DEVELOPMENT OF ELECTRODES FOR THE HIGH-LEVEL WASTE VITRIFICATION FURNACE

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ABSTRACT

In connection with the corrosion of molybdenum electrodes in vitrification furnaces concerning the reprocessing of high-level waste, the results are presented regarding the development of ceramic electrodes made of high glass-resistant tin dioxide base materials and metallic chromium base alloy electrodes. A specially designed cell is described and used for corrosion tests of rod-type electrodes. The results of comparative corrosion tests of tin dioxide and metallic chromium base alloy electrodes in molten phosphate and borosilicate glasses with high ferrum oxide and sulphate ion contents at a temperature of 1,100-1,150°C are given.

In the pilot vitrification furnace (ceramic Joule melter), developed in the USSR, active waste can be incorporated into phosphate or borosilicate glasses. Molybdenum is used as an electrode material. However, when reprocessing waste with higher sulfur and ferrum contents, there is a problem with molybdenum electrode corrosion in phosphate glass which limits the service life of a vitrification furnace.

There are two possible solutions to the electrode corrosion problem:

- Reduction of waste fraction having a high content of aggressive components. The total sulfur and ferrum oxide contents of molten glass must not exceed 0.2-0.3 and 1.5-2.0 mass %, respectively;
- Replacement of molybdenum by more glass-resistant electrode materials. The many years of experience shows that tin dioxide (1, 2) and metallic chromium base alloys are the most corrosion-resistant as compared to other materials.

Taking into account the high glass resistance of tin dioxide and chromium base alloys, a basic electrode design has been developed.

The results of the development and corrosion tests of experimental tin dioxide and metallic chromium base alloy electrodes are discussed below.

The electrode incorporates a ceramic tin dioxide rod with a cooled stainless steel current lead (Fig. 1). To increase the electrical conductivity of the ceramic tin dioxide rod and to have a reliable electrical content between the rod and the current lead, the assemblage is heat-treated in an inert atmosphere (nitrogen or argon) up to a temperature of 950-1,000°C.

As a result of this treatment, the electrical resistance of the tin dioxide rod with the current lead decreased from 10-100 to 0.08-0.1x10^{-4} Ohm/m. The current lead is heat-treated and is placed in a cooler to stabilize its operation and eliminate a molten glass leakage in the region of the electrode introduction into the furnace. In its design, the metallic chromium-nickel alloy base electrode does not differ from the ceramic one.

For corrosion tests, a cell was developed (Fig. 2) comprising:

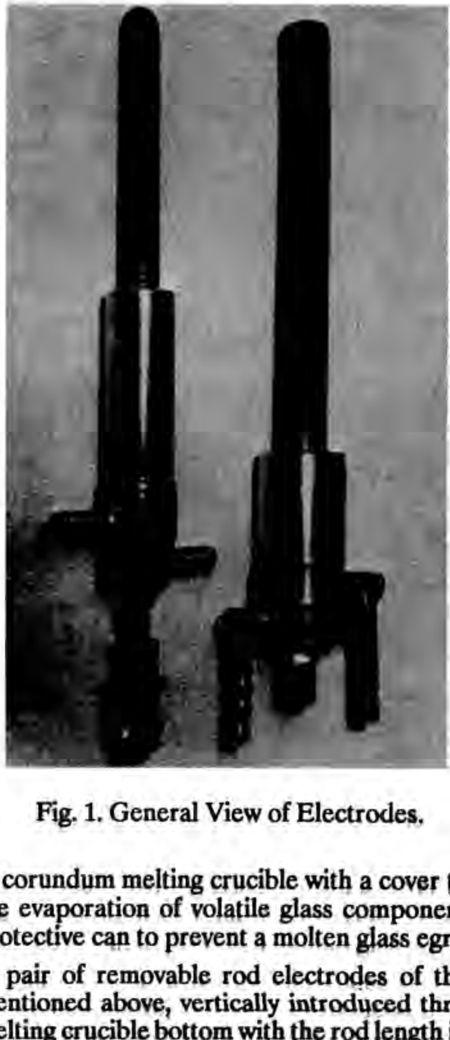

Fig. 1. General View of Electrodes.

- A corundum melting crucible with a cover to reduce the evaporation of volatile glass components and a protective can to prevent a molten glass egress;
- A pair of removable rod electrodes of the design mentioned above, vertically introduced through the melting crucible bottom with the rod length in molten glass equal to 135-140 mm;
- A furnace with silicon carbide heaters designed for preliminary glass-melting in the melting crucible.

The arrangement of the electrodes in the cell and their shape are the same as in the pilot furnace for high activity waste vitrification. The temperature was controlled with thermocouples immersed in the molten glass.

The corrosion resistance of the electrodes was estimated from the corrosion value (corrosion rate) that was calculated from a change in the electrode mass after testing according to the formula:

$$v = 8.76 \times 104 \frac{P}{S \cdot \tau \cdot d} \qquad \text{(Eq.1)}$$

where V is a corrosion value, mm/year;
P is a loss of the electrode mass during testing, g;
τ is a test duration, h;
d is a material density, g/cm^3;
S is an electrode area, cm^2.

Due to their porosity, the ceramic tin dioxide electrodes impregnated with glass during testing. To remove the glass from the electrodes, the tested specimens were treated for a long period of time with fresh portions of boiling nitric acid.

The table lists the conditions of the corrosion investigation as well as data on the electrode corrosion rate. Chromium base alloy electrodes (BX-4) were tested in borosilicate glass. For the sake of comparison, the data are given on testing a nickel base alloy electrode (USSR alloy, XH701-0). Fig. 3 illustrates the temperature distribution over the molten glass depth. Due to the solubility of nickel and chromium base alloys in molten alkaline phosphates, only ceramic tin dioxide electrodes were tested in phosphate glass.

As it is shown by corrosion tests in molten borosilicate glass containing ferrum oxide and sulphate ion in the amounts of 10.0 and 1.2 mass %, respectively, at a temperature of 1,150°C and current density of 0.3 A/cm^2, the corrosion rate of chromium base alloy electrodes is more than a factor of 3 lower than that of nickel base electrodes and is

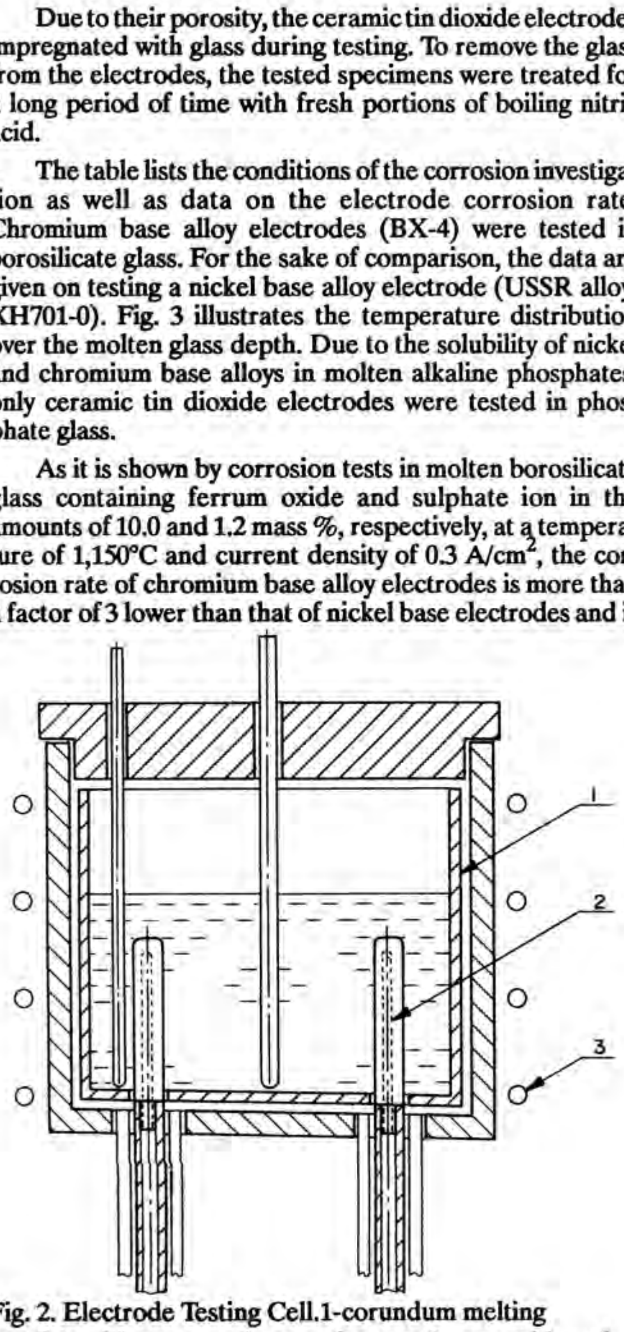

Fig. 2. Electrode Testing Cell.1-corundum melting crucible with cover and protective can, 2-removable rod electrodes, 3-furance with silicon carbide heater.

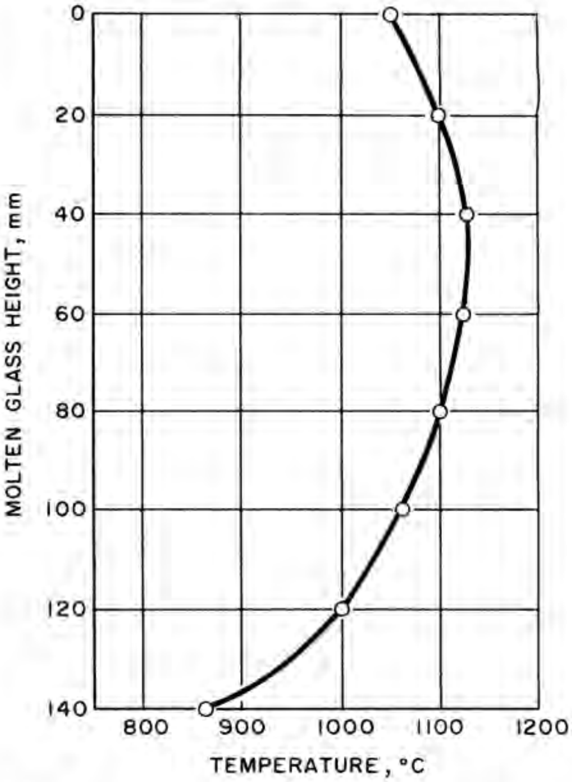

Fig. 3. Temperature Distribution Over Molten Glass Depth.

equal to 2.1 mm/year. There is a reduction factor of more than 2 in the nickel content of the chromium base alloy leads to a lower sulphide corrosion, which is due to a nickel-sulfur dioxide interaction in the molten glass to form low melting point nickel sulfides (Ni_3S_2, NiS, their melting temperatures are 650 and 850°C, respectively):

$$2Ni + SO_2 = 2NiO + NiS \ (2) \qquad \text{(Eq. 2)}$$

At the surface of a chromium base alloy electrode, a reaction takes place to form high-melting and low-soluble sulfide and chromium oxide:

$$6Cr + 3SO_2 = 2Cr_2O_3 + Cr_2S_3 \qquad \text{(Eq.3)}$$

It is shown by 100 h corrosion tests of tin dioxide electrodes with water-cooled current leads conducted in molten phosphate glass of higher ferrum oxide and sulfate ion contents at 1,100°C and current density of 1.0 A/cm^2 that:

- The electrical contact between the current lead and the ceramic tin dioxide rod worked in a stable manner without any variations in the electrical parameters;
- At the electric current density of 1 A/cm2, the corrosion of tin dioxide rods is uniform without any local attacks over the electrode length despite the non-uniform temperature distribution over the molten glass depth (Fig. 3);

- The average value of the rod tin dioxide electrode corrosion was 4.1 mm/year.

Thus, the tests in molten phosphate and borosilicate glasses showed that:

- Both ceramic tin dioxide and metallic chromium-nickel alloy electrodes are basically serviceable;
- Corrosion rates of tin dioxide and chromium base alloy electrodes are relatively low and equal to 4.1 and 2.1 mm/year, respectively.

To date, prolonged tests are being conducted of long rod tin dioxide and chromium base alloy electrodes in pilot furnaces for waste vitrification.

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TABLE I

Corrosion Testing Conditions and Electrode Corrosion Rates.

Electrode Material	Glass Composition								Test Temperature, °C	Current Density, A/cm^2	Test Duration, h	Corrosion Values, mm/year
	B_2O_3	SiO_2	CaO	Na_2O	Al_2O_3	P_2O_5	Fe_2O_3	SO_4^{2-}				
XH70H0	5.4	40.2	16.0	25.8	1.4	-	10.0	1.2	1150	0.3	31	7.5
BX4H									1150	0.3	80	2.1
SnO_2	-	-	-	22.7	21.8	48.8	6.2	0.5	1100	1.0	100	4.1