

# *Behaviour of metallic copper in the $KNO_3$ - $NaNO_3$ eutectic mixture at 300° C*

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The behaviour of metallic copper in an equimolecular mixture of  $KNO_3$  and  $NaNO_3$  at 300° C is discussed. As previously reported in the literature, under these conditions copper becomes covered with  $Cu_2O$ ; however, contact with the above bath for a sufficiently long time also causes an external, spontaneous growth of a  $CuO$  layer. Such conditions of surface oxidation are also obtained by suitable anodic polarizations. The metal covering scale, after the final oxidation state has been reached, is adherent and compact, and seems to be able to prevent practically any further corrosive processes.

## 1. Introduction

Though in recent years there has been a growing interest in electrochemical studies on molten salts, the literature relating to the behaviour of massive metals in these media is relatively poor, especially as compared with the literature on metal-gas systems at high temperature.

In particular the works by Gurovich and Matveeva [1-3], Swofford and Laitinen [4], Brough and Kerridge [5], Conte and Casadio [6, 7] and Notoya and Midorikawa [8, 9] on the behaviour of copper in molten alkali nitrates should be mentioned; in addition Marchiano and Arvia [10] have presented a thermodynamic treatment of the behaviour of copper in molten  $KNO_3$  in terms of potential- $pO_2$ ,  $-pO_2^-$  and  $-pO_2^-$  diagrams. From these works it results that, on the whole, copper in molten alkali nitrates is characterized by considerable stability [1-3] due to a spontaneous layer oxide formation [5]. Cathodic polarizations, relatively far away from the equilibrium potential, give rise to a chemical attack on the oxidized surface [4]. The oxide that spontaneously forms on copper in alkali nitrates (at least around 300° C) has been identified as  $Cu_2O$  [6, 7]. By means of suitable anodic polarizations,  $CuO$  also forms; this is evidenced by a characteristic passivation current peak [6, 8, 9]. Anodic polarizations sufficiently far from this passivation potential cause dissolution of copper due to

transpassivity, and consequent precipitation of  $CuO$  into the bath [7, 8].

This paper further contributes to the knowledge of the electrochemical behaviour of copper in the equimolecular mixture of  $KNO_3$  and  $NaNO_3$  at 300° C.

## 2. Experimental

In Fig. 1 the furnace with the cell and the devices for electrochemical measurements are outlined. The stainless steel hollow block that supports the beaker containing the eutectic mixture, also works as a 'thermal fly-wheel', thus enabling the working temperature to be stabilized within  $\pm 1.5^\circ$  C. The lead-throughs on the head-flange of the furnace allow the reference electrode to be immersed in and lifted from the molten bath, whereas the working electrode can be easily taken out of the furnace.

Potassium and sodium nitrates (Baker Analysed Reagent), have been utilized without further treatments. In fact, under our experimental conditions, we were able to notice that the utilization of the equimolecular mixture, previously filtered and preserved as described in the literature (for example, by Conte [6]), did not yield results appreciably different from those presented in this paper. Therefore 70 g of equimolecular mixture, after having been kept in an oven at 180° C for at least 48 hours, were put in a pyrex beaker (100 ml

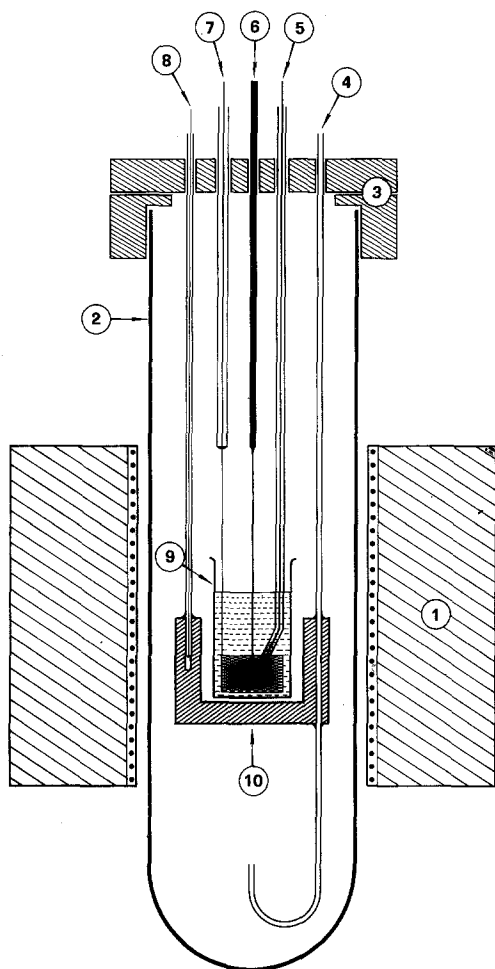


Fig. 1. Schematic view of the furnace and the electrochemical cell.

- (1) Anti-inductive electric furnace.
- (2) Alumina tube (8 cm diameter, 50 cm length).
- (3) Water-cooled metallic flange.
- (4) Input for the gaseous flux.
- (5) Electric lead for the reference electrode.
- (6) Electric lead for the working electrode.
- (7) Electric lead for the counterelectrode.
- (8) Electric leads for the measuring thermocouple (Chrome-Alumel).
- (9) Beaker containing the eutectic mixture.
- (10) Stainless steel hollow block.

in capacity), which was then placed into the furnace.

Prior to heating, an inert gas (Argon UPP) was made to pass through the space containing the electrochemical cell for at least 12 hours; this flow of argon was maintained during the tests.

The reference electrode, of the all-glass type described by Inman [11], consisted of a silver

wire immersed in an equimolecular mixture of  $(K, Na)NO_3$  plus 0.1 mol of  $AgNO_3$ .

The counterelectrode, with a geometric surface of about  $40\text{ cm}^2$ , was a platinum ribbon suitably shaped and placed against the inner side of the beaker.

The working electrode, finally, was made up of a wire (1.8 mm diameter) of commercial copper (99.8% purity; major impurities: Si 0.1%, Fe 0.05%). Before being utilized, the electrode was pickled in dilute  $HNO_3$ , then washed in distilled water and then in acetone. The surface immersed in the molten bath was about  $2\text{ cm}^2$ .

An electrometer with an input impedance greater than  $10^9\ \Omega$  and a potentiostat with a function generator were used for the electrochemical measurements. The polarization curves were directly recorded by means of an  $x$ - $y$  apparatus; the potential-time curves were recorded, utilizing the output with calibrated 'zero-offset' of the electrometer, by means of a  $x$ -time apparatus: in such a manner a sensitivity of  $8\text{ mV cm}^{-1}$  was obtained on a paper strip of the recorder.

In every test new baths and new working electrodes were used.

### 3. Results and discussion

It should be noted that the present graphs relating to the potential-time curves and to the polarization curves have been obtained by averaging various experimental results (at least 3 per every test), which had been processed by a desk computer and directly transcribed on a plotter according to a suitable program [12].

#### 3.1. Behaviour of copper under free-corrosion conditions

Fig. 2 shows the initial (Curve I) and long-term (Curve II) behaviour of the rest potentials of copper in  $(K, Na)NO_3$  at  $300^\circ\text{C}$ . One can see two characteristic potential plateaus: the first at about  $-0.680\text{ V}$  versus reference, which lasts about 30 min (Fig. 2, interval 'a'), and the second at about  $-0.440\text{ V}$  versus reference (Fig. 2, interval 'c'); the latter plateau remains constant (with small oscillations within  $\pm 5\text{ mV}$ ) at least for up to

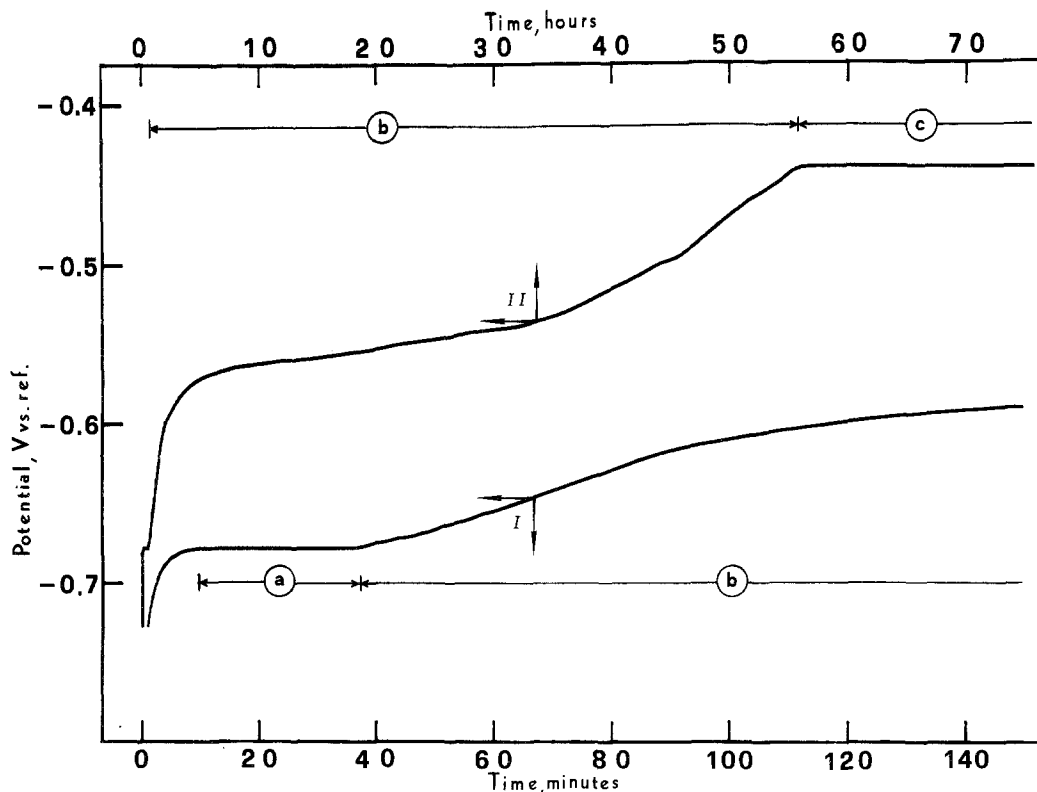


Fig. 2. Behaviour, as a function of time, of the rest potential of copper in  $\text{KNO}_3\text{-NaNO}_3$  at  $300^\circ\text{C}$ ; Curve I initial behaviour, Curve II long-term behaviour.

250 hours. Between the two plateaus (Fig. 2, interval 'b') the behaviour of the potential as a function of the time is rather complicated.

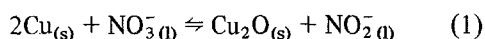
The X-ray diffractometric analysis made on corrosion products (by accurately scraping off the surface oxide scale which had formed due to the stay of the copper specimen in the molten bath), has shown the presence of  $\text{Cu}_2\text{O}$  on samples kept in contact with the bath for no more than about 20–30 hours, whereas the diffraction peaks of  $\text{CuO}$  can be seen on samples immersed for a longer time. The experimental difficulties encountered in these analyses did not enable us to determine a quantitative ratio between the two oxides observed, when both of them were present, even if one can state that the peaks of  $\text{CuO}$  become sharper and more definite as time of specimen immersion increases. Also the surface colour of the copper sample undergoes a series of alterations which depend on the immersion time, and roughly speaking, it changes from brown-red

(up to 10–15 hours of immersion), to brown (up to 25–30 hours of immersion), and finally to black.

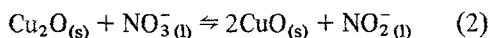
The above experimental evidence suggests that copper oxidized spontaneously first to  $\text{Cu}_2\text{O}$  and then to  $\text{CuO}$ ; to the author's knowledge, the latter remark has never been made in the literature.

The two rest potential plateaus, which have been noticed during the free-corrosion tests, can be related to two different conditions of electrochemical equilibrium on the electrode surface in the molten bath. The first is relevant to the couple  $\text{Cu}/\text{Cu}_2\text{O}$  (plateau at  $-0.620\text{ V}$  versus reference) and the second is relevant to the couple  $\text{Cu}_2\text{O}/\text{CuO}$  (plateau at  $-0.440\text{ V}$  versus reference). Under these conditions, copper might behave as an oxide electrode, i.e. as a sort of second-kind electrode. Moreover, according to the present state of the art, it is rather difficult to establish, quantitatively and qualitatively, which is, or which are, the oxidative species involved in

the process. In fact, it was first thought [4, 13, 14] that the primary product of the electro-reduction in molten alkali nitrates might be the oxide ion ( $O^{2-}$ ); however, it was later demonstrated [15, 16] that this ion is unstable in such a media and that it changes into peroxide ( $O_2^{2-}$ ) and superoxide ( $O_2^-$ ) ions, the latter being more stable [17-19]. Recently it has been stated [20], however, that the peroxide ion forms more easily in molten pure  $NaNO_3$ , whereas the superoxide ion forms especially in molten pure  $KNO_3$ . Of course, it is beyond the purpose of this work to deal with such considerations. Nevertheless it is interesting to try to present here, in a less descriptive way, the oxidation processes which take place on the surface of metallic copper immersed in molten alkali nitrates. To this end it seems correct to write the following probable overall reactions which take place in the system under examination:



and



where (s) = solid phase and (l) = liquid phase. As a first approximation, copper oxides are considered practically insoluble in molten alkali nitrates. (This assumption has been confirmed by the fact that, after the free-corrosion tests, no appreciable amounts of copper and/or copper compounds were found in the solidified bath). Moreover, according to [4], the final reduction product is assumed to be, under our operative conditions, the nitrite ion ( $NO_2^-$ ). The respective equilibrium electrode potentials can be associated with the above reactions:

$$E_1 = -\frac{\Delta G_1^0}{2F} - \frac{RT}{2F} \ln \left( \frac{a_{Cu_2O} a_{NO_2^-}}{a_{Cu}^2 a_{NO_3^-}} \right)_1 \quad (3)$$

and

$$E_2 = -\frac{\Delta G_2^0}{2F} - \frac{RT}{2F} \ln \left( \frac{a_{CuO}^2 a_{NO_2^-}}{a_{Cu_2O} a_{NO_3^-}} \right)_2 \quad (4)$$

where the symbols have their usual meanings, and the subscripts 1 and 2 refer to Reactions 1 and 2, respectively. If one assumes, in the case under examination, that the activities of the solid species are unity, and that the activity ratios of nitrite : nitrate ions are practically equal both in

Reaction 1 and in Reaction 2, one can write:

$$E_1 - E_2 = -\frac{1}{2F} (\Delta G_1^0 - \Delta G_2^0). \quad (5)$$

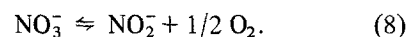
Since the values of the changes in the free energies of formation of  $Cu_2O$  and  $CuO$  are easily available in the literature, one can also write:

$$\Delta G_1^0 = \Delta G_{f,1}^0 + \Delta G_x^0 \quad (6)$$

and

$$\Delta G_2^0 = \Delta G_{f,2}^0 + \Delta G_x^0 \quad (7)$$

where  $\Delta G_{f,1}^0$  and  $\Delta G_{f,2}^0$  are the changes in the free energies of formation of  $Cu_2O$  and  $CuO$ , respectively, while  $\Delta G_x^0$  is the change in the standard free energy related to the formal reaction:



Therefore, the resulting equation is

$$E_1 - E_2 = -\frac{1}{2F} (\Delta G_{f,1}^0 - \Delta G_{f,2}^0). \quad (9)$$

Finally, from the data available in the literature [21], interpolated at 573 K, one can easily obtain from Equation 9 the difference between  $E_1$  and  $E_2$  ( $= +0.250$  V). It follows that, with the above assumptions and experimental conditions, the equilibrium potential of the couple  $Cu_2O/CuO$  should theoretically be more positive than the one of the couple  $Cu/Cu_2O$  by 0.250 V: in actual fact, the difference between the two experimental plateaus (Fig. 2) is about 0.240 V.

### 3.2. Behaviour of copper under external polarization conditions

Tests of potentiodynamic polarization have been carried out on copper samples kept in contact with the molten nitrate bath for increasing periods. Contrary to what has previously been stated in the literature [7, 8], the best reproducible results have been obtained at a potential scan rate less than  $1 \text{ mVs}^{-1}$ . Therefore, all the experimental data reported in the present paper have been obtained at a scan rate of  $0.2 \text{ mVs}^{-1}$ .

Fig. 3 shows the anodic polarization curves of copper in (K, Na) $NO_3$  at  $300^\circ \text{C}$ . The polarizations have been carried out starting from the rest potentials that had been reached by the electrodes after they had been kept immersed in the bath for

different times: in particular, Curve I refers to polarizations carried out after 10 min immersion ( $E_{\text{rest}}$  about  $-0.680$  V versus reference); Curve II refers to polarizations carried out after 6 hours immersion ( $E_{\text{rest}}$  about  $-0.570$  V versus reference) and Curve III refers to polarizations carried out after 50 hours immersion ( $E_{\text{rest}}$  about  $-0.440$  V versus reference). Beyond  $+0.200$  V versus reference the current density rises very rapidly, the transpassivity condition (i.e. anodic dissolution of copper) having been reached.

As can be seen in Fig. 3, if the copper electrode does not remain immersed in the bath for a suitable time, a current peak appears at about  $-0.500$  V versus reference (Fig. 3, Curve I and I'); after about one hours immersion this peak disappears (Fig. 3, Curve II and II'), though the current peak at about  $-0.030$  V versus reference stays practically at the same height. Finally, if the electrode is kept in the bath for some 50 hours,

the peak at about  $-0.030$  V versus reference is also no longer detectable (Fig. 3, Curve III).

At this stage it is worth noting that while the potential of the second anodic peak (taking into account the different experimental conditions) may be in good agreement with the data available in the literature and ascribed to the process due to the electrochemical oxidation of cuprous oxide into cupric oxide [6, 8, 9], the first anodic peak has been attributed to the probable presence of water in the molten alkali nitrate [8]. However, on the basis of considerations of free-corrosion processes, it seems more consistent to ascribe the first anodic peak to the oxidation process of metallic copper into cuprous oxide. To justify this hypothesis, some copper electrodes, which had just been immersed in the bath, were polarized at a fixed potential of  $-0.400$  V versus reference; the polarization was maintained for a suitable time (10–15 min), i.e. up to the point where the current

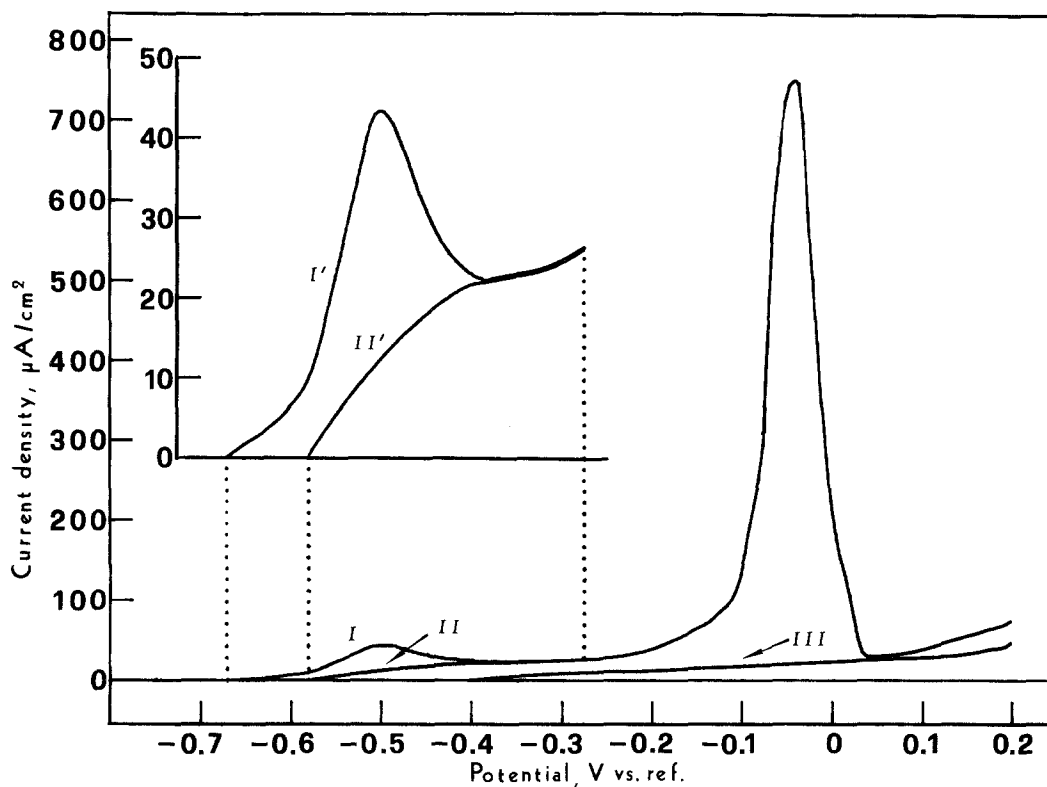


Fig. 3. Anodic polarization curves of copper in  $\text{KNO}_3\text{-NaNO}_3$  at  $300^\circ\text{C}$ . Scan rate:  $0.2\text{ mVs}^{-1}$ . Scanning starts from the rest potential reached after: Curve I: 10 min immersion; Curve II: 6 hours immersion; Curve III: 50 hours immersion. In the figure the initial lines of Curve I and II are also plotted (Curve I' and II', respectively) on ordinate scale ( $\times 10$ ).

density remains practically constant. After this polarization and on open circuit, the rest potential reached about  $-0.550$  V versus reference rapidly enough (in 10–15 min), while the subsequent potentiodynamic polarization repeated the behaviour of Curve II in Fig. 3.

Similarly polarizations at  $0.000$  V versus reference were carried out and, in subsequent potentiodynamic polarizations, behaviour analogous to Curve III in Fig. 3 was obtained.

Finally, the diffractometric analysis made on samples which had not been polarized beyond  $-0.400$  V versus reference showed only the presence of  $\text{Cu}_2\text{O}$ , whereas, when polarization was carried out beyond the potential of the second peak,  $\text{CuO}$  turned out to be also present.

As previously reported, the heights of the two anodic peaks decrease with the immersion time of the electrode in the bath. This behaviour is shown graphically in Fig. 4; while the height of the first peak decreases in a fairly regular way, until it disappears after about one hours immersion (Fig. 4, Curve I), the height of the second peak remains practically constant for 25–30 hours, then it decreases abruptly and, finally, it is negligible after

some 50 hours immersion. If one assumes that the height of the anodic peak (the other parameters being constant) is proportional, in the tests presented here, to the concentration of the oxidizable species present on the surface of the working electrode, one can state that during the first 50 min immersion, the copper electrode progressively covers itself with  $\text{Cu}_2\text{O}$  oxide (in other words, at this stage, the surface of 'bare' copper decreases). When the whole electrode is covered with oxide, the thickness of this layer starts increasing until it reaches a limiting dimension (after some 30 hours). At this stage, on the external surface of the electrode, a further appreciable oxidation process of  $\text{Cu}_2\text{O}$  into  $\text{CuO}$  spontaneously begins, which causes the height of the second anodic peak to decrease. Finally, after the second anodic peak has disappeared, one can deem that the whole external surface of the electrode is covered with  $\text{CuO}$ . The behaviour of the free-corrosion potential as a function of the time (two characteristic potential plateaus being present) proves the validity of this assumption, which is further verified by diffractometric analysis on the corrosion products.

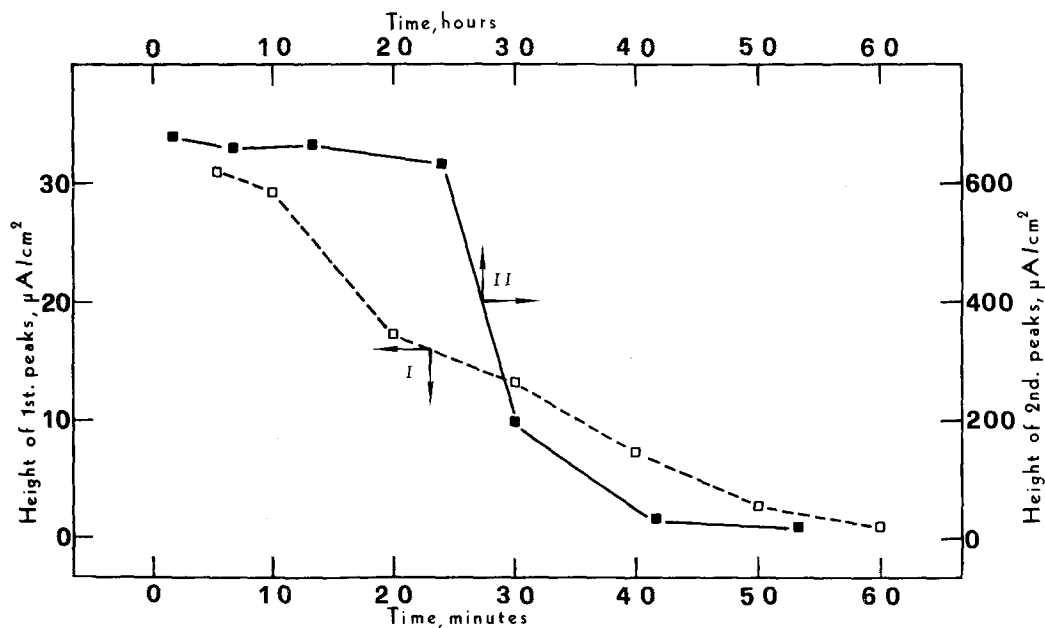


Fig. 4. Heights of the anodic current peaks as a function of the immersion time of copper specimen in  $\text{KNO}_3$ – $\text{NaNO}_3$  at  $300^\circ\text{C}$ . Curve I, dashed line: anodic peak at  $-0.500$  V versus reference; Curve II, continuous line: anodic peak at  $-0.030$  V versus reference.

Finally, it is interesting to point out that some copper samples, which had been oxidized until CuO had covered their surfaces (due to free-corrosion or anodic polarization), did not show, at least over 50 hours, any mass variations higher than  $10 \mu\text{g cm}^{-2}$  when they were taken out of the molten bath and placed in an atmosphere of  $\text{O}_2$  at  $300^\circ \text{C}$ . The fact that such remarkable stability conditions can be obtained, shows that the scale which forms can protect the copper in a quite satisfactory way.

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