559. *The Anodic Oxidation of Copper–Tin (Speculum) Alloys at Very Low Current Density.*

By (the late) S. E. S. El Wakkad, T. M. Salem, A. M. Shams ElDin, and Z. Hanafi.

The anodic oxidation of copper–tin alloys in alkaline solutions at very low current density is examined. It is shown that when speculum is forced from the hydrogen evolution potential to the oxygen evolution value, a less than unimolecular layer of stannous hydroxide is formed which is further oxidised to stannic hydroxide. This is followed by the formation of less than a unimolecular layer of cuprous oxide which is oxidised to cupric hydroxide. In acid solution the anode never rises to the oxygen evolution potential. It is shown that the alloys are more electronegative than their components, in agreement with Uhling and Woodside's conclusions in their study on steel. The alloys studied contained 45 ± 5% of tin.

In continuation of previous work [1] the anodic oxidation of copper–tin (speculum) alloys at very low current density has been investigated. Very little is known about the anodic oxidation of alloys in spite of their technical importance, and no relevant work has been published on speculum.

Copper–tin alloys, being simple-phase alloys, are corroded in a uniform manner and the corroded surfaces are very smooth. However, under some conditions, especially in acid solutions, the corrosion proceeds irregularly, so that the grains stand out in relief and the metal is rough. Copper–tin alloys were found to have a very high corrosion rate (at least 0·025 in. per day) in concentrated nitric acid. At first, the rate is high, but later decreases owing to formation of white metastannic acid on the surface.[2] In contact with copper–tin alloys, hydrochloric acid is one of the most corrosive of the non-oxidising acids. In sodium hydroxide solution, the corrosion rate was less than 0·01 in. per year at room temperature. The degree of aeration in this dilute solution was usually without appreciable effect. In non-oxidising alkaline salts, such as phosphates and carbonates, the copper–tin alloys are attacked at room temperature at rates less than 0·002 in. per year. The colour of the tarnish or corrosion product depends on the atmosphere.

Studies of the corrosion products of tin-bronze have shown the product to have decided periodicity. A cross-section of the corrosion layer on a 9 : 1 copper–tin alloy reveals

---

[1] El Wakkad, *et al.*, (*a*) *J.*, 1952, 461; 1953, (*b*) 3504, (*c*) 3508; 1954, (*d*) 3094, (*e*) 3098, (*f*) 3103; Electrochem. Soc. Meeting, Cincinnati, Ohio, May 1955.

[2] Bulow, "Corrosion Handbook," New York, 1948, where other references are cited.

alternate layers of red cuprite and green malachite.[3] Derge and Markus[4] studied the corrosion of tin alloys containing copper in solutions of sodium carbonate. Time–potential curves revealed promotion of passivity by the following cations: K^+, Li^+, NH_4^+, Ca^{++}, Fe^{++}, Cd^{++}, Mn^{++}, Ba^{++}, Bi^{++}, Mg^{++}, Cu^{++}, Pb^{++}, Zn^{++}, Ni^{++}, Ag^+. Oxygen induced passivity, but nitrogen increased the corrosion rate.

In the present study the anodic oxidation of speculum at very low current density was studied in acid and alkaline solutions. With an electroplated speculum anode and a very small polarising current a considerable time is required for the electrode to pass from the hydrogen to the oxygen evolution value, and so equilibrium potential can be measured at each stage of the polarisation. The results also show that stannous hydroxide is first formed over the surface of the speculum anode, followed by stannic hydroxide, cuprous oxide, and cupric hydroxide successively before evolution of oxygen.

From such a study it is shown that the alloys are more electronegative than their components.

EXPERIMENTAL

The electrical circuit and the electrolytic cell employed were as described by El Wakkad and Emara.[1a] The speculum electrodes were prepared by electrodeposition from a bath as recommended by Silman.[5] This was prepared by dissolving 80 g. of sodium hydroxide, 100 g. of $SnCl_4,5H_2O$, 12 g. of cuprous cyanide, and 28 g. of sodium cyanide in 1 l. of water, and adding 1 c.c. of 5% ammonia. The anodes were two copper and two tin electrodes placed alternately. Each pair of anodes was connected to a separate circuit including a resistance and an ammeter. The current imposed on the copper anodes was 6 mA/cm.², and that on the tin anodes was 7 mA/cm.². The total areas of the copper and tin anodes were 2 and 3 cm.² respectively. The anodes were coated with a film as recommended by the Tin Research Institute. The cathode was a platinum foil of 2 cm.² apparent area. Deposition was carried out in an electrically heated bath at 65° ± 2°, 15 minutes' heating giving satisfactory results. The electrodes were washed several times with conductivity water before being placed in their compartment.

Analysis of the deposited alloy gave Sn, 45 ± 5%. (This was checked by the Tin Research Institute, to whom we express our thanks.) Each experiment was carried out with a freshly prepared electrode from a fresh bath. The electrode was placed in such a position with respect to the cathode as to insure uniform distribution of the polarising current at the anode surface. The cathode was a platinum spiral about 2 cm. long and 0·1 cm. in diameter.

Measurements were made mainly in alkaline solution, *viz.*, 0·1N-sodium hydroxide (pH 13), 0·1M-sodium carbonate (pH 11·5), and 0·1M-sodium borate (pH 9·2), but also in 0·1N-hydrochloric and 0·1N-nitric acid. The solution in the cell was boiled before use and cooled in an atmosphere of pure nitrogen, to remove dissolved oxygen.

The polarising current used was 30 μA/electrode for the hydroxide solution and 1 and 3 μA for the carbonate and the borate solution, respectively. With acid solutions, currents up to 500 μA/electrode were used. In each solution each electrode was studied under those conditions, *viz.*, anodic polarisation, cathodic polarisation, and anodic decay. The procedure adopted in obtaining the corresponding curves was as described before.[1a]

The reference half-cell was a saturated calomel electrode prepared as described before.[1a] The electrolytic cell and the reference half-cell were kept in an air thermostat at 25° ± 0·01°. The e.m.f. was measured with a calibrated metre bridge and an Onwood mirror galvanometer having a sensitivity of 190 mm. per μA. All potentials quoted are on the hydrogen scale.

RESULTS AND DISCUSSION

Curve *A*, Fig. 1, is the characteristic anodic polarisation curve for speculum (45 ± 5% Sn) at 25° with a polarising current of 30 μA in 0·1N-sodium hydroxide; curve *A*, Fig. 2, is the same anodic polarisation curve in 0·1M-sodium carbonate solution for a polarising current of 1 μA/electrode. From these curves, which show the variation of the potential of the speculum anode with the quantity of electricity passed, it can be seen that, at first, there is a rapid initial build up of potential, ascribed, by analogy with the cases previously

---

[3] Calin, Fink, and Palushkin, *Trans. Amer. Inst. Mining Met. Eng.*, 1936, No. 693.

[4] Derge and Markus, *ibid.*, Tech. Publ. No. 1306, 1941.

[5] Silman, " Chemical and Electroplated Finishes," 1949, p. 323.

studied,[1a] to the charging of the double layer, which is followed by four well-defined arrests before evolution of oxygen. Measurements from a large number of polarisation curves give an average value for the double layer capacity of 550 μF/electrode for the speculum anode under investigation in the hydroxide solution of pH 13. In the carbonate solution, it was difficult to determine the capacity of the double layer because the potential of the electrodes, when made the cathode, was very near to the oxide potential at these extremely low currents (1 μA).

The first arrest after the charging of the double layer appears to start at —0·91 v in sodium hydroxide and at —0·72 v in carbonate solution. The second, third, and fourth arrests appear to start at —0·81, —0·30, ±0·00, and —0·61, —0·17, +0·03 v, in the two solutions respectively.

FIG. 1.

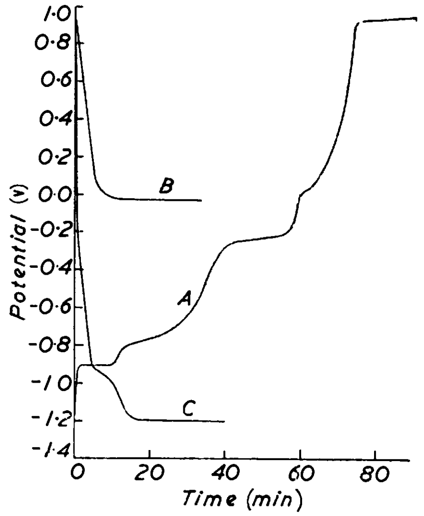
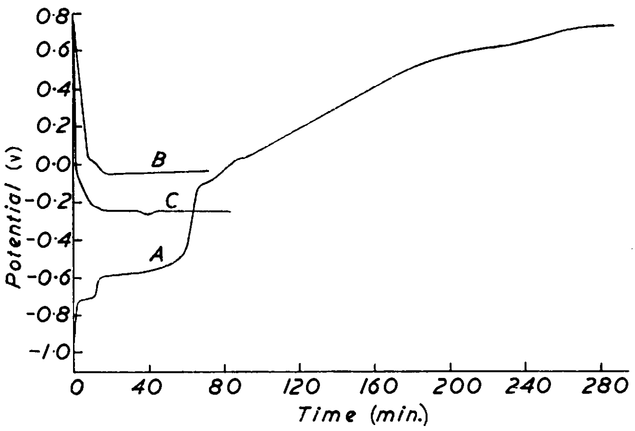


FIG. 2.



In the following Table are shown the starting potential of these four arrests in the two electrolytes as compared with the equilibrium potentials of the systems Sn–$Sn(OH)_2$, $Sn(OH)_2$–$Sn(OH)_4$, Cu–Cu_2O, and Cu_2O–$Cu(OH)_2$, which were obtained as follows: the free energies of $Sn(OH)_2$, $Sn(OH)_4$, Cu_2O, $Cu(OH)_2$, OH^-, and H_2O being taken respectively as —115,200, —266,000, —35,150, —85,500, —37,585, and —56,690 cal.,[6] the free energy changes of the reactions are :

$$Sn + 2OH' = Sn(OH)_2 + 2e;\ \Delta F = -40{,}030 \text{ cal.}$$
$$Sn(OH)_2 + 2OH' = Sn(OH)_4 + 2e;\ \Delta F = -35{,}630 \text{ cal.}$$
$$2Cu + 2OH' = Cu_2O + H_2O + 2e;\ \Delta F = -16{,}670 \text{ cal.}$$
$$\text{and} \quad Cu_2O + 2OH' + H_2O = 2Cu(OH)_2 + 2e;\ \Delta F = -3990 \text{ cal.}$$

and these give $E°_B$ (the potential value at the extreme alkaline range of pH) as —0·87, —0·77, —0·36, and —0·087 v for the above four systems respectively. By applying the ordinary equation for the variation of the potential of these systems with pH, the values given in the following Table are obtained :

	Starting potential (v) of arrests :				Equilibrium potential (v) of system :			
Solution	1st	2nd	3rd	4th	Sn–$Sn(OH)_2$	$Sn(OH)_2$–$Sn(OH)_4$	Cu–Cu_2O	Cu_2O–$Cu(OH)_2$
0·1N-NaOH	—0·91	—0·81	—0·30	±0·00	—0·81	—0·71	—0·30	—0·30
0·1M-Na_2CO_3	—0·72	—0·61	—0·17	+0·03	—0·72	—0·62	—0·21	+0·06

---

[6] Latimer, " The Oxidation States of the Elements and their Potentials in Aqueous Solutions," New York, 1938, pp. 35, 137, 170.

The agreement between the starting potentials of the four arrests as observed from the curves and the equilibrium values of the four systems leaves little doubt that these four steps in the anodic polarisation in such solutions correspond to the consecutive formation of stannous hydroxide, stannic hydroxide, cuprous oxide, and cupric hydroxide on the speculum anode before evolution of oxygen.

The standard condition for the alloy was taken to be the carbonate solution. The quantities of electricity utilised in the passivation of the alloys were found to vary from one solution to another. In the carbonate solution the quantity of electricity passed from the beginning to the end of the first step was about 600 microcoulombs. Comparison of this amount of electricity with that obtained in the case of the tin electrode alone [1b] shows that the alloys are of more electronegative character, as found also by Uhling and Woodside [7] in their study on steel.

The alloys prepared by electrodeposition are considered to have an area more or less comparable with those of both the tin and the copper electrode alone. Thus the quantity of electricity passed in the first step would liberate $1{\cdot}84 \times 10^{15}$ oxygen atoms. The diameter of the tin atom being taken as 3·04 Å (from its density), there would be about $1{\cdot}08 \times 10^{15}$ atoms of tin per true sq. cm. at the tin surface. From the value of the capacity of the double layer of the speculum anode, a rather rough estimate for the ratio of the real to the apparent area of speculum anode can be obtained. The capacity of the real area being taken as that estimated from previous work,[1a, 8] *viz.*, 100 μF per true sq. cm., the value for the ratio real : apparent area of our anode would be 5·5 : 1 and hence there would be about $5{\cdot}94 \times 10^{15}$ atoms of tin on the whole surface of our electrode. This shows that the quantity of electricity passed in the first step corresponds with the formation of a film of $Sn(OH)_2$ which is less than one molecule thick. However, it must be emphasised that these results are very approximate since part of the surface of the electrode is covered by copper atoms from the alloy.

Fig. 3.

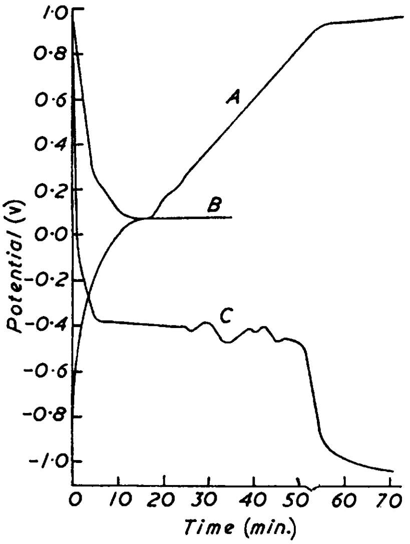
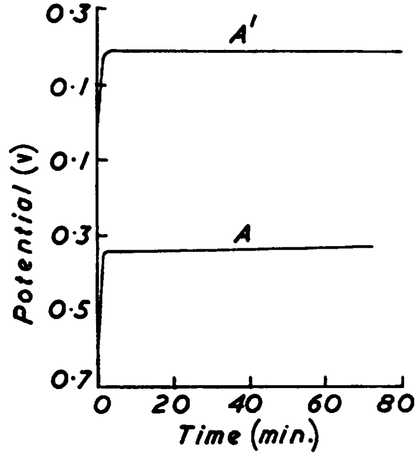


Fig. 4.



The quantity of electricity passed in the second step corresponds to the formation of a film of $Sn(OH)_4$ some two molecules thick; that passed in the third step is about 600 microcoulombs and is sufficient for the formation of less than one molecular thickness of cuprous oxide; and that in the fourth step indicates conversion of cuprous oxide film into cupric hydroxide.

---

[7] Uhling and Woodside, *J. Phys. Chem.*, 1953, **57**, 280.

[8] El Wakkad and Salem, *J.*, 1955, 1489.

The same conclusion as to the thickness of the oxides is reached for sodium hydroxide solution, thus confirming the above statement on the relative electrochemical behaviour of alloys and their constituents.

Curve *A*, Fig. 3, represents the anodic behaviour of the speculum alloy in 0·1M-sodium borate solution of pH 9·2, a polarising current of 3 μA per electrode being used. This curve shows the notable "shielding effect" of the steps $Sn-Sn(OH)_2$ and $Sn(OH)_2-Sn(OH)_4$ by the two following steps, $Cu-Cu_2O$ and $Cu_2O-Cu(OH)_2$. Thus it was rather difficult to record the two first steps although the polarising current was very much lowered. Thus it gives two steps whose starting potentials are at +0·05 and +0·18 v, as compared with −0·06 and +0·20 v for the second two systems at the same pH.

In 0·1N-hydrochloric acid (curve *A*, Fig. 4) the results indicate anodic dissolution of tin at about its reversible potential, a current up to 500 μA per electrode being used. Curve *A'*, Fig. 4, shows the characteristic anodic polarisation of speculum in a solution of nitric acid (pH 1) with a current of 500 μA per electrode. This was obtained when the current was switched on cathodically before the speculum electrode was dipped into the nitric acid solution.[1b] The solution was found to be turbid owing to the suspension of metastannic acid, confirming Bulow's results.[9] The potential of the speculum anode suggests anodic dissolution. The same potential was also found when using 0·01N-nitric acid. Pure copper also behaved similarly. The potential obtained does not coincide with any of the known potentials of copper. However, the constancy of the potential in both 0·1N- and 0·01N-nitric acid indicates dissolution to give some other ionic species than the usual one. This may be due to the oxidising effect of nitric acid.

The anodic decay curves (*B*, Figs. 1, 2, 3,) reveal that, on interruption of the polarising current when the anode is at oxygen evolution potential, the potential falls to that of the system $Cu_2O-Cu(OH)_2$ where it remains constant. This behaviour was explained on the basis that $Cu(OH)_2$ was not in direct contact with the metal.[1c]

The cathodic curve (*C*, Fig. 1) shows a value for the potential of $Sn-Sn(OH)_2$ which is explained by the increased solubility of tin oxides in such solutions. In case of sodium carbonate, curve *C*, Fig. 2, shows the reduction of copper oxides at negative potentials. This was explained by El Wakkad and Emara.[1c] With the very low polarising current used, the potential of the electrode remains for a long time at the arrest of $Cu-CuO_2$. Curve *C*, Fig. 3, obtained for the borate solution, shows that the potential of the electrode fell directly to the value of the system $Sn(OH)_2-Sn(OH)_4$ where it remained constant before evolution of hydrogen.

CAIRO UNIVERSITY, FACULTY OF SCIENCE, CAIRO, EGYPT.
EIN SHAMS UNIVERSITY, WOMEN'S INSTITUTE,
ZAMALEK, CAIRO, EGYPT.

[*Received, January 13th,* 1956].

---

[9] Bulow, "Corrosion Handbook," New York, 1948.