relatively low firing temperature of 900 °C and is based on frit A418 too.

In addition, glass-crystalline enamel 35M1 was prepared. It is based on a crystallizing sealing glass for copper. Its chemical composition lies in the system Li<sub>2</sub>O-ZnO-SiO<sub>2</sub> and has a CET (20...400 °C) of 168·10<sup>-7</sup>/K as described in literature [15]. Its application as enamel and study of crystallization conditions are described in [16].

Tests for resistance to oxidation were carried out by annealing the samples at varied temperatures and holding times in a laboratory muffle furnace in air. Samples were weighed and photographed before and after the test. In addition, coat thickness was measured (exacto FN, Electrophysics). An increase in mass served as a measure of oxidation.

Expansion coefficient CTE was determined in accordance with DIN 51177: 2008 using a Linseis dilatometer. Sample bodies were made by sintering at firing temperature.

**Results**

Enamel samples AS 5 on steel 1.4404 were annealed at 1000 °C for 5, 16, 22 and 66 hours as well as for 22 hours at 800 °C, 900 °C, 1000 °C and 1100 °C. Results are shown in figures 1 to 4. In figures 1 and 2 untested reference samples are shown below. The green glossy enamel shows a visually rippled surface due to spraying. Some samples exhibit small failures because of the contact with sample holders. Gloss decreases from 900 °C and becomes satin finished. With
increasing holding time the green colour first gets brighter and then becomes brownish.

Sample 6 (1100 °C) gets a thin layer except of the bottom right corner. This thin layer turned into brown-green. At this temperature oxidation cannot be stopped but reduced. This is proven by the fact of increased coating thickness after the test. Thereby the increasing thickness is an indication for oxidation. Unfortunately mass change of this series could not be determined because two samples had small chippings at the edge.

For series with increasing holding time at 1000 °C, mass increase is shown in Fig. 4. Mass increase of the unenamelled steel could not be measured because of scale chipped immediately after removal from furnace. An impression gives Fig. 3. The study is not yet complete and should be verified by repeated measurements.

![Figure 1: Steel 1.4404, enamelled with AS5 after annealing for 22 h](image)

![Figure 2: Steel 1.4404, enamelled with AS5 after annealing at 1000 °C](image)

![Figure 3: Steel 1.4404 without (left) and with enamel coating AS5 after 16 h at 1000 °C](image)

![Figure 4: Mass change after annealing](image)

The influence of inert additive cristobalite on CTE is shown in Figure 5, where frit A418 and lower softening enamel S7/3-5 are compared.
Exploring the vitro-crystalline enamel 35M1, crystallization conditions were varied and phase content determined. Optimal crystallization temperature of 900 °C was found at a crystallization time of 30 to 60 minutes. The main crystal phase is lithium zinc silicate, furthermore cristobalite and quartz were found. The value of CTE (20…400 °C) was determined with 140·10^{-7}/K. In a first annealing test at 1000 °C for 16 h, no optical changes of enamel on steel 1.4404 were seen. Change in mass could not be determined. The experiments will be continued.

**Conclusions**

In the described experiments it was shown, that enamelling of high-alloy steels for high temperature applications is possible. Application temperatures up to at least 900 °C are no problem, temperatures around 1000 °C possible. The adjustment of CTE must be taken into account for each steel type. For conventional high-temperature enamel it can be achieved via mill additions. In this case wet application is necessary. In the case of glass-crystalline enamel, the CTE can be adjusted by crystallization conditions of the frit. Therefore powder application is preferable.

For each application a reasonable coat thickness must be found. Although a large coat thickness offers a better protection against oxidation, it probably has a negative effect on thermal shock resistance despite adjustment of CTE.

Applications of high temperature enamels are mainly in the field of heat treatment plants and furnace construction. Other options are chimneys and exhaust pipes. Enamelling increases life of components and their strength in continuous use. Thus investment cost can be saved. If enamelled steel replaces Ni-based alloys, heat capacity of the furnace component decreases and energy costs could be reduced. Enamelling of firing grates would lead to reduction of scale, too.

**Figure 5: Dilatometric curves of frit A418 and slip S73-5**

![Dilatometric curves of frit A418 and slip S73-5](image)

**References**

/2/ Petzold, A.; Betzer, H.: Versuche mit Hochtemperaturemails auf legierten Stählen. Sprechsaal 93 (1960) 9, 252-255