Abstract: On the base of composite glass-ceramic coatings with high resistive in reduction media is developed enamel technology. This technology is applied for enamel of riser tube for casting machine of gas counter pressure. Developed mathematical model for casting formation in conditions of centrifugal casting is shown by comparison analysis between numerical results to adapt of enamel technology.

KEYWORDS: GLASS-CERAMIC COATINGS, ENAMEL RISER TUBE.

1. Introduction

The progress in the modern technologies is limited by the synthesis of new materials with extremal – and in some cases even with mutually incompatible properties. For example machine details and installations working in aggressive media at high temperatures should be characterized not only by an excellent corrosion resistivity but also by good thermomechanical properties. Some metals and metal alloys show very good thermomechanical behavior, however, their corrosion resistivity in respect to a number of aggressive media and especially in respect to molten metals is very poor. Materials with a high corrosion resistivity in metal melts and possessing simultaneously good thermomechanical characteristics are of utmost for the foundry, the nuclear energetics, the space ship building etc. The molten aluminium is one of the most aggressive reagents the nearly all metal melts; It possesses a very high affinity toward the oxygen, higher even than that of like Na, K etc. [1]. Moreover, it dissolves almost all metals giving alloys which composition vary within large limits [2]. The molten aluminium is also characterized by a high aggressivity toward other materials. For example, the silica glass corrodes very intensively in molten aluminium alloys because of the reduction of SiO₂ to elementary Si and the subsequent dissolving of the obtained Si in the melt. This process will continue up to reaching the equilibrium solubility of Si for the respective temperature. Since the solubility of Si in molten Al is significant (at the eutectic temperature it reaches a value of 11,7 wt.% [3]) in practice silica glass be fully corroded in molten Al is very low; The solubility of B in molten Al is 0,01 wt.% and that of P is only 0,001 wt.% at 800°C [3]. Carbon, some oxides like Al₂O₃, MgO, BeO and ZrO₂ as well as some non-oxide compounds like borides, carbides and nitrides show a good corrosion durability in respect to the molten aluminium, because of this a number of ceramic and composite materials (e.g. alumattinate ceramics, carbon clay materials) have been developed on their base [4 to 6]. However, the main disadvantages of all these materials are both their high fragility and gas permeability.

An alternative solution of this problem is by covering of metal details with appropriate protective enamels to obtain articles combining the good mechanical properties of the metals with the excellent thermal and corrosion resistivity of the oxide ceramics.

An effective protection of metal details could be achieved if the enamel coating is enough to mask defects like open pores, scratches, cracks etc. However, with increasing the thickness of the enamel coating the internal strain is growing up and the adhesion between the coating and the metal detail as well as the thermal shock resistance are getting worse.

The deposition of composite coatings of an appropriate combination of different layers could solve these problems and provide an effective protection of metal details. An attempt has already been made in this respect by using a composite coating consisting of a thermal resistant enamel and Al₂O₃ plaster [7]. However, the anticorrosion behavior of this coating is not good enough because of the relatively high content of SiO₂ in the applied enamel.

In the present contribution the efforts are directed in creating a new composite coating for protection of cast iron details from corrosion in reduction media and especially in molten aluminium. Accounting for the results of our previous investigation [7], now, enamels were synthesized with high B₂O₃ and P₂O₅ content and with an appropriate combination of reduction resistant oxides like ZrO₂, Al₂O₃ and MgO. The SiO₂ content in these enamels is very low or equal to 0. An especially high adhesion of the enamels was observed when on the surface of the cast iron details a thin crust of casting scale has been preliminary formed. Moreover, it turned out that the chemical resistivity of the synthesized enamel coating can sufficiently be enhanced if on the enamel layer a phosphate plaster reinforced by E-glass fibres is additionally applied.

2. Synthesis of glass ceramic enamels with a high resistivity in reduction media and deposition technology [8]

According for that oxides like Al₂O₃, B₂O₃, P₂O₅, MgO and ZrO₂ possess a high corrosion resistivity in reduction media a series enamels were synthesized in the system SiO₂-Al₂O₃-B₂O₃-P₂O₅-ZrO₂-MgO-CaO-BaO-Na₂O-K₂O. The synthesis of the enamels was carried out in superkanthal furnace at 1250°C in corundum crucible and two hours dwell time. The homogeneous melts thus synthesized were fritted by pouring into water.

For the deposition of the enamels coatings were prepared of the composition (in weight parts): enamel frit – 100, clay – 5, Na₂B₄O₇·10H₂O – 0,3, NaNO₃ – 0,01, Al₂O₃ – 30 and water – 50. The probe details were double coated with these slips and after drying they were fired in the temperature interval 800 – 850°C depending of the initial glassy frit. The slips consistency used enabled to form coatings with thickness of 0,12 to 0,15 mm.

3. Lab and pilot examinations of the composite coatings [8]
The lab examinations were carried out using cylindrical cast iron details with and without preliminary formed thin crust of casting scale. For the sake of brevity from now on this crust casting scale will be noted as a cer-met underlayer.

For each composition under investigation the maximal temperature differences ΔT1 and ΔT3 which the coating can endure at a single or fivefold heating and cooling into water with room temperature without determined. In Table 1 some composition of the enamels synthesized are presented which according to our lab examinations are characterized by an especially high corrosion resistivity in aluminium melt.

Table 1 Composition of enamels with a high corrosion resistivity in molten aluminium (in wt. %).

<table>
<thead>
<tr>
<th>N</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>ZrO2</th>
<th>MgO</th>
<th>CaO</th>
<th>BaO</th>
<th>Na2O</th>
<th>K2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>18</td>
<td>9</td>
<td>17</td>
<td>6</td>
<td>-</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>25</td>
<td>15</td>
<td>19</td>
<td>5</td>
<td>3</td>
<td>6</td>
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<td>40</td>
<td>5</td>
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<td>4</td>
<td>5</td>
<td>10</td>
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<tr>
<td>4</td>
<td>24</td>
<td>29</td>
<td>20</td>
<td>14</td>
<td>10</td>
<td>5</td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 2 summarizes data for the thermal expansion coefficients α, the glass transitions temperatures Tg and the softening points Tf of the enamels from Table 1. In the same table the firing temperature Tfiring of the coatings obtained by using the respective from Table 1 are given as well as the values of ΔT1 and ΔT3 which characterize the thermal shock resistance of these coatings. The (+) and (-) signs denote presence or absence of preliminary formed cer-met underlayer, respectively.

Table 2 Properties of the enamels from Table 1 and the coatings prepared with these enamels.

<table>
<thead>
<tr>
<th>N</th>
<th>Tg [°C]</th>
<th>Tf [°C]</th>
<th>Tfiring [°C]</th>
<th>ΔT1 (+)</th>
<th>ΔT1 (-)</th>
<th>ΔT3 (+)</th>
<th>ΔT3 (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85</td>
<td>430</td>
<td>520</td>
<td>800</td>
<td>480</td>
<td>700</td>
<td>380</td>
</tr>
<tr>
<td>2</td>
<td>105</td>
<td>400</td>
<td>470</td>
<td>820</td>
<td>450</td>
<td>680</td>
<td>350</td>
</tr>
<tr>
<td>3</td>
<td>118</td>
<td>380</td>
<td>430</td>
<td>850</td>
<td>500</td>
<td>750</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
<td>410</td>
<td>450</td>
<td>830</td>
<td>520</td>
<td>800</td>
<td>420</td>
</tr>
</tbody>
</table>

In the temperature interval 20 – 400°C the thermal expansion coefficients α of the glass enamels synthesized vary in the range of 120.10^-6 for non-silicate compositions to nearly 90.10^-6 °C^-1 for the enamel glasses coating SiO2. This means that the non-silicate compositions are especially suitable for deposition on cast iron details. (α of cast iron is the range of 125 to 130.10^-6 °C^-1.)

Moreover, the non-silicate compositions with a high P2O5 content, like compositions 3 and 4 for example, are characterized by a relatively low viscosity and tension in the temperature interval of 750 to 850°C which allows the deposition of enamel coatings of good equality at the metal surface. At this it turned out that the composition 4 which resembles a borophosphate low melting glass enamel but with an increased content of ZrO2 and MgO is characterized by the best coating as well as thermal and corrosion resistant characteristics among the enamels by us.

As seen from Table 2 the thermal shock resistance of the composite enamel coatings depends strongly on the presence of cer-met underlayer. For all enamels investigated the values of ΔT1(+) and ΔT3(+) are much higher than those of ΔT1(-) and ΔT3(-) (see Table 2), i.e. the coatings on cer-met underlayer possess better thermal shock behavior than those without such an underlayer.

The composite coatings were also examined at semi-industrial conditions in counter pressure casting machines. These examinations were performed in an Al-Si melt at 760±20°C. (The content of Si in the melt was 9 wt. %.) For this purpose 3 series of enameled cast tubes were prepared. For all series enamel 4 from Table 1 was used. The tubes from the first series were without cermet underlayer while these from second and the third series were with such an underlayer. On the tubes of the third series plaster reinforced by E glass fibers was additionally applied onto the enamel layer. The phosphate plaster represents a low hardening phosphate cement with a high Al2O3 content.

The thermal behavior of the coatings was examined by subjecting the tubes to thermal shocks from 760±20°C to room temperature and determining the number Nshock of the shocks which the coatings can endure without visible defects.

Moreover, the castings were tested at continuous in the Al melt. The anticorrosion properties of coatings were controlled by analyzing the amount of iron dissolved from the cast iron tubes in the melt.

For each type of coating the time interval tcont was determined during the content of iron in the melt remained lower than 0.2 wt. %.

The results of the pilot examinations are summarized in Table 3.

Table 3 Results of pilot examinations of the protected cast iron tubes.

<table>
<thead>
<tr>
<th>Series</th>
<th>tcont [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>70</td>
</tr>
<tr>
<td>II</td>
<td>280</td>
</tr>
<tr>
<td>III</td>
<td>360</td>
</tr>
</tbody>
</table>

As seen in Tables 2 and 3 the lab examinations as well as the pilot out that much better characteristics of the coatings are obtained in the presence of cer-met underlayer. At this coatings from the third series exhibits the best thermal shock resistance as well as anti-corrosion properties. They are comparable with those of the coatings produced by Dr. Riedelbauch & Stoffregen GmbH Company. The latter coatings represent a phosphate plaster reinforced with E-glass fibers.

4. Technological functionality of enamel Riser tube

Riser tube implemented the flow metal melt from furnace to mold in the casting technology with gas counter pressure Fig.1

Machine for casting - gas counter pressure

Fig. 1 Balevski – Dimov casting method and machine with gas counter pressure.

Fig. 2 – Centrifugal cast riser tubes ingots from iron 20 [9].

To detect the presence of void spaces and other defects castings were subjected to metal cutting on inner, outer and top surfaces. Machined castings (Fig. 3) were subjected to subsequent coating with glass-ceramic coating.

Fig. 3 – Processed risers 2 [9].

On Fig.4 are shown applied here of mathematical model [10] for comparison numerical analyze – temperature field of thin layer with
thickness 0.001m and length 1m at filling with melt: Fig. 4.a is temperature field of liquid metal [10] and Fig. 4.b – temperature field of model substance for adapted of the mathematical model [10] to the technology – enamel.

5. Conclusion
The results from industrial tests show that the composite enamel coatings and especially the triple layer composite coating: cer-met underlayer, enamel coating, phosphate plaster could give an effective anti-corrosion protection of the cast iron tubes in respect to the Al melt and its alloys. In this way the composite coatings could be consider as an alternative of the Al₂O₃-TiO₂ or carbon/shamot casting tubes up to now in the foundry, which main disadvantages are both their high fragility and gas permeability.

6. References