AD 683386

FSTC-HT-23-98-68

# U.S. ARMY FOREIGN SCIENCE AND TECHNOLOGY CENTER

JUN 17 1969

COMPOSITION AND PERFORMANCE PROPERTIES

OF HEAT RESISTANT COATINGS

COUNTRY: USSR

## TECHNICAL TRANSLATION

Distribution of this document is unlimited. It may be released to the Clearinghouse, Department of Commerce, for sale to the general public.

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va. 22151

49

AD 680 800

TECHNICAL TRANSLATION

FSTC-HT-23- 98-68

# COMPOSITION AND PERFORMANCE PROPERTIES OF HEAT RESISTANT COATINGS

by

A. A. Appen

SOURCE: TEMPERATUROUSTOYCHIVYY
NEORGANICHESKIYE POKRYTIYA
Chapter IV, (Russian)
1967, pp. 107-147

Translated for FSTC by ACSI

This translation is a rendition of the original foreign text without any analytical or editorial comment. Statements or theories advocated or implied are those of the source and do not necessarily reflect the position or opinion of the US Army Foreign Science and Technology Center. This translation is published with a minimum of copy editing and graphics preparation in order to expedite the dissemination of information. Requests for additional copies of this document should be addressed to the Defense Documentation Center, Cameron Station, Alexandria, Virginia, ATTN: OSR-2

UNCLASSIFIED
Security Classification

AD 688386

## DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Foreign Science and Technology Center
US Army Materiel Command
Department of the Army

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
Composition and Performance Properties of Heat Resistant Coatings

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Translation

5. AUTHOR(S) (First name, middle initial, last name)
A. A. Appen

6. REPORT DATE
7 MAR 68

7a. TOTAL NO. OF PAGES
45

7b. NO. OF REFS
N/A

8a. CONTRACT OR GRANT NO.

b. PROJECT NO.

c. 9223628 2301

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
FSTC-HT-23- 98-68

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
ACSI Control Number J-4433

10. DISTRIBUTION STATEMENT
Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
US Army Foreign Science and Technology Center

13. ABSTRACT

The requirements for, and the types of, long-term and short-term heat resistant coatings are discussed from the standpoint of their composition and performance. Particular attention is given to aluminum coatings.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED
Security Classification

# COMPOSITION AND PERFORMANCE PROPERTIES OF HEAT RESISTANT COATINGS

A. A. Appen

TEMPERATUROUSTOYCHIVYY
NEORGANICHESKIYE POKRYTIYA,
CHAPTER IV, (Russian)
1967, pp. 107-147

Heat resistant coatings are divided into two groups depending upon the coating and temperature of operation set forth by the requirements of practice: long-term coatings (from several hours to several years) and short-term coatings (seconds, minutes). The second type of coating has become particularly important during recent years due to the development of rocket technology. Short-term coatings are called upon to work under conditions of a high-speed gas flow at gas temperatures up to 2000° to 3000° or more. They must protect the construction metal parts from overheating and, in this way, preserve their sturdiness.

Consequently, they primarily must be outstanding in low heat conductivity. At the same time, they must be resistant for a short time to erosion and corrosion in gas streams that are of an explosive nature.

Different requirements are made on long-term coatings, but they work at lower temperatures. There are, at least six groups of such coatings:

1) Heat insulating;
2) Corrosion resistant which work in gas environments containing $O_2$, $H_2O$, $SO_2$, $Cl_2$ et al, in media of alloys and hot solutions, frequently, at high pressures;
3) Erosion resistant which function in gas streams contaminated by hard particles or in contact with mobile hard and liquid bodies;
4) Heat conducting;
5) Electric insulating;
6) Coatings with other special properties.

Frequently the same coatings must satisfy several of these requirements at the same time.

Heat resistant coatings can be classified into four basic types according to their composition: metal coatings, oxide, metal-like, and composite coatings.

## Metal Coatings

Table 29 shows several general conclusions concerning the formation of metal coatings from a melted state on iron and concerning the behavior of them when heated.

Metals, which do not interact with iron (group 4), adhere weakly to the surface since there is only a van der Waals mechanical bond. Generally speaking, no coating is formed in the absence of any wetting.* Activating admixtures are added to the fused metals in order to reinforce the bonds. For example, tin (up to 25%) or antimony (up to 10%) are put into the fused lead during lead plating.

Metals, which interact with iron (groups 1, 2, 3), under proper temperature conditions adhere firmly to the surface because of the chemical bonds which arise between the contiguous phases. However, even this circumstance has a negative aspect. Such metals are much more inclined to diffuse into the backing during operation at high temperatures. The reverse process then ensues rapidly - diffusion of iron into the coating. As a result of the interaction, solid solutions or intermetal compounds are formed and, in the final analysis, the poor effectiveness of coatings made from rare metals is due to precisely this destructive action of diffusion.

Table 29.

Nature of Interaction of Solid Iron with Elements in Dual Systems [135]

| Group | Elements | Nature of Interaction |
|---|---|---|
| 1. | V, Cr | Continuous solid solutions with α- iron (ferrite)are formed |
| 2. | Co, Ni, Rh, Pd, Ir, Pt, Au | Continuous solid solutions with γ- iron (austenite) are formed |
| 3. | C, N, P, B, As, Sb, Zn, Ga, In, Ge, Sn, Mn, Be, Al, Sc, Ti, Zr, Nb, Mo, W, Ta, Hf, Os, Ru, Mg | Limited solid solutions or compounds are formed |
| 4. | Ag, Cd, Hg, Tl, Pb, Bi, Li, Na, K, Rb, Cs, Ca, Sr, Ba | There is practically no interaction, i.e., they do not form either solid solutions nor intermetal compounds. |

* The formation of coatings from non-wetting metals is possible if the technology of the electrochemical precipitation of metals from water or melted salt solution is used.

There are metal coatings which play the special role of sealing layers against rapidly diffusing elements. For example, a layer of copper serves as an effective barrier to the penetration of carbon into the metals (iron, nickel, molybdenum, tungsten,et al). Figure 43 shown schematically the type of section when carbon is diffused into metals without a coating (a) and with a coating which has a thickness of h (b). The inhibiting capability of coatings is rated by the relative decrease of the depth of the diffusion layer $\frac{\Delta x}{x_0}$. As we can see from Figure 44, the copper coating has practically retarded the diffusion of the carbon into iron even at a thickness of approximately 3 mc. Chrome, nickel, and cobalt coatings inhibit diffusion by only 10 to 30% with this thickness [136].

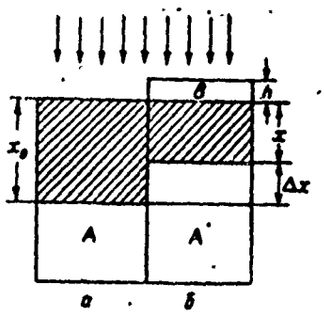



Figure 43. Diffusion of Carbon into Metal without Coating (a) and with Coating (b): h - thickness of coating; x - depth of diffusion layer under coating; A - metal; B - coating.

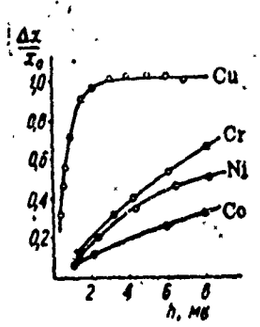



Figure 44. Diffusion of carbon into Iron Through coating composed of Copper, Chromium, Nickel, and Cobalt in a solid Carbonizer.

Temperature-950 to 980°C, time-6 hours, h-thickness of coating.

How do we explain the fact that the copper layer is so very effective? If we arrange the metals according to their increasing affinity to carbon, then we have the following sequence:

Cu, Co, Ni, Si, Al, Fe, Mn, Cr, W, Mo, V, Ti

Copper has the least affinity for carbon among the other metals in this series. This is one of the reasons for the weak diffusion of carbon in copper. The supposition has also been put forth that an electric field which prevents the penetration of carbon is formed on the surface of copper. Neither does copper interact with boron. The copper layer, with a thickness of 0.15 mm according to data [137], completely protects the steel from the penetration of boron at a temperature of 950° (time - 2 hours).

Tin is another example of an inert sealing layer. Coatings made of tin protect the metals from the penetration of nitrogen into them. Nitrogen is non-soluble in tin and does not form compounds with it at a temperature up to 800°. Therefore, there is no diffusion. Coatings made of palladium would be even more effective since nitrogen is non-soluble in palladium up to a temperature of 1400°. The absence of solubility means the absence of affinity.

Generally speaking, the speed of diffusion is connected in a complicated way with the affinity of the diffusing element to the metal backing. The reverse phenomenon is possible when not a weak, but a strong affinity serves as the reason for the delayed diffusion. This occurs when the speed of diffusion in an arising new phase is somewhat less than the speed of diffusion in the initial metal. At that time, a new phase which forms as a result of the action begins to play the role of the sealing layer. Carbon diffuses into molybdenum and tungsten with less rapidity than into iron, although the affinity to the former is greater because of the formation of carbides of molybdenum and tungsten in the surface layer.

Metal coatings, which have been applied to steel, are for the most part, distinguished by their high adhesion qualities and the way in which they can withstand mechanical and heat shocks well. They can be applied by almost all the existing methods, and it cannot always be easily stated which of the methods should be given preference. The effectiveness of a covering to service depends not only on its composition, but also on the method of application and reinforcement.

Here we will discuss coatings formed from a fused state by submerging articles into fusions by pulverizing metal fusions and by methods of welding seams.

Coatings made from easily fusible metals such as zinc, tin, lead, aluminum, and cadmium are applied by means of submersion. The technology of hot zinc plating, tin plating, and lead plating of iron has been developed for a long time and is in wide use [123]. However, these coatings do not assure protection of steel parts at high temperatures. Zinc coatings

are intended primarily for service under atmospheric conditions, tin coatings - in non-aggressive solutions and organic acids, lead coatings - in sulfuric acid vapor, and cadmium coatings - in sea water and in alkaline solutions. With regard to protecting iron from oxidation in gas environments in response to high temperatures, aluminum has the best properties in this respect.

Aluminum coatings, applied by submerging it in the fusion, is one of the most effective ways of protecting iron from oxidation even to temperatures of 1000 to 1100° [138]. Both solid solutions as well as specific compounds FeAl, $FeAl_2$, $Fe_2Al_5$, $FeAl_3$, $Fe_2Al_7$ are formed in the interaction of aluminum and iron. Of these, only the compound $Fe_2Al_5$ is melted congruently (without decomposing) at a temperature of 1173°. Temperatures for melting other compounds also lie below 1200°, and they are melted incongruently (with decomposition) and according to peritectic reactions [139].

Aluminum coating is also an excellent means of high temperature protection of alloyed steels and alloys based on nickel. Aluminum forms a number of compounds with nickel - $Ni_3Al$, NiAl, $Ni_2Al_3$, $NiAl_3$, and NiAl is the most interesting of them. It melts congruently only at a temperature of 1640° and is hardly even oxidized up to 1100°. To be more exact, a thin film of spinel $NiAl_2O_4$, which has outstanding protective qualities, must be formed on the surface [140].

The fused aluminum forms, in addition, effective protective coverings on titanium, molybdenum, niobium, and other metals. When titanium is submerged into a fusion of aluminum for 20 to 90 minutes (temperature 830 to 850°), diffusion coatings consisting of $TiAl_3$ and TiAl with a thickness of 60 to 110 mc are formed. The addition of up to 12% of silicon to the fused aluminum increases the protective properties of the coating. At 900 to 1000°, the heat resistance of titanium in the air after coating with aluminum and aluminum silicate is improved 30 to 35, and 80 to 150 times respectively [111].

It should be emphasized that the quality of aluminum coatings depends greatly on the method by which they are formed. Coatings, applied not by the submergence of the article in a fusion, but by pulverizing the fusion is much less effective because of the porosity. Only after the protected articles have undergone thermal treatment in a vacuum or in a neutral atmosphere is the protective action of the fused coatings significantly improved because of the rise of an intermediate diffusion layer.

If we make use of the methods of melting and fusing, the circle of materials, suitable for obtaining metal coatings, is basically increased somewhat. Different types of alloyed steels, nichrome, and other alloys on a nickel base, intermetallides, copper, molybdenum, tungsten, et al, may be used.

For example, steels and alloys, intended for electrical heating elements of resistance [141] and other heat resistant alloys can be used as heat resistant coatings on iron. They are made on the basis of the system Ni-Cr, Ni-Al, Fe-Cr-Al, Ni-Cr-Al, Fe-Ni-Cr-Al (Table 30). Spinels such as $NiCr_2O_4$, $NiAl_2O_4$ and their solid solutions, which even protect material from oxidation, are formed on the surface of such alloys.

Table 30.

Composition (% by weight) of Some Metal Alloys Based on Iron and Nickel which are Suitable for Use as Heat Resistant Coverings

| Сплав a | Fe | Ni | Cr | Al | Co | Mn | Si | C | Другие элементы b |
|---|---|---|---|---|---|---|---|---|---|
| № 3 | 67,5—63,5 | — | 25—27 | 6—8 | — | < 0,5 | <0,8 | 0,05 | 0,2—0,4 Ti |
| № 5 | 47—36 | 30—35 | 18—22 | 4—6 | — | — | 1,0 | 0,05 | — |
| Kh25N20S2 | 53—45 | 18—21 | 23—27 | — | — | 1,5 | 2—3 | 0,2 | — |
| c Сплав Смита | 55 | — | 37,5 | 7,5 | — | — | — | — | — |
| d Кантал | 67 | — | 25 | 5 | 3 | — | — | — | — |
| Kh18N25S2 | 56—49 | 23—26 | 17—20 | — | — | < 1,5 | 2—3 | 0,3—0,4 | — |
| Kh20N80 | — | 78—75 | 20—23 | — | — | < 1,5 | <0,5 | 0,15 | — |
| VKhN-1 | — | 60—50 | 35—40 | — | — | < 0,5 | 1,5—2,3 | 0,5—1,2 | — |
| KhN60YU | 19—26 | 58—55 | 15—18 | 2,6—3,5 | — | < 0,3 | <0,8 | < 0,1 | |
| Kh70YU | < 1,0 | 69—65 | 26—29 | 2,6—3,5 | — | < 0,3 | <0,8 | < 0,1 | |
| KhN77TYU | 1,0 | 76—75 | 20 | 0,75 | — | — | — | 0,06 | 2,5 Ti |

Key: a- Alloy
b- Other elements
c- Smith alloy
d- Kantol

The speed with which the better alloys oxidize even at a temperature of 1200° still remains low (increase of weight less than 1 $g/m^2$ hr).

Table 31.

Heat Resistant Intermetallides

| Intermetallide | Melting Point °C | Привес в воздухе при 1250°, (100 ч) г/м²·ч a | Intermetallide | Melting Point °C | Привес в воздухе при 1250°, (100 ч) г/м²·ч a |
|---|---|---|---|---|---|
| $TiBe_{12}$ . . . | 1430 | 0,30 | $YBe_{13}$ . . . | 1920 | — |
| $ZrBe_{13}$ . . . | 1930 | 0,62 | $WBe_2$ . . . | 1800 | 0,51 |
| $CrBe_2$ . . . | 1840 | 0,23 | $TaAl_3$ . . . | 1690 | 0,64 |
| $LaBe_{13}$ . . | 1810 | 0,20 | $NbAl_3$ . . . | 1660 | 0,22 |
| $TaBe_{12}$ . . . | 183[illegible] | 0,39 | NiAl . . . | 1640 | — |
| $MoBe_2$ . . | 171[illegible] | 0,26 | TiAl . . . | 1520 | — |
| $NbBe_{12}$ . . | 15[illegible] | 0,13 | CoAl . . . | 1630 | — |

Key: a- Increase in weight in air at 1250° (100 hr) $g/m^2$ hr.

Carbon has a very complicated influence on the stability of steels in the gas environment. It has been persuasively shown in literature [307] that the speed with which non-alloyed steels are oxidized under static conditions becomes slower as the amount of carbon in them increases. With regard to the resistance of high alloyed steels to erosion in gas streams, the monograph [304] draws reverse conclusions and recommends that the percentage of carbon in steels be very rigidly limited.

Several intermetallic compounds [142] have bright prospects. Beryllides [321] and aluminides [139] are among the intermetallides with a high heat resistance (Table 31).

Such metals as Cr, V, Co, Pt, et al, are precipitated from salt fusions on iron and steels by chemical and electrochemical methods. Chrome coatings are deserving of particualr attention. They have considerably high heat resistance in an oxidizing atmosphere, resistance to wear and tear, and resistance in many liquid aggressive environments. The properties of chrome coatings and methods of obtaining them have been described in detail in a monography by G. N. Dubinin [8].

The destruction of metal surfaces in gas environments usually occurs more or less equally throughout the entire surface or, to be more exact, at multiple points dispersed statistically evenly throughout the surface. Therefore, the protective action of the metal coatings can be quantitatively evaluated according to the increase in weight of the samples due to oxidation, per unit of surface or according to the loss in weight after removing the products of corrosion. At temperatures accepted as limiting for the use of coatings, the increase in weight of the protected samples amounts to approximately 0.1 mg/cm$^2$ hr. i.e., 1 g/m$^2$ hr. We can stipulate this figure to mean the limited acceptable norm of gas corrosion.

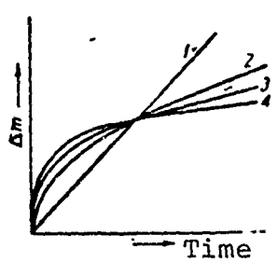



Figure 45. Standard Curves of High Temperature Oxidation of Metals and Alloys.

Dependent: 1- linear; 2- parabolic; 3- cubic; 4- logarithmic.

Here we should have a reservation. The dependence of the speed of oxidation of metal coverings, and of heat resistant

alloys, on time is usually not rectilinear (Figure 45). The connection between the increase in weight of metals $\Delta m$ and delayed time t at a given temperature is expressed for the various metals and alloys by four standard types of equations [143]:

| | | |
|---|---|---|
| Linear | $\Delta m = kt$ | (31) |
| Parabolic | $\Delta m^2 = k_1 t$ | (32) |
| Cubic | $\Delta m^3 = k_2 t$ | (33) |
| Logarithmic | $\Delta m = k_3 \lg t + k_4$ | (34) |

It was shown in the article [144] that the natural law underlying the oxidation of different types of heat resistant steels obeys either the logarithmic equation or an equation such as

$$\Delta m^n = kt \qquad (35)$$

where n varies from 1.27 to 2.06. The values k convey the idea of the constant of speed of oxidation.

The conditional norm for gas corrosion mentioned above should be considered as an average value computed at the initial period of service for the covering or material (for the first 100 hr).*

The process of corrosion in pure water or steam- and water-mixtures in heat power plants, even under high pressure (100 to 300 atm) at a temperature of 300 to 500° takes place much more slowly. Therefore, even the limited allowable norm of speed of corrosion is correspondingly lower: 0.1 $g/m^2$ hr. in ordinary and 0.01 $g/m^2$ hr. in atomic plants for the first 1000 hours; the difference $\Delta m = m_1 - m_2$ is considered to be the increase in weight of the sample where $m_1$ is the weight of the sample after testing, $m_2$ is the weight of the same sample after removing the parts of corrosion per 1 $m^2$ of surface and time 1 hour.

In evaluating the corrosion stability of metal coverings, attention must be paid to the nature of corrosion which can be equal, ulcerous, point, and intercrystallite. The speed of the uniform corrosion is frequently expressed by the depth of the disintegrated layer $\delta$ mm/yr. Conversion from units of $\Delta m$ $g/m^2$ hr. to units of $\delta$ mm/yr is done according to the formula:

---

* According to [303] the speed of oxidation of heat resistant steels containing approximately 25% Cr falls in due course to only a specific limit; after approximately 300- 500 hours of testing at 1100°, subsequent oxidation takes on increasing speed.

$$\delta = \frac{8.76 \cdot \Delta m}{\rho} \qquad (36)$$

where $\rho$ is the specific gravity of the corroding metal.

Units $g/m^2$ hr. and mm/yr differ numerically very little since the specific gravities of many metals and alloys are similar to the converted coefficient of 8.76.

Stainless chrome nickel steels have an excellent resistance to the action of water and steam at stringent parameters (temperature up to 500°, pressure 300 to 500 at) and some acid and alkaline solutions. For example, the best of them, Kh18N10T, Kh17N13M2T, Kh28N4, Kh23N28M2T, OKh23N28M3D3T, EI696 et al, as well as alloys of titanium and zircon, are quite economically feasible to use as a double layer clad rolled iron and as coatings. The latter are applied by melting and fusing. But since the fused coatings have high porosity (10 to 15%), to make them impenetrable for liquid media, they must be subjected to an additional treatment - chemical-mechanical, or thermal.

In chemical treatment with specially collected solutions, the pores are sealed with specific non-soluble compounds.

The mechanical cleaning with a blast of metal shot or rolling with rollers and scratch finishing are effective if the metal of the coating is sufficiently plastic.

Thermal treatment boils down to annealing the article in a reducing atmosphere, for example, in a CO environment at a temperature of 1000 to 1100°, as a result of which oxide films dividing individual particles of the metal are reduced, and the coatings bake and form clinkers.

The fused coatings can be made impenetrable for liquids by increasing the thickness of the layer to 0.6-1.0 mm.

There is no necessity here of comparing the resistance of specific types of steels and special alloys in different aggressive liquids. There is detailed textbook literature [145-301], and by making use of it, one may select materials which are the most acceptable for use under specific conditions.

Where resistant metal coatings, suitable for use both under normal as well as in comparatively high temperatures, belong to an independent wide class. They consist of carbide alloys of iron or cobalt with those metals (W, Cr, V, Ti, Mn et al) which forming carbides, gives a high degree of hardness and high resistance against abrasive wear and tear to the systems. They also include silicon in small amounts. Coatings, containing more than 3.5% carbon, or more than 3% silicon and 0.5% boron, belong to the type of metal-like coatings, and are

discussed below.

Table 32.

Composition of Selected Wear Resistant Iron and Cobalt Based Material Coatings

| Type of fused metals | Composition of Fused Layer or Fused Materials % by weight | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | Cr | W | V | Ni | other elements | Base |
| TBKKh - 10V | 1,57 | — | — | 7,2 | — | — | — | Mo 1,0; B 0,5 | Cobalt |
| R6F2K14M5 | 1,0—1,2 | <0,3 | <0,3 | 3,8—4,2 | 5,5—6,5 | 1,8—2,2 | <0,3 | Mo 5; Co 15 | |
| OM6* | 0,5—0,8 | — | — | 10—12 | — | — | — | — | |
| O3N - 400* | 0,18—0,22 | — | 4,0—4,7 | — | — | — | — | — | |
| PP - Kh 12* | 2,0—2,3 | < 0,4 | < 0,35 | 11,5—13,0 | — | — | < 0,35 | — | |
| PP - P 9* | 0,85—0,95 | < 0,45 | < 0,45 | 3,8—4,4 | 8,5—10,0 | 2,0—2,6 | — | — | |
| PP - R 18* | 0,7—0,8 | < 0,4 | < 0,4 | 3,8—4,4 | 17,5—19,0 | 1,0—1,4 | — | — | |
| Kh 34 | 1,8 | 1,4 | — | 34—37 | — | — | — | — | |
| SV-25Kh25116G7 | 0,2—0,3 | < 0,3 | 6—8 | 24—27 | — | — | 15—17 | — | |
| 3Kh2V8 | 0,3—0,4 | < 0,35 | 0,2—0,4 | 2,2—2,7 | 7,5—9,0 | 0,2—0,5 | < 0,30 | — | |
| 4Kh8V2 | 0,35—0,45 | < 0,35 | 0,2—0,4 | 7—9 | 2—3 | — | — | — | |
| 30Kh10G10 | 0,3—0,4 | 0,5—0,8 | 10,5—12,5 | 12—14 | — | — | — | — | |
| NP - 4Kh 13A | 0,35—0,45 | < 0,5 | < 0,6 | 12—14 | — | — | < 0,6 | — | |
| NP - G13A | 1,0—1,2 | < 0,4 | 12,5—14,5 | < 0,6 | — | — | < 0,6 | — | |
| Iron strip ChE | 3,3—3,6 | 1,3—1,4 | 0,2—0,4 | — | — | — | — | — | |
| ZhC - 400* | 0,30—0,35 | 0,15 | 1,8—2,0 | 5,0—5,5 | — | — | — | — | |
| ZhC - 500* | 0,4—0,8 | 0,6—1,0 | 3,0—3,5 | 10—15 | — | — | — | — | |
| Sormayt- 2 | 1,5—2,0 | 1,5—2,2 | 1,0 | 13,5—17,5 | — | — | 1,3—2,2 | — | Iron |
| Stellite V2K | 1,8—2,5 | 1—2 | 1,0 | 27—33 | 13—17 | — | < 2 | < 2Fe | |
| Stellite V2K | 1,0—1,5 | 2,5 | — | 28—32 | 4—5 | — | < 2 | < 2Fe | |

* Composition of fused layer

Table 32 shows the representative composition of some wear resistant metal coatings. Many of them also have a high degree of heat resistance. They are applied to the articles through welding in different variations for which special welding materials are used (electrodes, alloy fluxes) or alloyed steels and alloys of standard types (wire, strip).

The wear of metals is a complicated process depending upon a whole complex of diverse factors [304]. In practice, one encounters several varieties of erosion, abrasive, cavitation gas, electric, ultrasound et al. The question of which coating should be used in each specific case is resolved after conducting preliminary tests.

## Oxide Coatings

Oxide coatings can be both simple (one component) or complex.

The action of pure oxides on iron differs greatly. According to the data in [146], the oxides $SiO_2$, $TiO_2$, $Al_2O_3$, $B_2O_3$, NiO ZnO, CuO, applied on the surface in the form of suspensions, delays the process of oxidation of iron in air at temperatures of 800 to 1100°; on the other hand, the oxides $Na_2O$, PbO, MgO, CaO, BaO, accelerate gas corrosion. However, they are so aggressive only in a free state. In association with $SiO_2$, they lose, to a significant degree, their aggressive properties. For example, even sodium metasilicate $Na_2SiO_3$ has the property for protecting coatings even though it is not very effective.

Two classes of oxide coatings are formed from the fused state: glass-like and crystalline. But such a subdivision is not strictly adhered to; it is done only according to the sign of the predominating phase since glass-like coatings may contain crystalline particles and crystalline coatings frequently contain a significant amount of glass-like substances. The so-called sital enamels contain approximately 50% other phases.

### 1. Glass-Like Silicate Enamels

Silicate enamels in the form of artistic decorations on metals have been known since ancient times. For a long time, they have been used for enameling household dishes. However, in the last ten years, silicate enamels have become especially important in a new field - as an effective means of protecting chemical equipment from corrosion in acid, alkaline, and other aggressive solutions including high temperatures and pressures.

Silicate enamels are divided into two categories according to the sequence of application: primer and cover. Primer enamels are applied on metals with the first layer, coated enamels with a second and third layer, and if necessary, by subsequent layers. A primer assures that the coating will adhere to the metals; a coating upper layer must have high resistance to external aggressive atmosphere.

It has been recommended that primer enamels be used with the widest softening integral possible. This makes it possible to apply different coating enamels on one and the same primer. The softening interval is best expanded by mixing in a grist of two frit of different fusibility and by adding thinly ground quartz sand to the frit.

Table 33 shows the composition of some widely used priming enamels.

Table 33

Composition of Priming Enamels (Frit) on Steel and Iron (% by Weight)

| № грунтовой эмали 1 | $SiO_2$ | $Al_2O_3$ | $B_2O_3$ | CaO | $Na_2O$ | $K_2O$ | CoO | NiO | $MnO_2$ | $CaF_2$ | Другие компоненты 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2015 | 46,0 | 8,0 | 18,3 | 5,6 | 20,0 | — | 0,6 | 0,6 | 0,9 | — | F 2,6 |
| 3132 | 50,3 | 2,2 | 26,1 | 1,1 | 11,9 | 1,0 | 1,2 | 0,6 | 0,6 | 5,0 | — |
| 18 | 46,6 | 6,0 | 20,2 | — | 17,3 | — | 0,5 | 0,8 | 1,1 | 7,5 | — |
| 41 | 50,3 | 7,8 | 13,9 | — | 12,1 | 4,7 | 0,5 | 0,6 | 2,6 | 7,5 | — |
| 8ч | 58,0 | 4,0 | 19,3 | 4,0 | 14,0 | — | 0,2 | — | 0,5 | — | — |
| Ф-3 | 68,1 | 5,8 | 12,3 | 0,8 | 11,2 | 1,2 | 0,2 | — | 0,6 | — | — |
| 8 | 35,1 | 5,0 | 21,5 | 4,0 | 23,2 | — | 0,4 | 0,8 | 0,5 | 6,0 | $TiO_2$ 3,5 |
| СД * | 49,2 | 5,3 | 12,3 | 11,6 | 19,2 | — | 0,4 | 0,8 | 1,2 | — | F 3,4 |

* In manufacturing the complex Danburite enamel S.D., Danburite concentrate and calcium borate are used instead of the scarce boric acid or borax; therefore, the composition of the primer is characterized by a high percentage of CaO. The table shows the average composition obtained after mixing the three different frits [317].

Key: 1. Number of priming enamel
2. Other elements.

Primers 2015 and 3132 are intended for chemical equipment. When dross is being prepared, they are usually mixed in a ratio of 70:30. In addition, water (40 to 50%), clay (3 to 9%), ground sand (30%) and small admixtures of borax, sodium nitrite and others are put in the mill. The specific gravity of the dross is 1.68 to 1.69. Other ratios between the components of the dross are possible.

Primers 18 and 41 are used in the production of enamelware. Primers 8ch (fused) and F-3 (baked) are intended for items made of iron; the fused primer 3132 mixed with ground sand is also suitable for iron equipment.

Primer 8 is easily fused; its firing temperature lies in the interval of 780 to 800° [315].

At present, a study is being made of white primer-free enamel of steels; however, their results have not yet found wide application in process.

## Heat Resistant Enamels

In addition to their basic purpose - that of protecting metals from corrosion in liquid solutions - silicate enamels are widely used as a means of protecting metals for a long period of time from oxidation and deterioration in gas environments at temperatures of 600° and above; however, it must be acknowledged that prolonged and systematic research is required for developing the optimum formula for heat resistant enamel coatings.

All heat resistant enamels must have a high softening point since coatings which soften during their use, do not answer technical requirements. The higher the softening point of the enamels, the higher is the possible temperature for their use. But, as a rule, increasing the infusibility is accompanied by a decrease in their coefficient of thermal expansion $\alpha$ (c.t.e.), inasmuch as almost all infusible oxides lower the c.t.e. of the glass-like silicates. Moreover, the difference $\Delta\alpha$ grows between the c.t.e. of steel and enamel. Both these facts - the increase in the softening point of enamel and the increase in the difference of $\Delta\alpha$ - leads to a sharp increase in tension in the layer of enamel which shows up in its adhesion to steel. Therefore, in creating heat-resistant enamels, there is a constant worry about the requisite adherence of the enamel to the steel. Usually, this is limited by applying the enamel in the form of very thin layers (0.05 to 0.10 mm). Serious complications also arise in the firing process itself of high temperature enamels.

Table 37.

Compositions of enamels with increased alkali resistance to steel (weight %)

| № эмали a | $SiO_2$ | $ZrO_2$ | $TiO_2$ | $SnO_2$ | $B_2O_3$ | $Al_2O_3$ | ZnO | CaO | $K_2O$ | $Na_2O$ | $Li_2O$ | Сверх 100% F b |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 28 | 64 | — | — | — | — | 5 | 12 | — | — | 19 | — | — |
| 29 | 54 | — | — | 13,5 | 3,1 | 2,3 | — | 6,3 | — | 20,8 | — | — |
| 77 | 56 | 5 | 2 | — | 3 | 7 | 7 | — | — | 20 | — | 4 |
| 18 | 52 | 18 | 5 | — | 3 | — | — | 2 | 1 | 17 | 2 | 3 |

Key: a- Enamel No.
b- Over 100% F

The use of infusible frits is technically difficult. The most promising is the use of comparatively easily fusible frits to which refractory components are added in the grist. Refractory admixtures are oxides $SiO_2$, $Al_2O_3$, $ZrO_2$, $Cr_2O_3$, $CeO_2$, $La_2O_3$, $TiO_2$ et al, or minerals such as

zircon, diaspore, mullite, chromite, kaolin, feldspar et al [6, 122, 163].

Table 38 shows the composition of the most well known or recently suggested heat resistant enamels. They are all multi-components, but are divided into two groups: alkali alumo silicate and barium silicate.

Table 38.

Composition of Representative Heat Resistant Enamels on Steels, Frits, % by Weight

| Component | Number of Frit | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | — | 11 | 32 | 285 | 2/2 | 10 | 331 | 332 | — | 435 | — | — |
| $SiO_2$ | 74,5 | 42,0 | 56,5 | 51,1 | 63,3 | 58 | 38,5 | 37,5 | 43,0 | 37,00 | 31 | 29 |
| $TiO_2$ | 3,8 | — | — | — | 4,3 | — | — | — | — | — | 2 | — |
| $ZrO_2$ | — | — | — | — | — | — | — | 2,5 | — | — | — | — |
| $B_2O_3$ | — | 25,8 | 10,5 | 9,5 | 1,7 | 11 | 6,5 | 6,5 | — | — | 5 | 5 |
| $Al_2O_3$ | 2,5 | 5,6 | 8,4 | 19,8 | 2,8 | 10 | — | 1,0 | — | — | 1,5 | 1,5 |
| $Cr_2O_3$ | — | — | — | — | 0,4 | — | — | — | — | — | 21 | 21 |
| BeO | — | — | — | — | — | — | 2,5 | — | 2,5 | 3,10 | — | — |
| CaO | — | — | — | — | 4,8 | — | 3,5 | 3,5 | 4,0 | 4,15 | 2,5 | 2,5 |
| BaO | — | — | — | — | — | 3,5 | 44,0 | 44,0 | 42,5 | 47,25 | 33 | 33 |
| ZnO | — | — | — | — | — | — | 5,0 | 5,0 | 5,0 | 5,0 | — | 4 |
| MnO | — | 1,2 | 1,8 | — | — | — | — | — | — | — | 1,5 | 1,5 |
| CoO | 0,5 | 0,5 | 0,5 | — | 0,3 | 1 | — | — | — | — | 1,5 | 1,5 |
| NiO | — | 0,6 | 0,6 | — | 0,1 | 0,5 | — | — | — | — | — | — |
| $Li_2O$ | 4,65 | — | — | — | — | — | — | — | — | — | — | — |
| $Na_2O$ | 5,25 | 17,9 | 12,1 | 10,9 | 16,1 | 16 | — | — | — | — | — | — |
| $K_2O$ | 4,8 | 3,4 | 5,1 | 4,6 | 4,2 | — | — | — | — | — | — | — |
| $CaF_2$ | — | 3,0 | 4,5 | 4,1 | 2,0 | — | — | — | — | — | — | — |
| $P_2O_5$ | — | — | — | — | — | — | — | — | — | 3,50 | — | — |
| $MoO_3$ | — | — | — | — | — | — | — | — | 3,0 | — | 1,0 | 1,0 |

Table 38 [continued]

| Component | Dross, Part by Weight | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Number of Dross and Enamel | | | | | | | | | | | |
| | А-32 | А-19Н | Н-32 | Н-285 | № 7 | 10/20 | А-417 | А-418 | ЭВ-55 | № 108 | № 27 | ЭВ-300-60 |
| a Фритта . . | 100 | 100 | 88 | 100 | 50 | 100 | 70 | 70 | 70 | 97,5 | 100 | 100 |
| b Диаспор . . | — | — | 12 | — | 20 | — | — | — | — | — | — | — |
| c Хромит . . | — | — | — | — | 30 | — | — | — | — | — | — | — |
| $Al_2O_3$ . . . | — | 25 | — | — | — | — | — | — | — | — | — | — |
| $Cr_2O_3$ . . . | — | — | — | — | — | 20 | 30 | 30 | 30 | 15 | — | — |
| $CeO_2$ . . . | — | — | — | — | — | — | — | — | — | 37,5 | — | — |
| d Глина . . . | 5 | 10 | 8 | 7 | — | 5 | 5 | 5 | 5 | 7,5 | 5 | 5 |
| e Вода . . . | 40 to 50% more than the total weight of the dry component. | | | | | | | | | | | |

Key: a- Frit
b- Diaspore
c- Chromite
d- Clay
e- Water

Enamels A-19, No. 7, No. 10/20 are intended for enameling non-alloyed steels.

Enamels A-417, A-418, EV-55, 108, 27, EV-300-60 are applied on alloyed chrome nickle steels; they do not have to contain adhesion oxides CoO and NiO. The latter two types of enamels are distinctive in that the chromic oxide in it is introduced through the frit into the brew. Highly silicic enamel A-32 is intended for enameling the internal surface of pipes, since it has a comparatively small expansion coefficient [164]. The same defect is peculiar to the barium silicate enamels and, therefore, they are applied in a thin coating.

Heat resistant enamels are fired at high temperatures (1000 to 1250°). To escape excessive oxidation of unalloyed steels when they are fired we recommend that the surface of the item be treated in a nickel solution first (submerging in nickel).

The dross of heat resistant enamels is ground to a high degree of dispersion. Dross A-19 must leave a residue in the sieve of 6400 pref/cm$^2$ of no more than 1% of the weight of the frit; the residue of enamels A-417 and A-418 should not exceed 0.4 g per 50 ml of dross. Dross EV-55 is filtered through the seive with 10000 pref/cm$^2$. By recommendation of the authors, enamel No. 7 is ground less finely: residue 16 to 18% in a sieve 6400 pref/cm$^2$.

The alloy "Inconel," covered with enamel A-417, maintains its properties after 500 hours of operation at a temperature of 900°. The intensity of corrosion of steel 3, protected by enamel No. 7, at 870° in the air amounts to 0.5 mg/cm$^2$ hr.,

while corrosion of unprotected steel under the very same conditions is 19 $mg/cm^2$ hr. [165].

Cover 108 is recommended for chrome nickel parts of nuclear reactors [166]. It is outstanding in its low coefficient of absorption of thermal neutrons (less than 3 barns).

## Improving the Quality of Enamel Coatings

Despite the successes achieved which are known at the present time, enamels still do not answer the ever-increasing level of requirements placed on them by our practice. In particular, there have been no enamels created which resist well enough the action of hot alkaline solutions, solutions of hydrofluoric acid and fluorides, phosphoric acid and phosphates, fused metals and salts.

One can approach the solution of these problems by essentially improving the quality of the silicate enamels now in use. This can be achieved in several ways:

improving and expanding the formula of the frit, for example, by using rare oxides and rare-earth elements;

by introducing into the enamel, several oxygen-free compounds such as silicides, borides, carbides, intermetallides, thinly dispersed metal powders; in the form of ground admixtures;

by crystallizing enamel coatings;

by replacing the metals.

## Expanding the Frit Formula

Among the oxides which have components which hold promise, but are still not used very much in the production of enamels are $Li_2O$, $ZrO_2$l, $P_2O_5$, $TiO_2$, $SnO_2$, SrO, $La_2O_3$, CeO, $Fe_2O_3$, MnO et al.

Lithium oxide is the strongest flux among the alkalis while $Li_2O$ is not so easily decomposed by water reagents as the other alkalis. The use of $Li_2O$ makes it possible to combine high water and acid resistance of the enamels with a high coefficient of expansion and easy fusibility - very important indices for enameling steel equipment. A comparison of the three qualities of enamels 143 and 72 are shown in Table 40 from which it is evident that enamel 72, containing $Li_2O$ (Table 34), has quite an advantage over enamel 143. The effect of the two alkalis (EDShCh) is much more suitable for use in the $Li_2O$ + $Na_2O$ vapor, than in the $Na_2O$ + $K_2O$ vapor.

Table 40.

Comparison of Properties of Enamels 143 and 72 [73]

| Number of Enamel | Properties | | |
|---|---|---|---|
| | $\alpha_{20-400} \cdot 10^7$ | Loss of weight (%) | Viscosity at 1000° (nv) |
| 143 | 101.5 | 0.087 | 12 800 |
| 72 | 108.5 | 0.075 | 1 150 |

Its present high cost prevents the wide use of lithium in the production of enamels. The use of the same natural lithium minerals (spodumene, lepidolite) does not give a good enough effect because of the low percentage of lithium in them (mo more than 4.5%).

Because of its properties, strontium oxide occupies the intermediate place between CaO and BaO, but is closer to the latter. In comparison with CaO, it has a greater fluxing action, lowering the viscosity of the fusions in the area of the firing temperature (lower than 1000°). The partial replacement of CaO by SrO (up to 4 wt. %) somewhat improves the chemical stability of glass. Consequently, the use of SrO opens up the possibility of decreasing the percentage of alkalis in coatings - reserves for additional improvement of chemical stability. At the present time, strontium oxide is used in the form of the natural mineral of celestine containing 92 to 97% $SrSO_4$ in the production of glazed coatings on ceramics [150].

Celestine is still not used in enamel technology. The high percentage of the harmful component $SO_3$ (28.6%) in celestine makes it difficult to use it in production. In order to remove part of the $SO_3$, celestine should first be baked with silica and coal [151].

Ferric and particularly ferrous oxide lowers the viscosity and firing temperature of enamels considerably when it contains almost 20% FeO, and up to 10% $Fe_2O_3$ [152]. Since they are effective fluxes, these components make it possible to increase the chemical stability of enamels by decreasing the concentration of alkalis. As we have already noted above, ferric oxide also improves the adhesion of the coatings and their wetting ability. Manganese oxides MnO and $Mn_2O_3$ affect the properties of enamels in much the same way as ferric oxides.

Ferric and mangenese oxides are materials which are economically easy to obtain, the first in the form of pyrite cinders and the second in the form of pyrolusite. Besides this, they improve the technological qualities of enamels. Therefore, they are recommended for use in those cases when the black color of the enamels is not contraindicated. Later we will speak of some of the reservations concerning this (Ch. V, # 1).

Zirconium oxide improves the chemical stability of glass and enamels with respect to the different reagents (water, acids, carbonic and caustic alkalis). In this sense, zirconium oxide is a component of almost universal action. Zirconium oxide exerts a very favorable affect on alkali resistance of enamels. However, $ZrO_2$ increases the firing point of enamel sharply and, therefore, $Si_2O$ is put into the composition of the coating instead, or as an admixture in the grist.

Titanium dioxide is chemically only a somewhat less stable material than $ZrO_2$ and $SiO_2$. On the other hand, in silicates it acts, to some extent, as a flux and, consequently, belongs to a number of very useful components of enamels. The joint additions of $TiO_2$ and $Fe_2O_3$ affect the properties of enamels very favorably [153]. They can be introduced in the form of a mineral ilmenite of titanium-containing metallurgical slag.

Chromium oxide is notable for the fact that together with its positive effect on chemical stability of enamels, it sharply improves their coating power. Enamels containing even a small amount of chromium oxide (1 to 2%) are distinct for their very smooth surface, uniformity of the layer, and the lovely external affect.

The effect of oxides $SiO_2$, $TiO_2$, $ZrO_2$, and $Cr_2O_3$, introduced in the grist, on acid and alkali resistance of enamel coating 7 is shown in Figures 47 and 48 [73].

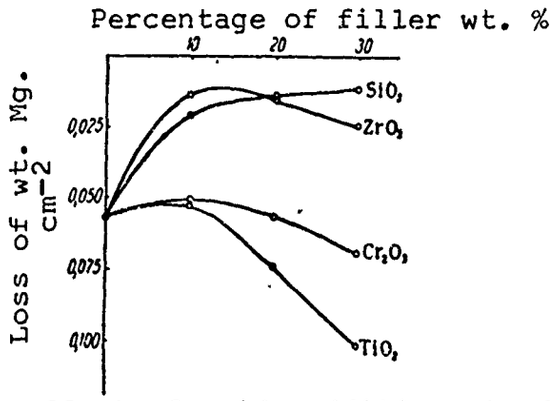



Figure 47. The effect of oxide additives to dross on the stability of enamel coating in 10% boiling $H_2SO_4$ (4 hours)

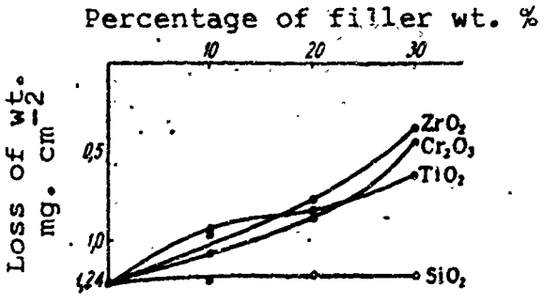



Figure 48. The effect of Oxide additives to dross on the stability of enamel coating in boiling 2 n. Solution of NaOH (4 hours).

Tin dioxide has been known for a long time in practice as an excellent damper of enamels. But, it was only ascertained in recent years that the addition of $SnO_2$ as with $ZrO_2$ sharply increased the alkali resistance of enamels and, with respect to the effectiveness of its effect on the moisture resistance of $SnO_2$ glass, it stands in first place; it has no peer among all the other tested oxides [154].

A very clear-cut positive effect on the alkali resistance of glass of lanthanum oxide $La_2O_3$ [155] and on the acid resistance of niobium oxide $Nb_2O_5$ and tantalum oxide $Ta_2O_5$ has been noted [156].

Almost no study has been given to the effect of rare earth elements oxides on the properties of enamels.

Phosphoric anhydride $P_2O_5$ is of interest as a component on the basis of which glass which is resistant to hydrofluoric acid and HF fumes is synthesized [157, 158]. Phosphoric glass such as $ZnO - Al_2O_3 - P_2O_5$, $Li_2O - MeO - La_2O_3 - Al_2O_3 - P_2O_5$, $Li_2O - La_2O_3 - Al_2O_3 - SiO_2 - P_2O_5$ et al can be used as easily fusible coating which protect metal from the action of phosphorous. With regards to fluorides, since they are strong fluxes, they make it possible to lower the amount of alkalis and increase the percentage of silicon in enamels. Therefore, it is considered feasible to put up to 3% fluorine into the composition of acid-and alkaline resistant enamels.

Investigators have the problem of further improving the formulas for frit so that they can find the best combination of effective components among the tremendous number of variations for each of the specific requirements of industry.

Many of the above-mentioned oxides ($TiO_2$, $ZrO_2$, $SnO_2$, $CeO_2$, $P_2O_5$) and fluorides, as components of enamels, also have another purpose. Their use in industry makes it possible to obtain opaque (non-transparent) white enamels with a high coefficient of whiteness (Ch. V, # 4).

## Use of New Ground Admixtures

Various ground admixtures (fillers) are widely used to adjust the properties of glass-like enamels (frit). Chemically stable oxides or minerals of the oxide type are used as ground admixtures as we have indicated above. Among the latter, clay and kaolin exerts a specific and somewhat unexpected effect on the chemical stability of enamels. According to data [149], admixtures of ground clays must be reduced to the minimum since they reduce the acid resistance of enamels.

At present, there is the problem of expanding the assortments of fillers at the expense of new types of substances - dispersion metals and alloys, oxygen-free infusible compounds, intermetallides etc. Admixtures of some thinly dispersed metal powders and oxygen-free compounds such as silicides, borides, carbides, nitrides, which, to a certain extent, have high melting points and solidity and are diathermal and conduct electricity, can give new properties to enamels. They have high erosion resistance as well as chemical stability in cold and heated acids and alkalis, and are resistant to the action of smelt.

The introduction of oxygen-free fillers as ground additives in a number of cases, does not change the technological process of applying the coatings but, at the same time, strengthens the adherence of the enamels to metals and decreases brittleness. Moreover, the firing temperature changes very little and sometimes even drops.

Thus, under ordinary temperatures (850 to 900°) in the air, enamel coatings with admixtures up to 30% of metal silicon and zircon metallic powders are formed. Good enamel coatings are obtained by adding $NoSi_2$, $TiSi_2$, $CrSi_2$, $TiB_2$, $ZrB_2$ et al. Results of an X-ray analysis shows that during the firing, fillers interact with melted frit only slightly. This makes it possible to add, to a certain degree, valuable properties of fillers to enamel coatings [73].

The acid resistance of enamels is increased considerably when metallic silicon is added (up to 5-10%) (figure 49). The addition of metallic zircon improves their alkali resistance (Figure 50) and $ZrB_2$ exerts a very useful affect in this respect.

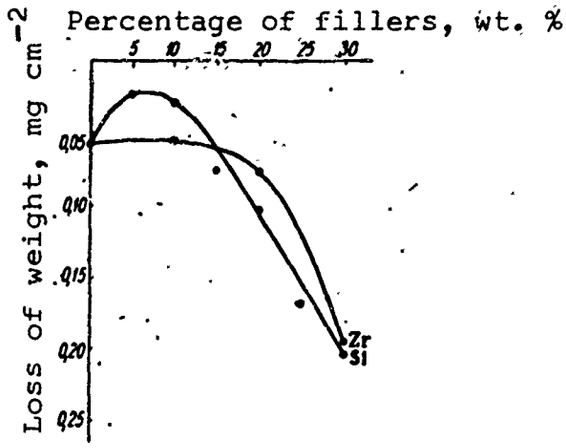



Figure 49. The effect of admixtures of zircon and silicon powders to dross on the stability of enamel coatings in a 10% boiling $H_2SO_4$ (4 hours).

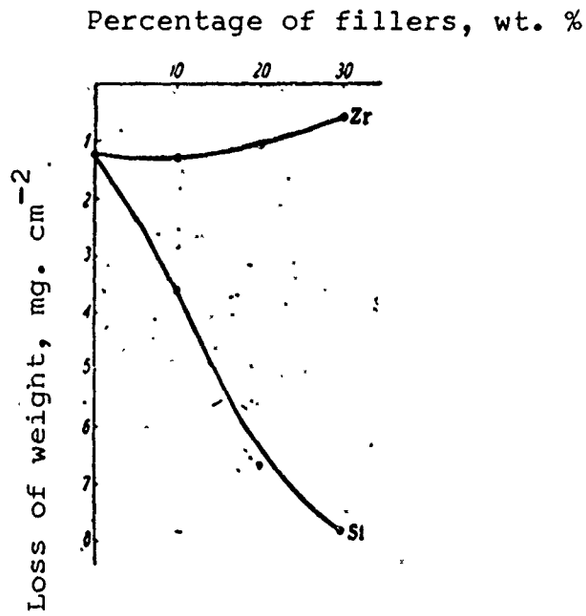



Figure 50. The effect of admixtures of zircon and silicon powders to dross on the stability of enamel coatings in boiling 2n. Solution of NaOH (4 hours).

We have noted the positive effect of admixtures of silicon, zircon, and other oxygen-free fillers on the bending strength of enamel coatings, adherence ability, and thermal resistance.

Thus the first experiments show that metal-like ground admixtures improve the thermal and mechanical properties of enamels and at the same time, may preserve and even increase their chemical resistance. It is possible that enamels will be obtained which will contain high heat resistance, thermal resistance, and erosion resistance in gas environments along with chemical resistance in hot aggressive solutions and fusions.

## Sitallization of Enamel Coatings

Additional possibilities in the field of enameling have opened up due to the creation in recent years of new glass crystal silicate materials, called sitals. Sitals are products of the thin crystallization of silicate glass which have a number of valuable properties, particularly, high mechanical stability. In order to obtain thinly dispersed crystalline materials after crystallization, admixtures of substances which are capable of easily forming multiple centers of crystallization are put into the glass. Such admixtures are colloid particles of metals (Au, Ag, Cu, Pt, Pd, Rh), oxides $Li_2O$, $TiO_2$, $CeO_2$, $P_2O_5$, $ZrO_2$, $Cr_2O_3$, ZnO; sulfides of iron, zinc, copper; fluorides et al. Small fine crystaline particles, which cling to each other, develop around the centers of crystallization when there has been appropriate thermal treatment. Sitals can also be obtained through liquation with subsequent crystallization which divides the liquid phases (borosilicate systems). The optimum size of the small crystalline particles varies from several hundreds angstroms to 1 micron.

However, the sitals which are known in the glass industry have not been successfully used as coatings for metals because of the high viscosity of the initial glass, the high temperature of their crystallization, and the disparity of their coefficients of expansion etc. Therefore, new compositions of sitallizing glass which would answer all requirements placed on coatings, must be developed.

The first samples of glass crystalline (sital) coatings have already been obtained at present. They are a special form of crystallized silicate enamels with a large percentage (50% or more) of thinly dispersed evenly divided crystalline phase.

The American firm["Pfaudler] was the first to announce the creation of sital enamels; however, they have not reported on

details of the technological process and composition [159].

The following composition of sital enamels (Table 41) has been recommended in dissertation [160, 161].

Table 41.

Composition of Sital Enamels (Wt. %)

| № покрытия | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $B_2O_3$ | MgO | CaO | $Li_2O$ | $Na_2O$ | FeS | Сверх 100% F |
|---|---|---|---|---|---|---|---|---|---|---|
| 24 | 64,0 | 10,0 | — | 4,0 | — | 4,7 | 8,0 | 9,3 | — | 10,0 |
| 32 | 61,0 | 10,0 | — | 4,0 | — | 4,7 | 8,0 | 9,3 | 3,0 | 10,0 |
| 55 | 58,5 | 6,5 | 16,6 | — | 2,5 | 1,0 | 4,8 | 10,1 | — | 1,0 |

Key: a- No. of coatings
b- Above.

Usually, enamels 24 and 32 are fired at a temperature of 800 to 840°. Sitallization (crystallization) of the formed coating is done according to an individual cycle. The articles slowly, with a speed of 150 deg/hr., are heated to a firmness temperature (630 to 650°). At the firmness temperature, the coverings are crystallized for 2 hours. LiF, $CaF_2$, and NaF are separated during the crystalline phase. The introduction of small admixtures of FeS (up to 3%) help obtain a more thinly crystalline structure of the coverings.

Enamel 55 must be sitallized at 550° for 4 hours.

Sital coverings, in contrast to the ordinary silicate enamels, have a quite high (3 to 5 times) degree of impact resistance, improved microsolidity, and resistance to attrition, and higher resistance to sharp changes in temperature (Table 42).

Table 42.

Comparison of Properties of Glass-Like and Sital Enamels

| Property | Number and Type of Coatings | | | |
|---|---|---|---|---|
| | Glass-like 24 | Sital 24 | Glass-like 32 | Sital 32 |
| Average Linear coefficient of thermal expansion $\alpha \cdot 10^7$ 1/deg (200-400°) | 96 | 108 | 100 | 106 |
| Microhardness, kg/mm$^2$ | 534 | 938 | 514 | 947 |
| Impact resistance, kGm | 0.37 | 1.178 | 0.249 | 1.135 |
| Thermal Resistance, °C | 190 | 290 | 210 | 370 |

According to [161], the thermal resistance of sitallized enamel is reached even at 600° instead of the 100° for glass-like enamels. The wear and tear of sital enamels 24 and 32 even in dry sand is lower than steel-3 by 2.4 times [160].

The results of a study of resistance of sital enamels to acids is less well defined. The resistance of glass to acids after crystallization increases in the majority of cases, but may decrease. The nature of the change in the acid resistance is determined by the composition of the glass.

The operating temperature of glass crystalline enamels, compared with ordinary enamels, may be increased by 200 to 400°.

## Replacing the Metallic Backing

Glass enamel coatings for steel are usually not resistant enough to thermal and mechanical shocks. Since they have a comparatively small coefficient of expansion ($\approx 90.10^{-7}$), low heat conductivity, and high degree of brittleness, as compared to steel, they frequently chip off from convex outside surfaces during operation. Subsequent research is required which would be directed to improving the formula for the enamels. At present, it has been established that this problem is most effectively being resolved by replacing steel and iron as construction materials with titanium and its alloys.

From the economic point of view, titanium is a material with prospects. The production of titanium is increasing rapidly, and its cost is dropping. Consequently, there are reliable premises for wide application of titanium, at least in the form of sleeves, bushings, and other auxiliary armature in chemical machine construction.

Among the metals suitable for enamelling, titanium possesses very advantageous properties. It has a great affinity for oxygen, a high melting point, comparatively low coefficient of expansion, and is a modulus of elasticity. The combination of these qualities, the role of which will be discussed later in Chapters VI, and VII, makes it possible to apply enamels with a high overall content of silica and other refractory and chemically resistant oxides to titanium. The formula for the enamels for titanium can vary widely. According to data [309], frits contain the following: $SiO_2$ 55 to 75%, $ZrO_2$ 0 to 5%, $TiO_2$ 2 to 20%, $Al_2O_3$ 2.5 to 8%, $B_2O_3$ 0 to 15%, CaO 0 to 9%, $Li_2O$ 0 to 5%, $Na_2O$ 5 to 10%, $K_2O$ 0 to 5%, $CaF_2$ 0 to 7%, and $Cr_2O_3$ 0 to 2%. In order to improve the chemical stability, admixtures of $SiO_2$, $Al_2O_3$, $ZrO_2$, $TiO_2$, $CeO_2$, and $Cr_2O_3$ in amounts up to 40% are added to the dross during grinding. The technology of enameling titanium does not differ basically from the enameling of steel. Firing is done in an air atmosphere with a wide range of temperatures. Infusible enamels are fired at temperatures up to 1300° without the appearance of burnt-over areas; an undercoat of primer is not required. In addition, the coating will adhere excellently to metal even when the layer is 1 mm thick. According to the results of measuring the mechanical properties of samples prior to and after enamelling, we can reach the conclusion that during the firing time of enamel, at least at temperatures up to 1000°, the mechanical characteristics of the metal change insignificantly.

Heat resistant enamels for titanium have a much better resistance in aggressive gas environments, in acids, and in alkalis than the enamels for ferrous metals and alloys. They are even resistant in such an aggressive environment as $TiCl_4$ vapor at a temperature up to 1000° and scarcely change at all in boiling strong acids taken in maximum active concentrations (20% HCl, 30% $HNO_3$, 10% $H_2SO_4$). The loss of weight in a boiling solution of 2 n. NAOH for 8 hours does not exceed 0.8 mg/cm$^2$.

## 2. Crystalline Coatings

At present, oxide crystalline coatings without glass-like bands or with a small amount of residual glass have begun to be widely used. To the former belong coatings consisting of refractory simple and complex oxides such as: $Al_2O_3$, $Cr_2O_3$, $ZrO_2$, $CeO_2$, $TiO_2$, $MgAl_2O_4$ etc. and, to the latter, belong some silicate coverings: mullite $3Al_2O_3 \cdot 2SiO_2$, forsterite $Mg_2SiO_4$, and zircon $ZrSiO_4$ etc.

Crystalline oxide coatings are applied from the pulverizing of rods or of powders. A considerable open porosity, reaching 20%, is inherent in all oxide coatings applied by the pulverizing method. Therefore, they cannot be an effective medium for protecting metals from corrosion in gas environments and in liquids and fusions which penetrate through the pores. Such coatings are used, for the most part, as an electro- and thermoisolating ones. The porosity of coatings with the same composition depends upon several technological factors and, to some extent, needs adjusting.

Work [167] has shown that the following contributes to compression of gas flame coatings applied from a rod: increasing the pressure of the air, which disperses the fusion, i.e., increasing the speed of flight of the particles; increasing the angle of dip of the stream axis to the surface to be covered; decreasing the distance from the nozzle of the little pistol to the surface to be covered; and decreasing the speed with which the rod is supplied.

Along with the porosity of the covering, even their properties are changed. Therefore, in expressing qualitatively specific qualities, one must also indicate what kind of porosity they answer. The characteristics of certain properties of representative oxide coatings are shown in Table 43.

Table 43.

Properties of Oxide Crystalline Coatings

| Материал покрытий a | Открытая пористость, % b | Объемный вес, г/см³ c | Средний коэффициент расширения 20—700° d | Модуль упругости E, кГ/мм² e | Предел прочности при изгибе, кГ/мм² f | Микротвердость, кГ/мм² g | Коэффициент теплопроводности $\lambda \frac{ккал}{м \cdot ч \cdot град}$ при 500°С в аргоне (P=300 мм) h | Температура плавления, °С i |
|---|---|---|---|---|---|---|---|---|
| k Окись алюминия j | 5,0 | 3,10 | 77,0 | 3100 | 150 | 1090 | 0,230 | 2050 |
| l Двуокись циркония (стабилизированная) | 12,0 | 4,97 | 98,5 | 5300 | 87 | 675 | 0,145 | 2500 |
| m Двуокись титана | 10,0 | 3,20 | 89,5 | 3600 | 92 | 455 | 0,280 | 1830 |
| n Двуокись церия * | 6,5 | 5,90 | 105,6 | 1900 | 51 | 310 | — | 2600 |
| Окись хрома | 5,5 | 4,20 | 67,1 | 7200 | 67 | 590 | 0,560 | 2275 |
| o Закись никеля | 9,0 | 5,30 | 102,4 | 6600 | 115 | 440 | — | 1990 |
| p Циркон ($ZrSiO_4$) | 8,0 | 3,44 | 42,0 | 2100 | 107 | 455 | 0,210 | 1675 |
| q Шпинель ($MgAl_2O_4$) | 9,5 | 3,01 | 83,5 | 2200 | 48 | 610 | 0,165 | 2135 |
| r Форстерит ($Mg_2SiO_4$) | 5,0 | 2,66 | 88,6 | 2850 | — | 650 | — | 1860 |
| s Ильменит ($FeTiO_3$) | 7,0 | 3,52 | 143,8 | 3100 | 84 | 315 | — | 1440 |

* At high temperatures it becomes $Ce_2O_3$.

Key:
- a- Material of coatings
- b- Open porosity, %
- c- Volume weight, g/cm³
- d- Average coefficient of expansion 20 to 70°
- e- Modulus of elasticity E, kG/mm²
- f- Limit of bending stability, kg/mm²
- g- Microhardness kG/mm²
- h- Coefficient of heat conductivity, λ = kkal/m.hr. deg. at 500°C in argon (P = 300 mm)
- i- Melting point, °C
- j- Aluminum oxide
- k- Zirconium dioxide (stabilized)
- l- Titanium dioxide
- m- Cerium dioxide*
- n- Chromium oxide
- o- Nickelous oxide
- p- Zircon ($ZrSiO_4$)
- q- Spinel ($MgAl_2O_4$)
- r- Forsterite ($Mg_2SiO_4$)
- s- Ilmenite ($FeTiO_3$)

The modulus of elasticity of many porous oxide coatings is 2 to 3 times less than the modulus of elasticity of glass-like enamels. Therefore, they withstand even greater deformation from bending without causing collapse. The main defects of such coatings is their poor adhesion to metals. Relatively good

adhesion to ordinary steel is achieved by giving the surface an abrasive stream treatment and subsequently applying a sub-layer of Nichrome. The coatings should not be more than 0.5 to 0.6 mm thick since thick layers chip off easily from metal. A preliminary heating of the surface to 180-200°, increasing the pressure of the dispersing air, and increasing the angle of dip of the gas-air stream to 90° aids in adhesion.

According to data [168], gas-flame coatings are distinctive for their low thermal conductivity - 5 to 10 times less than the thermal conductivity of the same materials taken individually from the metal in the form of volume samples of comparative porosity. Thermal conductivity drops considerably when the pressure of the surrounding gas environment is lowered and becomes the least in vacuum (Figure 51). The zirconium dioxide is one of the best of the various materials for its least thermal conductivity.

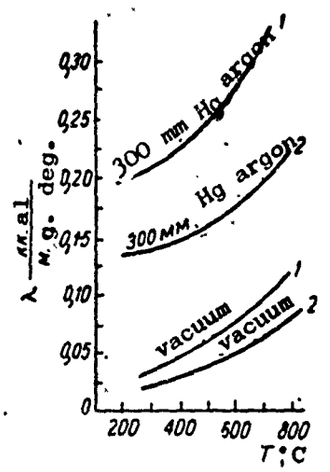



Figure 51. Thermal Conductivity of Coatings made of aluminum oxide (1) and Zirconium Dioxide (2).

## Metal-Like Coatings

Metal-like coatings are those which consist of metals and their silicides, borides, carbides, and nitrides.

Moreover, the face cannot always be drawn between the metal-like compositions, since the percentage of silicides, carbides, and nitrides in the layer of the metal-like coatings may be small. The possible conditional border between the metal and metal-like coatings has been mentioned above. Generally speaking, a special role in the formation of metal-like coatings is assigned to boron and carbon, and it is obviously preferable to introduce the boron, carbon, and silicon

into the composition of laminated compositions in a combined form (borides, carbides, silicides). However, this question still requires study.

At present, special attention is being paid to the invention of coatings based on silicides, borides, and carbides of d-transitional metals (metal-like compounds).

A description of the conditions for synthesis and the properties of these compounds became an object of new chapters in inorganic chemistry. Materials, created on the basis of metal-like compounds, begin to take on added significance in technology. Since they are very infusible, they occupy an intermediate position between metals and metal oxides because of these properties. Their high degree of hardness and suitable thermal emission characteristics are of special interest to industry in addition to their infusibility. Moreover, the increased thermal and electrical conductivity is frequently associated in them with high resistance to acids, alkalis, fused metals, and gas aggressive environments [169].

Some of them possess a considerable and even high resistance to cinders [170]. They can add these new qualities even to coatings.

Table 44 shows the most important properties of metal-like infusible compounds compared with corresponding pure metals.

The majority of compounds melt at temperatures higher than 2000°. The highest melting point among all the substances is tantalum and hafnium carbides. Due to the high degree if hardness and high melting point, carbides are appropriate components of wear-resistant coatings which withstand intensive heat in the absence of oxygen. They are used to protect parts of jet engines, cutting instruments etc. However, the temperature range of resistance of carbides to oxidation, with the exception of SiC, does not exceed 1000°. Therefore, conditions for their prolonged service at higher temperatures are limited by weakly oxidizing and neutral environments or vacuum. According to their resistance to oxidation at 900°, carbides can be placed approximately as follows in a series:

$$Cr_3C_2 > TiC > ZrC > NbC > Mo_2C > WC$$

As a rule, borides of infusible metals are more resistant to oxidation than carbides. The series of cinder resistance at 700-1000° is as follows:

$$ZrB_2 > TiB_2 > NbB_2 > W_2B_5 > Mo_2B_5$$

## Table 44.

### Properties of Metal-Like Infusible Compounds and Initial Metals

| Металлы и соединения a | Температура плавления, °C b | Микротвердость, кг/мм² c | Работа выхода электронов φ, ев d | Удельная электропроводность $\varkappa_{20°}$ 1/ом·см e | Теплопроводность $\lambda_{20°}$ ккал/м·ч·град f | Средний коэффициент расширения в интервале 20—1100° C $\alpha \cdot 10^7$ g |
|---|---|---|---|---|---|---|
| Ti | 1 725 | 160 | 3,95 | 20 800 | 14,0 | 93 |
| $TiSi_2$ | 1 540 | 820 | — | 59 250 | — | — |
| $TiB_2$ | 2 980 | 3 370 | 3,95 | 69 400 | 51,8 | 81 |
| TiC | 3 140 | 3 000 | 2,35 | 19 100 | 31,7 | 77 |
| TiN | 2 950 | 2 160 | 2,92 | 40 000 | 16,6 | 93,5 |
| V | 1 900 | 65 | 4,12 | 38 500 | 30,0 | 97 |
| VSi | 1 670 | 1 090 | 3,26 | 15 050 | — | — |
| $VB_2$ | 2 400 | 2 080 | 3,88 | 52 600 | 49,3 | 75 |
| VC | 2 830 | 2 090 | 3,85 | — | 21,1 | — |
| VN | 2 050 | 1 520 | — | 11 700 | 9,7 | 81 |
| Cr | 1 860 | 150 | 4,58 | 52 900 | 57,6 | 80 |
| $CrSi_2$ | 1 550 | 1 200 | 3,78 | 1 095 | — | — |
| $CrB_2$ | 1 960 | 1 800 | 3,36 | 17 540 | 21,0 | 111 |
| $Cr_3C_2$ | 1 890 | 1 300 | — | 13 330 | 16,5 | 117 |
| CrN | disintegrates | 1 090 | — | 1 560 | 10,1 | — |
| Zr | 1 830 | 100 | 3,90 | 24 390 | 15,9 | 63 |
| $ZrSi_2$ | 1 700 | 900 | 3,95 | 13 200 | — | — |
| $ZrB_2$ | 3 060 | 2 250 | 3,70 | 60 240 | 36,7 | 69 |
| ZrC | 3 530 | 2 600 | 2,18 | 20 000 | 18,0 | 67 |
| ZrN | 2 980 | 1 980 | 2,92 | 74 400 | 11,9 | 72 |
| Nb | 2 450 | 180 | 3,99 | 63 690 | 41,0 | 72 |
| $NbSi_2$ | 1 950 | 1 050 | 4,34 | 19 900 | — | — |
| $NbB_2$ | 3 000 | 2 590 | 3,65 | 29 400 | 30,2 | 61 |
| NbC | 3 480 | 1 960 | 2,24 | 19 600 | 19,8 | 65 |
| NbN | 2 050 | 1 400 | — | 12 820 | 3,2 | — |
| Mo | 2 625 | 250 | 4,30 | 190 300 | 126,0 | 55 |
| $MoSi_2$ | 2 030 | 1 200 | 4,02 | 46 300 | 41,7 | 51 |
| $Mo_2B_5$ | 2 100 | 2 350 | 3,38 | 40 000 | 23,0 | — |
| $Mo_2C$ | 2 690 | 1 500 | — | 14 100 | 5,8 | — |
| $Mo_2N$ | disintegrates | 630 | — | 50 500 | 15,4 | 62 |
| Hf | 2 130 | 115 | 3,53 | 33 300 | — | 61 |
| $HfSi_2$ | 1 750 | 930 | — | — | — | — |
| $HfB_2$ | 3 250 | 2 900 | — | 60 200 | 37,4 | 57 |
| HfC | 3 890 | 2 600 | 2,04 | 22 250 | 22,4 | 67 |
| HfN | 2 980 | 1 640 | — | 30 400 | — | 69 |
| Ta | 2 900 | 180 | 4,12 | 68 000 | 46,8 | 65 |
| $TaSi_2$ | 2 200 | 1 400 | 4,42 | 21 700 | — | 88,5 |
| $TaB_2$ | 3 100 | 2 500 | 2,89 | 26 740 | 18,5 | 51 |
| TaC | 3 880 | 1 600 | 3,14 | 23 750 | 12,5 | 83 |
| TaN | 3 090 | 1 060 | — | — | 7,4 | — |
| W | 3 350 | 350 | 4,50 | 181 800 | 136,8 | 45 |
| $WSi_2$ | 2 160 | 1 070 | 4,04 | 80 000 | — | — |
| $W_2B_5$ | 2 300 | 2 660 | 2,62 | 23 250 | 24,5 | — |
| WC | 2 870 | 1 780 | 4,58 | 51 200 | — | — |
| WN | disintegrates | — | — | — | — | — |

Key:
- a- Metals and compounds
- b- Melting Point °C
- c- Microhardness kG/mm²
- d- Electron yield φ, ev
- e- Specific electro-conductivity $\varkappa$ 20° 1/om·cm

[key to Table 42 continued]

f- Heat conductivity $\lambda$ 20° kkal/m.hr. deg.
g- Average coefficient of expansion in interval of 20 to 1100°C $\alpha.10^7$

Among the borides that are of special interest are: $ZrB_2$ a resistant compound in such aggressive media as melted iron, copper, magnesium, and zinc; $TiB_2$, $CrB_2$ - compounds which are quite resistant to the action of melted zinc and aluminum [108].

These borides may be used to synthesize appropriate protective coatings.

Boride coatings have an even greater abrasive wear resistance than carbides. Boride layers, since they have a high degree of hardness, are outstanding for their small degree of brittleness compared with carbides and, consequently they are more resistant to abrasive grains and chip off less [171].

Molybdenum disilicide is outstanding among the silicides which have the best resistance to oxidation. Coatings protecting infusible materials (molybdenum, tungsten) from oxidation at temperatures up to 1800° over the course of several hundreds of hours are obtained based on molybdenum disilicide [172]. In order to improve cohesion and resilience of coatings, molybdenum disilicide is combined with other silicides along with metals - chromium, aluminum, boron, neobium, and tungsten [173].

Molybdenum disilicide is also a very important component of protective coatings for graphite and carbographite materials (Ch. VIII). But, it is still not in use to protect steel since a reaction occurs between iron and $MoSi_2$ which destroys the coating.

Silicides of other metals are less resistant to oxidation and, because of their stability in the temperature interval of 800 to 1100°, they are located as follows in a series:

$$MoSi_2 > NbSi_2 > TiSi_2 > TaSi_2 > FeSi_2 > CoSi_2 > CrSi_2 > ZrSi_2 > WSi_2$$

Compounds which combine a high melting point with a low electron yield may be used to obtain coatings with an intensive thermal emission of electrons [174]. Such compounds as ZrC, and Hfc, since they are applied in the form of paste on backing made of infusible metal, assure a high degree of compactness of emission streams (up to 20 a/cm$^2$) for sufficiently long periods of service. They are recommended for use in the form

of coatings or compact articles as cathodes - thermal emitters in electron guns of powerful generators [175]. Because of their qualities, they excel the cathodes that are in wide use at the present time and which are made of lanthanum hexaboride $LaB_6$.

All the compounds listed in Table 44 are suitable only for coatings with a high degree of electro-and thermal conductivity; borides have a higher degree of electro and thermal conductivity compared with carbides. Electro-and thermal conductivity of some compounds is even sometimes two-three times higher ($TiB_2$, $ZrB_2$, $VB_2$ et al) than the initial metals. This quality assures high resistance of coatings made of metal-like compounds to frequent sharp temperature changes.

Coatings made of metal-like infusible compounds are applied by fusing and melting, and are also formed in the diffusion absorption of surfaces by silicon, boron, carbon, and nitrogen.

Combinations of carbides, borides, and silicides with metallic components are most frequently used in practice to form metal-like coatings. For example, foreign literature also mentions coatings such as Ni - $Cr_3C_2$, Ni - $CrB_2$, Ni - $ZrB_2$, Si - TiC, Co - WC, Cr - Ni - B, Ni - TiC - $Cr_3C_2$ et al [176, 177].

Among the borides, chromium boride CrB gives the greatest degree of hardness to ferroboride alloys [178]. Table 45 compares the hardness of coatings, obtained by smelting mixtures of different borides with iron powder on to steel-3 in a ratio of 1:1.

Table 45.

Hardness of Alloys of Borides and Iron

| Boride | CrB | MoB | WB | $VB_2$ | $ZrB_2$ | $TaB_2$ | $NbB_2$ | $TiB_2$ | $MnB_2$ |
|---|---|---|---|---|---|---|---|---|---|
| Hardness according to HRA | 84.4 | 80.5 | 79.5 | 79.0 | 75.5 | 75.2 | 71.8 | 69.0 | 60.0 |

Table 46 shows the composition of some carbide-boride-silicide smelted materials used in the form of electrode rods with a coating, smelted mixtures, cast powders, and powdered wire (pp); components of smelted mixtures are chromium carbide CrC, chromium boride CrB, tungsten carbide WC, and iron, nickle, silicon powders, [129, 178, 322]. Cast powder is prepared by crushing brittle cast alloys and by other methods [130].

Table 46.

Carbide-Boride-Silicide Smelted Materials Based on Iron, Nickel, and Chromium (hard alloys)

| | Material | Состав наплавленного слоя или наплавляемого материала (вес. %) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C | B | Si | Mn | Cr | Ni | Fe | W | другие примеси b |
| c | Электрод ГК-15* | 7,63 | — | — | — | 54,38 | 14,14 | 23,65 | — | — |
| d | Электрод БХ-2* | 0,55 | 7,67 | — | — | 31,29 | — | 60,00 | — | 0,35 |
| e | Электрод ХР-19* | 7,30 | 5,20 | — | — | 36,64 | — | 50,90 | — | — |
| f | Электрод КБХ-45* | 5,10 | 2,21 | — | — | 29,79 | — | 63,06 | — | — |
| g | Электрод Т-590* | 3,6 | 1,5 | 0,6 | 1,2 | 26,0 | — | 67,1 | — | — |
| h | Электрод ЦН-8* | 0,15 | — | 8,5 | 1,5 | 21,0 | 11,5 | 57,5 | — | — |
| i | Наплавочная смесь БХ* | 0,12 | 7,65 | — | — | 35,0 | — | 57,5 | — | 0,1 |
| j | Наплавочная смесь КБХ* | 2,6 | 0,9 | — | — | 24,9 | — | 71,0 | — | 0,8 |
| k | Наплавочная смесь КБХ-45* | 3,60 | 2,82 | — | 0,6 | 18,65 | — | 71,86 | — | — |
| l | Наплавочная смесь 115-ФС* | 1,95 | 3,59 | 19,42 | — | 26,27 | — | 48,86 | — | — |
| m | Литой порошок ЛП-1 | 4,60 | — | 1,83 | 6,94 | 30,00 | — | 56,6 | — | — |
| n | » » ЛП-3 | 5,25 | 5,2 | 0,22 | 0,77 | 39,18 | — | 49,35 | — | — |
| o | » » ЛП-6 | 0,42 | 2,8 | 5,19 | 0,06 | 13,20 | 78,3 | — | — | — |
| p | » » КХН | 11,30 | — | — | — | 73,70 | 15,0 | — | — | — |
| q | » » С17 | 0,58 | — | 15,80 | 0,72 | — | — | 82,9 | — | — |
| r | Пп-У30Х25Н4С4 (сормайт № 1) | 3,0 | — | 4,0 | < 1,5 | 27 | 4,0 | 59,5 | — | <1,5 |
| s | Пп-НХ15Р4 (колмоной) | 0,75 | 3,5 | 4,5 | — | 15 | 70 | 4,5 | — | — |
| t | Пп-Х10В14 | 4,5 | — | < 0,5 | 0,4 | 11,0 | — | 67,6 | 16,0 | — |
| u | Пп-У35Х10В14 | 3,5 | — | 0,6 | 0,4 | 10 | — | 71,5 | 14,0 | — |
| v | Сталинит | 8—10 | — | < 3,0 | 13—17 | 16—20 | — | 60—50 | — | — |

* Composition of fused layer

Key:

a- Composition of Smelted Layer or Smelted Material (weight %)
b- Other mixtures
C- Electrode GK-15*
d- Electrode BKh-2*
e- Electrode KhR-19*
f- " KBKh-45*
g- " T-590*
h- " TsN-8*
i- Fused mixture BKh*
j- " " KBKh*
k- " " KBKh-45*
l- " " 115-FS*
m- Cast powder LP-1
n- Cast powder LP-3
o- " " LP-6
p- " " KKhN
q- " " S17
r- Pp-U30Kh25NS4 (sormayt No. 1)
s- Pp-NKh15R4 (kolmonoy)

t- Pp-Kh10V14
u- Pp-U35Kh10V14
v- Stalinite

Carbide-boride fused materials based on iron, nickel, and chromium have a high degree of hardness - from 78 to 85 according to HRA. For comparison sake, let us note that the hardness of the layer made of a hard alloy of stalinite equals 77.

Coatings, smelted from a mixture of 115FS, are resistant to both abrasive wear and tear and corrosion ($SO_2$, $H_2SO_4$). The presence of nickle improves the heat resistance of the coatings and their resilience. For example, a resilient coating is formed from fused mixture A-8 consisting of CrB 50%, Fe 35%, and Ni 15%. Fused mixture No. 9 is only a little less effective: CrB 10%, MnB 40%, Fe 50%. Mixtures A-8 and No. 9 were fused on the beater used in mine mills, and showed high quality resilience in tests [178].

The carbide-metallic fused mixture "slavyanite," consisting of ferrochromium 37.7%, ferromanganese 10.8%, iron chips 47.1%, petroleum coke 4.4% is manufactured on an industrial scale. This mixture is filled with tubular electrodes.

Fused carbide materials containing tungsten, molybdenum, vanadium, and titanium are less economical but have better wear resistance.

A carbide coating formed from fused relite was particularly hard. Relite is an eutectic mixture of WC and $W_2C$. It contains 95 to 96% tungsten and 3.7 to 4.2% carbon, and is used as a filler in tubular electrodes. During fusion, only the steel tube is melted; the grains of relite remain unmelted and are in the form of inclusions in the iron die.

Metal-like coatings can also be applied by gas-flame and plasma fusion of fibers, rods, and powders. For example, heat resistant coatings, built up on boride, chromium, nickel, and silicon bases, can be applied by fiber fusion [179]. Sinters of CrB and Ni powders, which have for the most part a particle dispersion of less than 10μ, are prepared in advance. The powders are sintered in a hydrogen environment at about 1450°. The sinters are ground up and powders with different ratios of CrB/Ni; from 95/5 to 50/50, are obtained. Other components may be added to these powders. The coating, consisting of ground up sinters of CrB - Ni such as the 50/50 (95%) and silicon (5%), tested and showed good protective qualities. The mixture is also sintered, ground up, and mixed with an organic batch in hot rollers and formed at a temperature of 140° into a fiber with a diameter of 3 mm. Plastic POV-30 (alloy - 70%, polyethylene plus 30% of polyizobutylene) is used as the organic

binder for obtaining an elastic fiber. Twenty parts of the preparetion PVO-30 are taken to 80 parts of powder. It is recommended that the fused coating be flashed with a gas flame (the welding temperature is 1400°). This compresses it and firmly attaches it to the steel. After compaction, the coating takes on an excellent erosion resistance.

Recently, such materials for coatings as the so-called self fluxing alloys such as "kolmony," with a fusing temperature of approximately 1000 to 1125°, have been successfully used. Such an alloy is AMS-4775A. The make-up of the alloy (Wt %) is as follows: Ni 65 to 67, Cr 13 to 20, Fe 3 to 5, Si 3 to 5, B 2.75 to 4.75, C o.6 to 1.3. In addition to these components, several other alloys contain cobalt, copper, molybdenum, and tungsten. They are made in the form of bars of powders, and are applied on steel, for the most part, by fusing them, and subsequently flashing off [297].

Many self-fluxing alloys are distinctive because of their very high resistance to abrasive wear and tear and to different types of corrosion. Their wear resistance is due basically to the percentage of boron and carbon. Boron also reduces the infusible oxide films on the surface of metallic particles and in combination with silicon, forms up to 1% mixture of borosilicate glass which has a very favorable effect on the process of forming the coating. By forming easily fusible compounds and eutectics with nickel, boron and silicon ensure the possibility of obtaining practically pore-free coatings by means of flashing off. The thermal expansion of these alloys can be easily coordinated within the tolerance permitted with the expansion of steel. This circumstance makes it possible to obtain coatings that are up to 2 to 3 mm or more thick.

Self-fluxing alloys have also found use in a mixture with carbides. In addition, carbides (up to 70%) prove to be inclusions in the die made from the alloy, and improve its wear resistance to an even greater extent.

Materials based on tungsten and titanium carbides with a cobalt binder have a special resistance to abrasive wear and tear [313]. The best of them reach a hardness of 87 to 92 according to HRA (table 47).

These materials are obtained by pressing and caking the appropriate powders; they contain a high degree of hardness and cutting properties even at red heat temperatures (red resistance), exceeding the high speed cutting steel types P9, P18, et al in this respect. Admixtures of TiC and TaC improve the cutting qualities of the materials.

Table 47.

Especially Hard Materials and Coatings

| Type of Material | Composition of Material, Wt.% | | | |
|---|---|---|---|---|
| | WC | Co | TiC | TaC |
| BK-2 | 98 | 2 | — | — |
| BK-6 | 94 | 6 | — | — |
| BK-8 | 92 | 8 | — | — |
| BK-15 | 85 | 15 | — | — |
| T30-K4 | 66 | 4 | 30 | — |
| T15-K6 | 79 | 6 | 15 | — |
| T5-K12 | 83 | 12 | 5 | — |
| TT7-K12 | 81 | 12 | 4 | 3 |

In recent years, the dross method has been worked out for applying metal-like coatings which are similar to the method of enameling which is widely used in industry. According to foreign literature data [180], ground metals and other materials are first individually or collectively dispersed in a liquid media (in water or xylol with polyvinyl alcohol; in a nitro-cellulose lac, diluted with acetone or ether; in a toluene solution of polyizobutylene; in triclorethylene, et al). Preparation of the ingredients is different - two or more components are joined in one suspension or two or more suspensions are prepared which are applied in alternate layers. If oxidation of the metallic components must be prevented during the firing time, a neutral atmosphere is used.

The Ni-Cr-Si system, containing a constant amount of boron (3 to 5%), was discussed in detail in work [181]. The aim was to find the composition forming a coating on steels from the available and highly productive technology of enameling The authors pointed out that four-component mixtures of thinly dispersed powders of Ni, Cr, Si, and B with particles no larger than 40 mc easily form high quality heat resistant coatings. Easily fusible eutectics, possibly with a melting temperature below 1000° which serves as a binder tightly fastening the small crystals of other components together, are formed during the heating of these mixtures.

Figure 52 shows that the area for forming heat resistant coatings is limited by the composition. The following composition of 1M is optimum according to the technological and protective qualities: Ni - 70, Cr - 20, Si - 5, B - 5 wt. %. The dross consists of a mixture of Ni - Cr - Si - B - 100wt. parts, bentonite - 2 wt. parts, and water - 45 wt. parts.

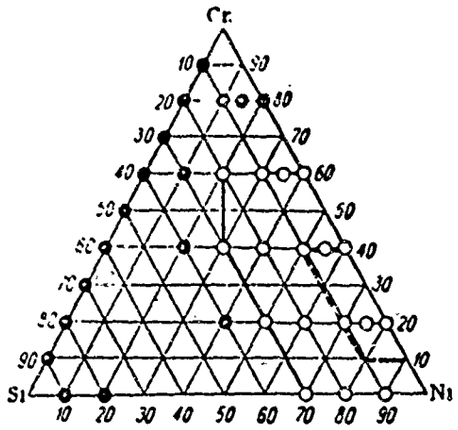



Figure 52. Temperature for forming coatings on Steel-3 formed on the system Ni - Cr - Si with an admixture of 10% boron.

O - 1150 to 1250°C; ● - more than 1250°C;

The broken line shows the area of heat resistant coatings with optimum technological properties.

In order to prevent oxidation of metallic components, it is expedient to utilize alcohol diluted by water in a ratio of 1:1 instead of water. The dross is milled in a spherical ceramic mill for 24 hours. Before using, the dross is filtered through a sieve 0075 (5476 pref/cm$^2$), and is applied on the article by pulverization. The article with the dross coating is dried, and then fired at a temperature of 1140 to 1160° in an electric stove in an atmosphere of argon or in a vacuum. The coating is applied and fired in three successive layers whose total thickness is 0.1 to 0.5 mm. It effectively protects the steel from oxidation for a long time. An increase in weight, because of oxidation of a sample from steel-3 with a coating for 60 hours, is approximately 200 times less than the sample without the coating (Figure 53, 54). The coating withstands any bending quite well and takes impacts as well. Its resistance to deterioration is 10 to 14 times higher than quartz glass. It raises the efficiency of steel somewhat. For example, the prolonged stability of steel EI-572 L with a coating is maintained at 650° on the same level as steel without a coating at 600°. If we compare the life of samples under load until collapse, then the effectiveness of the coating shows up considerably. During optimum test parameters, the life of the steels increase several tens of times (Table 48).

Table 48.

The effect of coating 1M on Prolonged stability of steel EI-572L at 650°

| Samples | Tension kG/mm² | Time until collapse | Удлинение, % a | Сужение, % b | Remarks |
|---|---|---|---|---|---|
| c Без покрытия | 30 | 18,5 | 6,4 | 7,8 | |
| | 28 | 76 | 5,0 | 7,4 | |
| | 25 | 124 | 7,2 | 9,8 | |
| d С покрытием | 30 | 38 | 13,8 | 13,7 | |
| | 28 | 313 | 10,0 | 9,4 | |
| | 25 | 5000 | 5,0 | -- | e Снят без разрушения |

Key: a- Elongation, %
b- Compression, %
c- Without covering
d- with covering
e- Removed without disintegration.

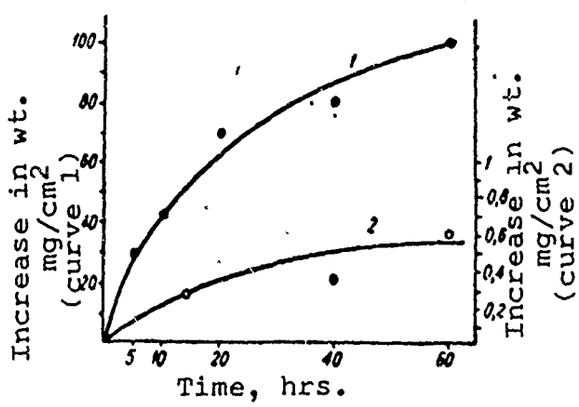



Figure 53. Speed of Oxidation of Steel-3 in Air at 900°: 1 - without coating; 2 - with coating 1M.

Photographs not reproducible

Figure 54. Microstructure of coating 1M Prior to (a) and After (b) testing for heat resistance at a temperature of 900° for 500 hours.

1- metal, 2- intermediate layer; 3- coating (x 500).

Yield strength, during elongation, is increased 25% under these same conditions, cyclic strength is increased 25%, and thermal resistance is quadrupled [182].

Abrasive resistance and heat resistance of borosilicide coatings is improved even more if chromium carbide $Cr_3C_2$ is put into the composition. The coating KM, composed of $Cr_3C_2$ (60%) and a mixture of Ni - Cr - Si - B (40%), is formed in argon or a vacuum at 1180 to 1220° [183]. The dross method can also be used to obtain coatings on systems Ni - $Cr_3C_2$, Ni - $CrB_2$, Ni - Cu - Fe - B, Fe - Ni - Cr - B, Co - Cr - W - B et al.

The basic shortcoming of carbide and boride metallic is the narrow annealing interval. Low heat applied to the parts during annealing (20 to 30°) will cause stains to form, so strict control should be maintained over the technological annealing process. We should also be sought to reduce the annealing temperature.

In order to expand the annealing intervals, it has been recommended that such a composition of complex mixtures would be selected which would have as great a difference as possible between the temperatures of the beginning and ending of fusing. It is desirable to anneal within the results of this temperature difference not exceeding the liquidus point. Hard non-fusible or crystallized particles prevent the easily slideable fusion from running off the walls of the article through gravity forces and capillary forces creating the premise for obtaining

thick layered coatings (up to 0.5 to 1.0 mm).

Metal-like coatings of different compositions can be applied according to the dross technology; the higher the annealing temperature permitted and the smaller its size, the greater selection of formula will there be. Wide introduction to industry of the dross method of applying metal-like and metallic coatings evidently is a matter for the very near future.

## Cermets and Mixed Type of Complex Coatings

A narrow definition is given to the term "cermets," namely: cermets are coatings consisting of oxides or silicates and metals.

The simplest in composition of the groups of cermet coatings is probably metal-oxide coatings such as Ni - MgO, Cr - $Al_2O_3$, Si - $TiO_2$, Al - $Al_2O_3$ etc., even though they have not been completely worked out technologically.

Coatings consisting of oxygen-free non-metallic compounds such as SiC, $B_4C$, $Si_3N_4$, BN in combination with specific other fusing binders belong to the category of cermets.

Mixed type of coatings are of complex composition. Oxides, silicates, metal powders, intermetallides, carbides, borides, silicides and other compounds may be a part of their composition as refractory components. Glass enamels, slag, and other fusible silicates serve as binders which ensure that the coatings will be hermetically sealed.

In 1952, D. Mur and his co-workers [184] suggested that a glass-chromium cover, composed of a mixture of glass-like frit and a thin metallic chromium powder, be used to protect molybdenum. Later on, he suggested a similar type of coating to protect steel. In this case, they used an alloy of the following composition ground into a powder as a filler: Ni 65 to 75%, Cr 13 to 29%, B 3 to 5%, Fe, Si, C (Total)up to 10%. Glass frit with the following composition was the binder; SiO 37.5, $ZrO_2$ 2.5, $B_2O_3$ 6.5, $Al_2O_3$ 1.0, CaO 3.5, BaO 44.0, and ZnO 5.0%. Coating M-60, containing 90% alloy powder and 10% frit, turned out to be the best [185]. Usually, the dross was prepared in water with the addition of 5% clay. The specific gravity of slag was 3.25. Annealing was done in the atmosphere with a low percentage of oxygen. Annealing temperature was 1040 to 1100°.

Obvious disintegration of the iron, protected by coating M-60, was observed only after 350 hours at 985°. The average coefficient of expansion of M-60 coating in an interval of 20 to 500° equaled $135 \cdot 10^{-7}$.

Glass-metal coatings combine the properties of glass and metal. They have excellent advantages compared with the purely oxide enamels. There is now the problem of a detailed study of their nature and properties, expansion of their formula, and determination of the fields in which it can be used in engineering.

A study was undertaken of the system "chrome-glass" as a coating for steel-3 [186]. The chromium was used as a powder with a particle dispersion of less than 20 μ. Experience showed that glass-metal coatings are inclined to flake off. In order to avoid this flaking, careful control must be exercised over the annealing cycle. In a correct annealing cycle for a coating, chromium particles must be equally distributed in the glass mass (Figure 55). Flaking will occur if the coating is heated up. At first, the chromium particles aggregate, then the glass is almost completely separated from the chromium and melts on the surface. The chromium with a small amount of glass residue separates out on the steel with a solid layer up to 100 mc or more thick. To inhibit the flaking process, it is preferable to use heterogeneous slag-like binders with a structural viscosity. The authors have used glass-slag 366 with the following composition (wt. %): $SiO_2$ 58, $TiO_2$ 6, $ZrO_2$ 3, $B_2O_3$ 20, $Al_2O_3$ 5, BeO 3, CoO 5.

Photographs not reproducible

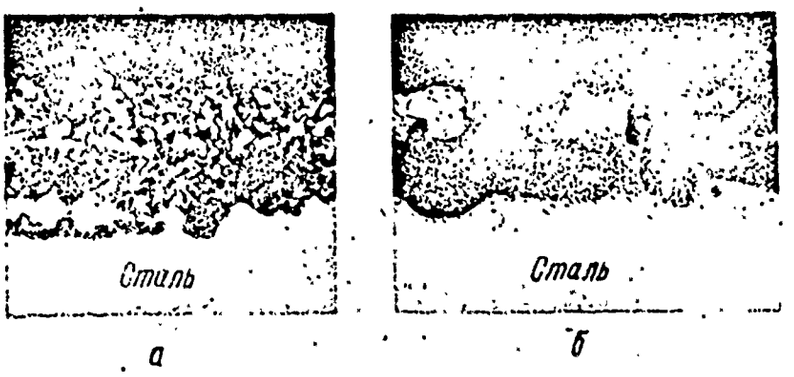



Figure 55. Structure of Glass Chromium Cover:

dark sections - glass-like or crystallized binder; light grains - metallic chromes;

a- normal structure; b- structure in flaking off stage.

Water suspensions of dross were prepared from a mixture of glass and chromium powder. The admixture which prevented the particles from precipitating, was bentonite (2%). The dross was milled until it passed through the sieve 10000 pref/ $cm^2$ without leaving a residue. Annealing temperature varied from 1200 to 1350°, and was done in a neutral atmosphere (argon). Table 49 shows some properties of glass chromium coatings.

Table 49.

Properties of Glass Chromium Coatings

| a № покрытия | b Состав в вес.% | | e Температура размягчения | f Удельный вес | g Модуль упругости E, кГ/мм² | h Коэффициент Пуассона | i Средний коэффициент линейного расширения α·10⁷·(20–600°) | j Удельное объемное сопротивление ρ, ом·см² (22°) |
|---|---|---|---|---|---|---|---|---|
| | c стекло | d хром | | | | | | |
| 1 | 50 | 50 | 1090 | 2,93 | 7930 | 0,245 | 72,0 | 16,8 |
| 2 | 40 | 60 | 1120 | 3,92 | 8400 | 0,305 | 76,0 | 2,7 |
| 3 | 30 | 70 | 1150 | 4,54 | 10740 | 0,291 | 78,0 | 0,62 |
| 4 | 20 | 80 | 1190 | 4,97 | 13380 | 0,257 | 87,0 | 0,60 |
| 5 | 10 | 90 | 1250 | 5,48 | — | — | 95,0 | — |
| 6 | 5 | 95 | 1330 | — | — | — | 96,5 | — |

Key:

a- No. of Cover;
b- Composition by Wieght %
c- Glass
d- Chromium
e- Softening point
f- Specific gravity
g- Modulus of elasticity E, $kG/mm^2$
h- Poisson's ratio
i- Average coefficient of linear expansion $\alpha \cdot 10^7 \cdot$(20 to 600°)
j- Specific volume resistance $om \cdot cm^2$ (22°)

Obviously, in adding chromium to glass, an increase in its coefficient of expansion occurred along with an increase in infusibility which is very important for successfully enameling the steel. Coatings No. 4 to 5 turned out to be the best for their protective qualities. Steel-3, protected by these coatings, scarcely oxidized at all at temperatures up to 100°, if there were no random defects in the cover layer (the increase in weight was less than 0.01 $mg/cm^2 \cdot hr$).

Unfortunately, there still has been no success in selecting such a silicate binder to the chromium as a filler which would ensure sufficient aggregate pyrosuspension resistance. When glass-chromium coatings are fired, it is difficult to avoid blemishes caused by flaking off.

Not one of the other metals in combination with glass can be compared in their protection action with chromium (Table 50). Only metallic silicon formed glass silicon cover which, at 900°, has approximately the same heat resistance, but even at 1000° the silicon becomes an ineffective component. Such metals as Ni, Co, Nb, Mo, W, Pd, Rh, Zr, in a mixture with glass forms very poor protective layer. Steel samples with these coatings disintegrate more or less evenly throughout the entire surface even in the course of the first 24 hours [187].

Table 50.

Heat Resistance of Steel-3 with Coatings made of Mixtures of Metal Powders or Oxygen-Free Compounds (70%) with a Silicate Binder (30%)

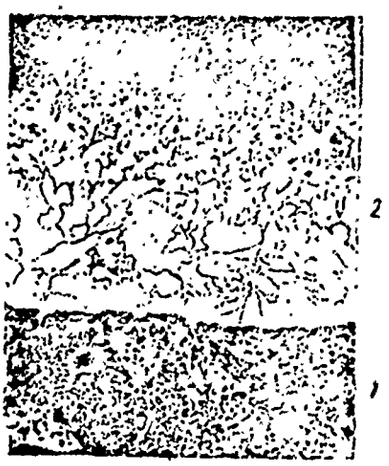
| Компонент наполнитель a | Средняя температура формирования покрытия b | С П- вес, мг/см²·ч средний за 15 ч | | Компонент наполнитель a | Средняя температура формирования покрытия b | С Привес, мг/см²·ч средний за 15 ч | |
|---|---|---|---|---|---|---|---|
| | | 900° | 1000° | | | 900° | 1000° |
| Без покрытия d | — | 8,45 | — | Pd . . . . . | 1050 | 1,07 | |
| Si . . . . . | 1260 | 0,01 | 2,2 | Rh . . . . . | 1300 | 1,33 | |
| Cr . . . . . | 1280 | 0,01 | 0,01 | Zr . . . . . | 1360 | 0,63 | |
| Ni . . . . . | 1180 | 0,36 | | B . . . . . | 1060 | 5,06 | |
| Co . . . . . | 1250 | 0,21 | | $CrB_2$ . . . . . | 1250 | 0,04 | |
| Nb . . . . . | 1380 | 0,12 | | $Cr_3C_2$ . . . . | 1350 | 0,04 | |
| Mo . . . . . | 1320 | 3,03 | | $MoSi_2$ . . . . | 1400 | 0,46 | |
| W . . . . . | 1340 | 0,85 | | | | | |

Key:

a- Filler component
b- Average Temperature for forming coating
c- Increase in weight mg/cm$^2$.hr, average for 15 hours.
d- Without coating

Among the metal fillers, the one which seems to hold the most prospects evidently is thinly dispersed Nichrome (Ni - 80%, Cr - 20%). A coating consisting of 50% nichrome and 50% glass-slag 366 was tested on samples made of alloyed steel EI-929 at 950° for 1500 hours, and displayed very good protective qualities. It eliminates ulcerous steel corrosion, and decreases the probability of cracks appearing in the metal [188].

Coatings containing oxygen-free chromium compounds ($CrB_2$, $Cr_3C_2$) have good protective action. Work [189] studied the effectiveness of coatings formed on the basis of $Cr_3C_2$. Easily fusible borosilicate glass was used as the binder. This fusion almost completely separates on the surface in the form of fine droplets during annealing in an atmosphere of argon at a temperature of 1240°. The cover layer was formed from $Cr_3C_2$ and of the products of its interaction with iron (Figure 56). Thus, the silicate fusion here plays a temporary role of flux, for the most part. We may judge the high effectiveness of the carbide coatings made of $Cr_3C_2$ - 90%, and glass - 10%, by Table 51.




**Photograph not reproducible**

Figure 56. Micro structure of carbide coating: 1- steel; 2- coating.

Table 51.

Effectiveness of Protection of Steel-3 with Chromium Carbide Coating from Oxidation in the Air

| Sample | Increase in weight, $mg/cm^2$ for 200 hours. | | |
|---|---|---|---|
| | 900° | 950° | 1000° |
| Without coating | 250 | 310 | 260* |
| With the coating | 0.52 | 0.91 | 5.2 |

* for 70 hours

Glass-metal coatings may also be used to protect iron [190]. In this case, instead of chromium a more easily fusible metallic component is selected since glass-chromium coatings are extremely infusible. It is true that this results in some decrease in the heat resistance of the coat but, all the same, it remains effective. The following formula has been suggested (wt. %): metallic component: Ni 70, Cr 20, Si 5, B 5;

glass slag: $SiO_2$ - 28.6, $B_2O_3$ - 4.9, $Al_2O_3$ - 0.8, $Cr_2O_3$ - 23.0, CaO - 2.7, BaO - 33.7, ZnO - 3.8, MnO - 1.2, CaO - 1.0.

30 - 5 parts of glass slag are taken to 70 - 95 parts of the metallic component. The dross is prepared in the same way as in the case of glass-chromium compositions. The coating is fired at a 1000 to 1100° in an atmosphere of argon or nitrogen. At a temperature of 900°, they decrease the speed with which the iron is oxidized by 30 to 40 times (Figure 57).

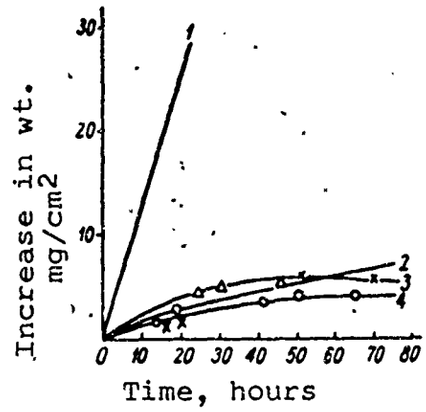



Figure 57. Curves showing the Oxidation of Iron in Air at 900° Protected by glass-metal coatings:

1- unprotected sample; 2- coating 50/50; 3- coating 30/70; 4- coating 5/95. (The numerator shows the percentage of the binder, and the denominator shown the percentage of metallic mixture).

The process of diffusion, recrystallization, and chemical interaction occur during the annealing process and during the exposure of the samples on the dividing line "coating-iron." The essence of the processes has not yet been studied, but their actuality has been proved by microphotography (Figure 58). Judging by the prints obtained on the PMT-3 instrument, a certain middle zone changing from metal to the coating is outstanding because of the great amount of microhardness. The coating is 0.1 to 0.2 mm thick, and the coefficient of linear expansion lies within the range 110 to $120 \cdot 10^{-7}$ (in the area 20 to 700°).

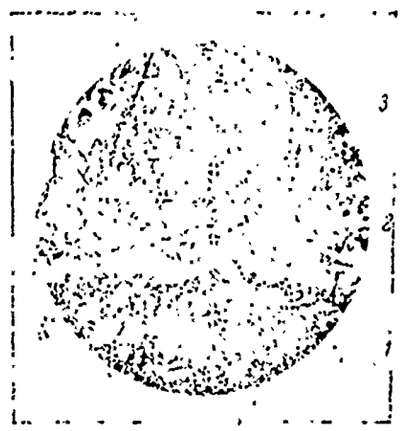
In recent years, glass-metal pyropastes and pyrosuspensions have been used in the new field of technology as the intermediate layers when ceramics and glass with metals are soldered. Mixtures of a powder of boronsilicate glass ($SiO_2$ - 38%, $B_2O_3$ - 57%, $Na_2O$ - 5%) with metal powders (Ni, Cu, Mn) in a ratio of 60:40 and with methyl alcohol were tested with this aim in mind in work [191]. The soldered joint was annealed at a temperature of 1200° under a pressure of 0.43 kg/cm$^2$.

It turned out that glass-metal soldered seams have a high shear strength. The strength of the glass manganese soldered seam at room temperature is 1054 kg/cm$^2$. When the temperature is increased, the stability diminishes, but at 1037°, it is still maintained at 91 kg/cm$^2$. The resilience of such systems was also high.

Alumosilicate glass in combination with copper oxide and iron powder (glass - 20%, CuO - 26%, Fe - 54%) forms a pyropaste recommended for welding ceramics to steel through an additional intermediate layer of nickel [192].

Electric conducting solders, which combine a high conductivity of metal with the ability of glass to soften when heated and to seal different materials hermetically, were obtained on the system "glass - silver" [193].

Generally speaking, there are possibilities for creating glass-metallic and glass cermet pyropastes, which are very different in composition, which are intended for soldering ceramics and glass to metal [194].




**Photograph not reproducible**

Figure 58. The microstructure of glass metallic coating on iron:
1- iron; 2- transition layer; 3- coating.