

REACTION PRODUCTS AND CORROSION OF MOLYBDENUM ELECTRODE IN GLASS MELT CONTAINING ANTIMONY OXIDES AND SODIUM SULFATE

#JIRÍ MATĚJ*, ANNA LANGROVÁ**

*Laboratory of Inorganic Materials, Joint Workplace of the Institute of Chemical Technology, Prague and the Institute of Rock Structure and Mechanics ASCR, v.v.i., Technická 5, 166 28 Prague 6, Czech Republic

**Institute of Geology, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague 6, Czech Republic

#E-mail: Jiri.Matej@vscht.cz

Submitted June 12, 2012; accepted August 20, 2012

Keywords: Molybdenum electrode, Corrosion, Glass melt, Antimony oxides, Sulfate

The products on the interface of a molybdenum electrode and glass melt were investigated primarily at 1400°C in three model glass melts without ingredients, with 1 % Sb₂O₃ and with 1 % Sb₂O₃ and 0.5 % SO₃ (wt. %), both under and without load by alternating current. Corrosion of the molybdenum electrode in glass melt without AC load is higher by one order of magnitude if antimony oxides are present. The corrosion continues to increase if sulfate is present in addition to antimony oxides. Isolated antimony droplets largely occur on the electrode-glass melt interface, and numerous droplets are also dissipated in the surrounding glass if only antimony oxides are present in the glass melt. A comparatively continuous layer of antimony occurs on the interface if SO₃ is also present, antimony being always in contact with molybdenum sulfide. Almost no antimony droplets are dissipated in the glass melt. The total amount of precipitated antimony also increases. The presence of sulfide on the interface likely facilitates antimony precipitation. The reaction of molybdenum with antimony oxides is inhibited in sites covered by an antimony layer. The composition of sulfide layers formed at 1400°C approximates that of Mo₂S₃. At 1100°C, the sulfide composition approximates that of MoS₄. Corrosion multiplies in the glass melt without additions through the effect of AC current, most molybdenum being separated in the form of metallic particles. Corrosion also increases in the glass melt containing antimony oxides. This is due to increased corrosion in the neighborhood of the separated antimony droplets. This mechanism also results in the loosening of molybdenum particles. The amount of precipitated antimony also increases through the effect of the AC current. AC exerts no appreciable effect on either corrosion, the character of the electrode-glass interface, or antimony precipitation in the glass melt containing SO₃.

INTRODUCTION

The basic mechanism of molybdenum corrosion in glass melt is its oxidation by glass components that act as corrosion depolarizers. Except for lead oxide, they represent minor glass components introduced as refining and coloring agents. The most common refining agents are antimony trioxide (introduced together with sodium nitrate) and sodium sulfate. As a result of the addition of nitrate, antimony is present in the glass melt as both Sb(III) and Sb(V). Sulfur is present as sulfate. The corrosion of molybdenum in glass melts containing antimony oxides was studied mainly in papers [1-3]. The effect of sodium sulfate was studied in papers [1, 4]. In the case of Sb₂O₃, its reduction up to metal occurring on the electrode surface was described. Isolated droplets of antimony in neighboring glass were also found [1, 5]. In addition to separated antimony, layers of oxidation products were found on the surface, their presence likely dependent on the conditions. Oxide layers with thickness from 10 to 40 µm were found [2]. The presence of layers containing Mo, O and Ba was described in another paper [3]. A thick layer of a product corresponding

best to the composition of barium molybdate was also found in paper [5]. Needles containing molybdenum and sulfur were found near the molybdenum surface [1]. Layers corresponding best to the composition of Mo₂S₃ were found in paper [4], where the electrodes were allowed to cool down freely in the glass melt. On the basis of voltammetric measurements, the mechanism of molybdenum oxidation was first suggested for lead glass melt [6], and more recently for glass melts containing antimony oxides [2]. This mechanism involves molybdenum oxidation to Mo(III) as the first step, followed by oxidation to MoO₂ on the surface, or to Mo(VI). More recent electrochemical measurements [7] have confirmed that mechanism. In glass melt containing SO₃, molybdenum oxidation to Mo(III) was suggested as the most probable, based on a comparison of the overall current in potentiostatic measurements with the calculated corrosion current [4]. This is in accordance with the found composition of the sulfide layer (and does not exclude its additional oxidation).

As for the effect of alternating current, a rather marked increase was found above 1 A.cm⁻² in glass melt with antimony trioxide [1]. The accelerating effect of AC

was confirmed in paper [3]. The amount of precipitated antimony also increases through the effect of alternating current [5]. On the other hand, little or no effect of alternating current was found in glass melts containing SO_3 [1, 3]. The relatively large effect of alternating current in the addition-free glass melt above 0.9 A.cm^{-2} [3] is worthy of interest.

In addition to molybdenum oxidation by antimony oxides, precipitated antimony may be another cause of molybdenum corrosion. Depending on temperature, this secondary corrosion may lead to the formation of the intermetallic compound Mo_3Sb_7 or to the heavy intercrystalline corrosion of molybdenum material, followed by loosening of the molybdenum particles above 940°C [8]. The embrittlement of molybdenum was also observed in glass melt containing SO_3 [1].

The heavy neck corrosion of the molybdenum electrodes by precipitated antimony was observed in electric melting of the glass, refined by a combination of antimony trioxide and sulfate. The causes of antimony accumulation and neck formation at relatively low temperatures near the glass surface were the subject of another paper [9], wherein it was suggested that sulfate has a stimulating effect on antimony precipitation. The subject of the submitted paper concerns, above all, what effect the presence of sulfate in glass melt containing antimony oxides has on the character of the molybdenum – glass interface and antimony precipitation, dependent on AC load, and also a comparison with the behavior in addition-free glass melt.

EXPERIMENTAL

The behavior of molybdenum electrodes was investigated in two model glass melts with basic composition of 16 Na_2O , 10 CaO , 74 SiO_2 (wt. %) modified by the addition of 1 wt. % Sb_2O_3 , and 1 % Sb_2O_3 + 0.5 % SO_3 , the ratio of the major components remaining unaltered, and compared with behavior in basic glass melt without additions. Model glasses were melted at 1450°C . Antimony oxides were introduced as Sb_2O_3 + NaNO_3 in an equivalent ratio, SO_3 as sodium sulfate. The composition of the prepared glasses was checked by the RFA method.

The experiments were carried out under loading by alternating current with a current density of 1.5 A.cm^{-2} (50 Hz), and also without loading. A pair of parallel electrodes in the form of molybdenum wires 1.2 mm in diameter, protected by silica glass capillaries except free bottom ends, 20 mm in length (0.765 cm^2), was introduced vertically in a crucible containing 75 g of glass melt. The duration of the experiments was 7 h. The temperature was reduced by 200°C at the end of exposure, and the electrodes together with the layer of adjacent glass were withdrawn from the crucible, embedded into epoxy resin and cut perpendicular to their axis. Diameter losses were

measured under a microscope on finely ground cuts. Selected cuts were used for preparation of the specimens for electron probe microanalysis. Specimens for the determination of precipitated antimony were prepared in a special series of experiments.

The amount of precipitated antimony was determined by a previously developed method [5]. The withdrawn electrodes with the adjacent layer of glass melt up to 20 mm above the glass level were crushed and mill ground (material of exposed electrodes is very brittle) into particles several micrometers in diameter, i.e., up to a diameter comparable with that of the smallest antimony droplets. Metallic antimony was extracted by boiling in concentrated sulfuric acid. 1 g of the thoroughly mixed specimen was extracted during 1 h in 10 ml of the acid. The amount of extracted antimony after rarefying was determined by the AAS method, unlike in paper [5]. As a certain amount of antimony oxides are leached from glass even under the described conditions, blank values for ground original glass were subtracted from the results. The blank values did not exceed 14 % of the lowest total value. The efficiency of antimony extraction was estimated to be about 90 % of the amount of precipitated antimony [5].

RESULTS AND DISCUSSION

Figures 1 to 5 show the glass-electrode interface in back-scattered electrons. In the glass melt containing just antimony oxides (Figure 1), only isolated antimony droplets occur on the interface, and many isolated antimony droplets are scattered in the surrounding glass. If the glass melt also contains SO_3 , a comparatively compact antimony layer occurs at the interface, and the amount of antimony droplets in the glass melt is minimal (Figure 2). A more or less compact layer of molybdenum sulfide, which is always in contact with the

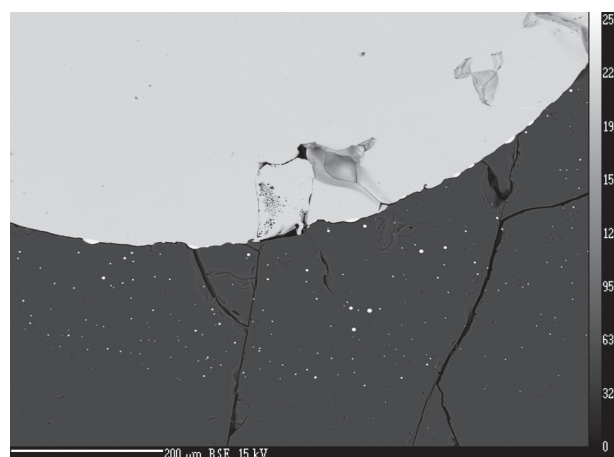


Figure 1. Isolated antimony droplets at molybdenum electrode (above) and numerous droplets scattered in the glass melt. 1 % Sb_2O_3 , no current load.

antimony, occurs at the interface. Although the antimony layer lies under the sulfide one, some solitary antimony droplets do occur on the outer periphery of the sulfide layer, as well as at the released particle. The character of the interface in glass melt containing SO_3 does not change, even under loading by alternating current (Figure 5). The picture shows a site with a rather thick antimony layer. It is obvious that the sulfide layer has formed by crystallization of an originally liquid layer at a temperature when antimony (with m. p. of 630°C) still remains a liquid. The outer antimony droplets may have formed during this solidification. The corrosion channel formed by secondary molybdenum corrosion by antimony represents evidence that liquid antimony is permanently present on the molybdenum surface. The described behavior shows that sulfide plays a significant role in the precipitation of antimony on the molybdenum electrode. Antimony likely precipitates together with sulfide. A more detailed explanation would demand additional investigation.

The results of a microanalysis of some sulfide layers are summarized in Table 1. The composition of the layers formed at specimens exposed at 1400°C corresponds comparatively well to that of Mo_2S_3 , as it has been found similarly in the same glass melt containing only SO_3 at the same temperature [4]. Like in the quoted paper, the layer formed at this temperature contains a comparatively large amount of sodium. This supports the assumption of the presence of an originally liquid multicomponent layer. 0.2 – 0.4 % Sb has also been found. Other components, i.e. 0 – 0.04 % Si and 0.06 – 0.126 % Ca found in the layer and not given in Table 1 may be attributed to contamination of the specimen surface by surrounding glass. On the other hand, the composition of the product on specimens exposed at 1100°C , when the first antimony droplets start to appear, corresponds best to that of MoS_2 . These products also contain almost no sodium. Different conditions, especially temperature and cooling rate, may then be the cause of contradictions in compositions found in different papers, e.g., in [1] vs. [4]. It may also be seen from Table 1 that the composition of the sulfate

layer formed at 1400°C without alternating current is somewhat nearer to Mo_2S_3 than the composition of the layer formed under a current load.

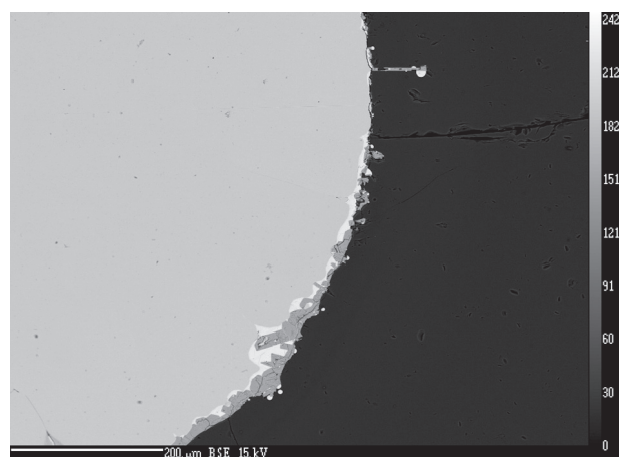


Figure 2. Comparatively continuous antimony layer underneath a sulfide one on a molybdenum electrode (left) formed in glass melt containing 1 % Sb_2O_3 and 0.5 % SO_3 , without current load.



Figure 3. Irregular molybdenum corrosion in glass melt containing 1 % Sb_2O_3 at current load of 1.5 A.cm^{-2} , with numerous metallic particles scattered in the glass (left).

Table 1. Composition of sulfide layers on molybdenum electrode.

Conditions	Composition					
	Na	Sb	S	Mo	S*	Mo*
1100°C , 0.4 A.cm^{-2} **	0.34	1.17	37.37	60.91	38.02	61.98
1100°C , 0.4 A.cm^{-2} **	0.43	0.91	41.02	60.96	40.22	59.78
1400°C , without current	2.81	0.38	33.48	70.81	32.10	67.90
1400°C , without current	2.98	0.19	32.41	71.59	31.16	68.84
1400°C , 1.5 A.cm^{-2}	2.93	0.40	32.15	69.20	31.72	68.28
1400°C , 1.5 A.cm^{-2}	2.70	0.40	27.88	68.33	28.98	71.02
Composition of Mo_2S_3	–	–	–	–	33.39	66.61
Composition of MoS_2	–	–	–	–	40.06	59.94

* values re-calculated to 100 % Mo + S

** sulfide particles on a loosed antimony drop

Another phenomenon occurs on an uncovered molybdenum surface under the effect of alternating current. Figure 3 shows irregular molybdenum corrosion in glass melt containing antimony oxides. The interface shows projections with gradually narrowing necks. Figure 3 and especially Figure 4 show that darker molybdenum particles are loosened in the end, in addition to white round antimony droplets. Irregular corrosion of the same type under the effect of alternating current has already been observed by Hwang et al. [10], who found no antimony on the molybdenum surface. Figure 4 shows, however, that a hemispheric antimony droplet is present on the top of almost every molybdenum projection. It may be seen from Figure 6 that the loosening of molybdenum particles under the effect of alternating current also takes place in the glass melt without additions. However, the molybdenum – glass interface is relatively smooth in that case, and obviously another mechanism is at work. Corrosion of the same type has also been observed in two glasses with a different basic composition containing no corrosion depolarizers [11].

The corrosion losses are given in Table 2. Corrosion without AC load is increased by one order of magnitude if antimony oxides are present. Corrosion continues to

increase if SO_3 is also present. The corrosion multiplies through the effect of alternating current in the addition-free glass melt and increases considerably in the glass melt containing antimony oxides, while alternating current exerts no effect in the glass melt also containing SO_3 , similar to what was found in the glass melt containing only SO_3 [1]. In comparison with paper [4], the lower corrosion losses found in the presented paper may be explained by the protective effect of the antimony layer covering a considerable part of the electrode surface if SO_3 is present. Table 3 shows the results of measuring the concentration of the components engaged in the corrosion process in the vicinity of the electrode surface. Despite the comparatively large scatter (cf. the repeated measurements), it can be seen that the concentration of molybdenum is considerably lower at sites covered by an antimony layer. In accordance with that, the consumption of antimony oxides decreases. It is then obvious that the electrode is protected by an antimony layer against

Table 2. Diameter losses Δr and amounts of precipitated antimony m at different conditions (1400°C, 7 h).

Addition	Current density [A.cm ⁻²]	Δr [μm]	m [mg]
none	0	0.9	–
none	1.5	4.5	–
Sb ₂ O ₃	0	7.0	8.0
Sb ₂ O ₃	1.5	12.2	16.0
Sb ₂ O ₃ + SO ₃	0	17.0	18.5
Sb ₂ O ₃ + SO ₃	1.5	17.1	18.9

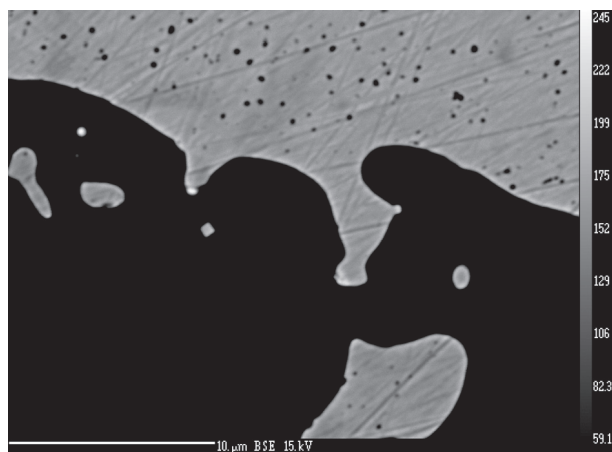


Figure 4. Detail of Figure 3 showing white antimony droplets on the tops of molybdenum projections and darker loosened molybdenum particles.

Table 3. Concentrations of engaged components c_i near to glass metal interface at different conditions after 7 h at 1400°C.

Additives, current density	Distance [μm]	c_i [wt. %] (free surface/covered surface)		
		MoO ₃	Sb ₂ O ₃	SO ₃
none, 0	5	0.71* (0.69; 0.73)	–	–
	50	0.36* (0.36; 0.36)	–	–
	500	0.06* (0.13; 0.00)	–	–
none, 1.5 A.cm ⁻²	5	1.08* (0.84; 1.32)	–	–
	50	0.85* (0.78; 0.92)	–	–
	500	0.00* (0.00; 0.01)	–	–
Sb ₂ O ₃ , 1.5 A.cm ⁻²	5	1.40/0.72	0.00/0.38	–
	50	0.31/0.00	0.25/0.99	–
	500	0.22/0.00	1.03/0.97	–
Sb ₂ O ₃ + SO ₃ , 1.5 A.cm ⁻²	5	1.33/0.89	0.32/1.04	0.04/0.05
	50	0.21/0.05	0.88/1.11	0.14/0.16
	500	0.52/0.00	0.69/0.94	0.17/0.18

* average from the values in brackets

oxidation by antimony oxides, and the presence of metallic antimony does not accelerate its precipitation. The concentration of SO_3 also decreases towards the interface, but less rapidly, and the effect of the covering by antimony is inconclusive.

Table 2 also involves the results of the determination of precipitated antimony. It can be seen that the amount of precipitated antimony increases if SO_3 is also present in the melt, especially in the current-free state. It may be stated that the amount of precipitated antimony is affected by both the presence of SO_3 and alternating current, and roughly parallels the loss in diameter. Alternating current does not exert a considerable effect on either diameter loss or antimony precipitation if SO_3 is present in the glass melt. The increase in antimony precipitation takes place despite the possibly competitive molybdenum oxidation by sulfate. This is in accordance with the increased occurrence of precipitated antimony at the

interface, stated above. Hence, the presence of sulfate in the glass melt resulting in the presence of sulfide on the electrode – glass interface probably promotes antimony precipitation. It has been found through investigation of the cathodic behavior of a molybdenum electrode in various glass melts [12] that, at the shift of the potential from its rest value towards more negative ones, the amounts of both precipitated antimony and precipitated lead show an expressed minimum. The respective potentials of those minima correspond to the potentials where molybdenum oxidation stops. The precipitation of metals on a molybdenum electrode in glass melt is probably facilitated by the presence of molybdenum compounds on the molybdenum surface.

Corrosion increases through the effect of alternating current most in glass melt without additions, and less in melt containing antimony oxides. Alternating current exerts no effect if SO_3 is also present. In the first case, the effect of alternating current probably corresponds almost solely to the amount of loosened particles of metallic molybdenum. A rough comparison in Figure 6, of the average sum of the diameters of loosened particles at different sites with the radius loss, confirms this presumption. The loosened particles may be oxidized solely by a limited amount of the dissolved oxygen. This effect of alternating current could be associated with a potential shift to extremely negative values during the cathodic half-period in glass melt containing no electro-active components. A more accurate and supported explanation would demand more detailed study. The accelerated corrosion in the sites of galvanic cells formed by solitary antimony droplets and by the neighboring uncovered molybdenum surface seems to be the most probable explanations of the irregular corrosion observed in the glass melt containing antimony oxides. Dévay et al. [13] confirmed a considerable increase in cell current through the effect of alternating current in the case of steel corrosion in water solutions.

Minute antimony droplets can be observed a relatively great distance from the electrode in glass melt without SO_3 (Figure 1) even if no alternating current is applied. This can then hardly be explained by the additional oxidation of loosened molybdenum particles by antimony oxides. The most probable explanation is the additional oxidation of molybdenum dissolved in a lower oxidation state resulting in the formation of Mo(VI) and metallic antimony. The presence of SO_3 leads to the formation of sulfide on the molybdenum electrode. This likely facilitates a reduction of antimony oxides on the electrode. Moreover, molybdenum dissolved in a lower oxidation state could be additionally oxidized preferably by SO_3 instead of antimony oxides. This is why no antimony precipitates in the surrounding glass melt.

The enhanced precipitation of antimony on the electrode surface leads to greater covering of the electrode by the metal. As a consequence, irregular corrosion

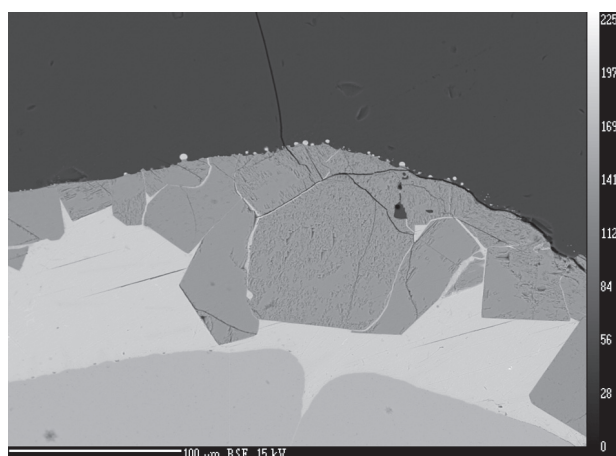


Figure 5. A thick and crystalline sulfide layer with antimony droplets above and continuous antimony layer below, formed in glass melt with 1 % Sb_2O_3 and 0.5 % SO_3 at current load of 1.5 A.cm^{-2} . Secondary molybdenum corrosion by antimony is visible on the very bottom.

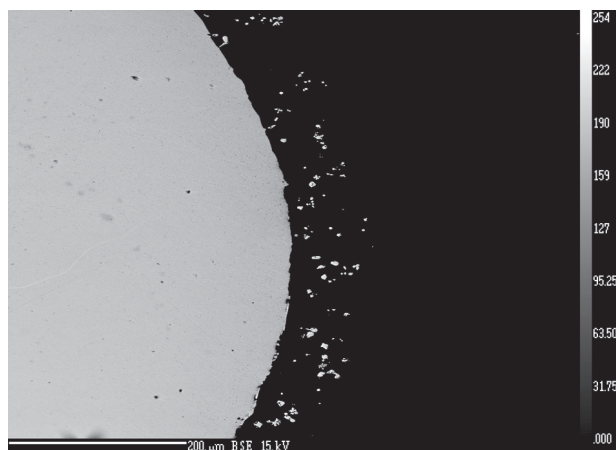


Figure 6. Scattering of fine molybdenum particles into glass melt (right) in addition-free glass melt under current load of 1.5 A.cm^{-2} .

under the effect of alternating current as described above is absent. On the other hand, the increased secondary corrosion by metallic antimony visible in Figure 5 is another consequence of the addition of sulfate to glass melt containing antimony oxides.

CONCLUSION

- The corrosion of the molybdenum electrode in the described model glass melt without load by alternating current increases by an order of magnitude if antimony oxides are present. The corrosion continues to increase if SO_3 is also present.
- The electrode-glass interface changes considerably if SO_3 is present, in addition to antimony oxides. While presumably isolated antimony droplets occur on the electrode-glass interface, and numerous antimony droplets are dissipated in the surrounding glass melt if only antimony oxides are present, a comparatively compact antimony layer, which is always in contact with molybdenum sulfide, occurs on the electrode. The occurrence of dissipated antimony droplets in the surrounding glass is minimal. The total amount of precipitated antimony increases. The presence of sulfide on the electrode probably facilitates antimony precipitation. Corrosion reactions are hindered on the sites covered by an antimony layer.
- Similarly to the glass melt containing only SO_3 , the composition of the sulfide layer formed after exposure at 1400°C approximates that of Mo_2S_3 . This product contains some wt. % of Na. The composition of products formed at 1250°C approximates that of MoS_2 .
- Corrosion in the addition-free glass multiplies through the effect of alternating current, with most molybdenum being loosened in the form of metallic particles. The corrosion also increases, even if not so markedly, in glass melt containing antimony oxides.

Irregular attack takes place in that case, the corrosion being considerably increased in the neighborhood of isolated antimony droplets. This mechanism also results in the loosening of molybdenum in metallic form. The amount of precipitated antimony also increases through the effect of alternating current. To the contrary, alternating current does not exert any considerable effect on either the corrosion, antimony precipitation, or character of the electrode – glass interface, if SO_3 is present in addition to antimony oxides.

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