ACID CORROSION OF A GLASS—CRYSTALLINE ENAMEL COATING

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Development of various branches of the chemical industry and intensification of the technological processes require new construction materials, including silicate coatings for the safe and protracted protection of metal from acid corrosion. A glass—crystalline enamel coating is one of these materials.

As a result of investigations, we synthesized a composition of a crystallizable enamel in the system Li₂O—Na₂O—Al₂O₃—SiO₂ containing additions of TiO₂ and MgO, and we developed the technology for obtaining a glass—crystalline coating for pipes that exhibited improved mechanical and thermal properties after heat treatment.

A study of the acid corrosion was necessary for evaluating the suitability of such a coating for use in aggressive media. To do this, we obtained an enamel coating with a thickness of 0.5–0.6 mm in the fused and recrystallized states on round plates with a diameter of 70 mm made from mark 10 steel. To obtain the thickness of the coating, we applied one ground-coat and two layers of glass—crystalline enamel, each of which was melted at 920°C for 5 rain. The heat treatment, for the purpose of effecting crystallization, was performed at 720°C for 2 h.

X-ray structural and electron-microscopic analysis indicated that the fused coating has a zonal structure and that it contains 3–5% of a mineral phase. It was identified as α-quartz (3.35 Å) and rutile (3.24 Å); these crystals are 1–2 μ in diameter and fill the liquation regions of the enamel, which is indicative of partial crystallization of the coating during firing.

Heat treatment leads to quantitative and qualitative changes in the mineralogical composition of the coating. The total amount of crystalline phase is increased and constitutes approximately 20–25%. A quartz—like phase with a lithium composition (3.40 Å), cristobalite (4.09 Å), an insignificant amount of sodium silicate (3.10 Å), and a phase of a conjectured composition (2.693 Å) are formed in the coating.

One percent of cryolite was added to the enamel on milling for improving the technological properties (reduction of melting temperature and viscosity). The effect of this additive on chemical durability was also studied. The amount of clay and ammonium molybdate in all of the coatings was identical (5 and 0.5 parts by weight per 100 parts of enamel).

To determine the chemical durability, we subjected the enamel both in the fused and recrystallized states to the protracted action of a boiling 20% solution of hydrochloric acid. To obtain kinetic curves of acid corrosion of the coating, fresh samples obtained under identical technological conditions were subjected to the continuous attack of acid for 8, 16, 24, 36, 78, 102, 126, and 150 h. The samples were placed in porcelain vessels by arranging them vertically in relation to the reagent. The ratio of the area of the tested surface to the volume of acid was 1: 10. After the exposure, the samples were repeatedly (about five times) washed in boiling distilled water, dried by rubbing, dried at 120°C for 1 h, and heated...
at 400°C for 2 h. After cooling in a desiccator, the samples were weighed to an accuracy of 0.0001 g. The weight loss was determined in mg/cm². The results obtained are presented in Fig. 1 and Table 1. The number of the coating corresponds to the curve on the figure.

Glass-crystalline coatings with and without cryolite additions give kinetic corrosion curves of the \( \tau \)-type \[I\] after secondary heat treatment as a result of the unidentical corrosion resistance of the glassy and crystalline phases (curves 3 and 4). At the start of the process (0–60 h), the general nature of the growth rate of corrosion follows a parabolic law, then (60–150 h) it is altered to linear.

It follows from the obtained leaching dependence of the coating that, during the 0–60 h period (the parabolic portion of the curve), there occurs a selective leaching of the unstable constituents of the coating (sodium silicate and the residual glass phase impoverished in silica). The silica in the enamel is consumed in this case by the formation of minerals: quartz-like phases with a lithium composition of the petalite type or higher silica phases up to the ratio \( \text{Li}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 = 1 : 1 : 15 \), sodium silicate, a double magnesium–lithium silicate, and cristobalite. At the same time, the unstable components of the enamel are leached out with the formation of a protective film, the thickness of which is continuously increased.

During the period of acid attack from 60 to 150 h, a natural corrosion process occurs in which the film is removed and dissolved; this is indicated by the linear portions of the kinetic curves. Leaching processes also occur which maintain a constancy in film thickness, i.e., the growth rate of the film in regions is equal to its rate of removal.

The corrosion rate in the linear region (90–150 h) is an order of magnitude less than in the parabolic region. It characterizes corrosion stability of the enamel coating during protracted use and can be the basis for calculating the corrosion of the surface. The greatest corrosion rate was found for a recrystallized coating with and without cryolite for the period 0–8 h (0.965 and 1.550 mm per year respectively, curves 3 and 4 in Fig. 1). However, the addition of cryolite on milling the glass-crystalline enamel composition is effective, since the technological properties are improved and the acid resistance is reduced only during the first period of attack (0–8 h); this is a consequence of the fact that, during the short period of forming the enamel coating on the metal, the particles of cryolite do not form a monolithic framework with the particles of the enamel frit.

The corrosion rate of the fused enamel coating (curves 1 and 2) gradually acquire a linear nature, which is characteristic of highly acid-resistant liquating compositions of glass–enamel coatings, where the main glassy phase is stable to the reagent. The leaching is attributed to the slip additions and, in the given case, to partial crystallization during melting.

The obtained kinetic curves of acid corrosion of a glass–crystalline enamel coating, both fused and recrystallized, are characterized by the fact that the loss in weight, and, hence, the corrosion rate in the initial regions, is great (0.061–0.388 mg/cm²). After 50–60 h, there is a sharp decrease in the slope of the curve, which characterizes the good protective properties of the forming film. A similar nature for the kinetic curves is found for the kinetic curves of high acid-resistant apparatus glasses such as Pyrex, Vycor, etc. \[I\]. The corrosion characteristics of the losses in the given case should be determined from