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Electrochemical behaviour of cobalt in aqueous solutions of different pH

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Abstract

A systematic study of the corrosion and passivation behaviour of cobalt in aqueous solutions of different pH was carried out. Open circuit potential measurements, polarization experiments and electrochemical spectroscopic (EIS) investigations were employed. The experimental results show that the metal surface is always covered by a native passive film which consists of CoO. The formation of the oxide film obeys a two-electron charge transfer process. The dissolution of the barrier film is controlled by the pH of the solution. In neutral and basic solutions the barrier film is stable. In these media a barrier film thickening with the formation of secondary layer is considered. In acidic solutions, the passive film is unstable and dissolves via a pure chemical process. The mechanism of the corrosion and passivation processes taking place at the electrode/electrolyte interface in the different solutions is discussed. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to confirm the electrochemical measurements and the suggested mechanisms.

1. Introduction

Due to their importance in many industrial applications, the iron group metals (Fe, Co and Ni) have been subjected to intensive investigation concerning their electrochemical behaviour in aqueous solutions. In particular, the electrochemical behaviour of cobalt has still not been thoroughly investigated and contradictory results are reported.

The corrosion and passivation behaviour of cobalt in aqueous solutions depend on the composition and pH of the solution [1–6]. In the presence of chloride ions pitting corrosion was reported to take place depending on the concentration of these ions and the applied potential [6–9]. The effect of halides on the electrodissolution of the iron group metals has been widely investigated [10–15]. These studies focused on the kinetics of the electrodissolution of the metal in its active region. The interpretations of the results were based on the specific adsorption of anions on the metal surface [14–17]. For cobalt, no systematic investigations on the electrochemical behaviour have been reported. Most investigations have been carried out in basic solution where a stable passive film is formed on the metal surface [18–21]. It was suggested that the anodic oxidation of cobalt in alkaline solutions takes place in two stages which correspond to the transition stage Co/$Co(OH)_2$ followed by $Co(OH)_2/Co(OH)_3$. The formation and growth of $Co(OH)_2$ were studied by the analysis of current transients at different constant potentials. It was claimed that the anodic oxidation of cobalt in basic solutions results in the formation of $Co(OH)_2$ as a first oxidation step, which is then further oxidized to Co_3O_4 and CoOOH at more positive potentials [19]. The potential–current polarization curves were associated with three different anodic peaks corresponding to $Co(OH)_2$, Co_3O_4 and CoOOH, at increasing anodic potentials, respectively [20].

The electrochemical behaviour of cobalt in carbonate/bicarbonate solutions was investigated in order to clarify the reasons why carbonate and bicarbonate ions have considerable effect on the corrosion and passivation of cobalt [21–23]. The anodic oxidation of the metal in these solutions in the potential range of the active/passive transition is strongly dependent of the hydrodynamic conditions and the pH of the solution [22]. The composition of the surface layer depends on the OH^- to HCO_3^- concentration ratio, and the passivation of cobalt at higher anodic potentials is mainly due to the formation of Co_3O_4 [23]. In neutral and basic solutions, the anodic oxidation of cobalt involves active dissolution potential region, a primary passivity potential region related to the formation of CoO layer and a secondary passive potential region in which a duplex layer of CoO/Co_3O_4 structure is formed [19, 24–27].

In the present investigation, the corrosion and passivation behaviour of cobalt in aqueous solutions at different pH is investigated. The corrosion parameters are calculated and the mechanisms of the corrosion and passivation processes in the three solutions in different media are discussed.

2. Experimental details

Massive cylindrical spectroscopically pure cobalt rods (Goodfellow Cambridge Ltd) were mounted in glass tubes of appropriate diameter by epoxy resin leaving a circular front surface area of 0.32 cm^2 to contact the solution and used as working electrodes. The test electrolytes were buffer solutions covering the pH range 1–13 prepared from analytical grade reagents and triple distilled water according to the composition presented in Table 1. Before each experiment, the working electrodes were mechanically polished using successive grades emery papers down to 1200 grit, rubbed with a smooth polishing cloth then washed with triple distilled water and immersed in the test electrolyte. In this way the working electrode front surface acquired a reproducibly bright appearance. The pH of the solution was measured and controlled by a sensitive pH-meter. The electrolytic cell was a three-electrode, all-glass, double-walled cell, with a large area platinum counter and Ag/AgCl/Cl^- (3 M KCl) reference electrodes. Whenever it was required, the reference electrode was separated by an electrolyte bridge with Luggin capillary tip, filled with the test solution.

The open-circuit potential was controlled and recorded separately from the moment of electrode immersion in the test solution until it reached the steady state and up to the specified time (~180 min) by means of a high impedance digital automatic recording multimeter. The potentiodynamic experiments were carried out using a potensiostat/galvanostat interfaced to a computer, with a program which enabled direct compensation of ohmic overpotentials. Electrochemical impedance spectroscopic investigations were performed by using an excitation amplitude was 10 mV peak-to-peak in a frequency domain from 0.1 to 10^5 Hz. The electrode surface was analysed by X-ray photoelectron spectroscopy (XPS) and examined by means of a scanning electron microscope, SEM. Except otherwise stated all experiments were carried out in naturally aerated solutions at constant room temperature of ~25 °C. All potentials were measured against and referred to the Ag/AgCl/Cl^- reference ($E° = 0.197$ V vs NHE). Details of experimental procedures were as described elsewhere [28–30].

3. Experimental results

3.1. *Open-circuit potential behaviour of cobalt in naturally aerated solutions*

The open-circuit potential of cobalt electrodes was recorded in aqueous solutions covering the pH range 1–13. Representative results in acidic (pH 1), neutral (pH 7) and basic (pH 13) solutions are shown collectively in Figure 1. The results reveal that the electrochemical behaviour of cobalt in basic solutions is different from its behaviour in acidic or neutral solutions. In acidic solutions (pH 1–6), the open-circuit potential of the metal does not change with time; its value is dependent of the solution pH and becomes more negative as pH increases. In neutral solutions (pH 7), the open-circuit potential reaches its steady state in less than 15 min. In basic solutions (pH 13), the open-circuit potential shows two arrests. The first occurs at a steady value of about −800 mV which extends over 70 min and jumps to the second arrest which occurs at a more positive steady value (−111 mV) and extends over more than 5 h. The results show clearly that the cobalt electrode undergoes a steady corrosion process in acidic solutions and the electrode potential is a linear function of the solution pH (cf. Figure 2). Such a linear function can be represented as [29]:

$$E_{ss} = \alpha - \beta \text{ pH} \tag{1}$$

where α is the steady state potential at pH 0 and β is the slope of the linear relationship. The value of α was found to be equal to −240 mV. The slope of the linear relation

Table 1. Compositioin of the buffer solutions

pH	Composition
1 (H_3PO_4)	100 ml 0.48 M H_3PO_4
1 (H_2SO_4)	100 ml 0.1 M H_2SO_4
1 (HCl)	100 ml 0.1 M HCl
2	65 ml 0.1 M potassium biphthalate + 8 ml 1 M HCl + 295 ml H_2O
3	65 ml 0.1 M potassium biphthalate + 3.8 ml 1 M HCl + 780 ml H_2O
4	50 ml 0.1 M potassium biphthalate + 1 ml 0.1 M NaOH + 50 ml H_2O
5	50 ml 0.1 M potassium biphthalate + 23.6 ml 0.1 M NaOH + 49 ml H_2O
6	50 ml 0.1 M potassium biphthalate + 48 ml 0.1 M NaOH + 15 ml H_2O
7	50 ml 0.1 M potassium biphthalate + 47.8 ml 0.1 M NaOH
7	50 ml 0.1 M KH_2PO_4 + 25 ml 0.1 M NaOH + 35 ml H_2O
8	50 ml 0.1 M KH_2PO_4 + 47 ml 0.1 M NaOH + 8.5 ml H_2O
9	100 ml 0.2 M KH_2PO_4 + 103.5 ml 0.2 M NaOH
10	100 ml 0.2 M KH_2PO_4 + 105.2 ml 0.2 M NaOH
11	100 ml 0.2 M KH_2PO_4 + 115.2 ml 0.2 M NaOH
12	100 ml 0.2 M KH_2PO_4 + 163.7 ml 0.2 M NaOH
13	100 ml 0.1 M NaOH

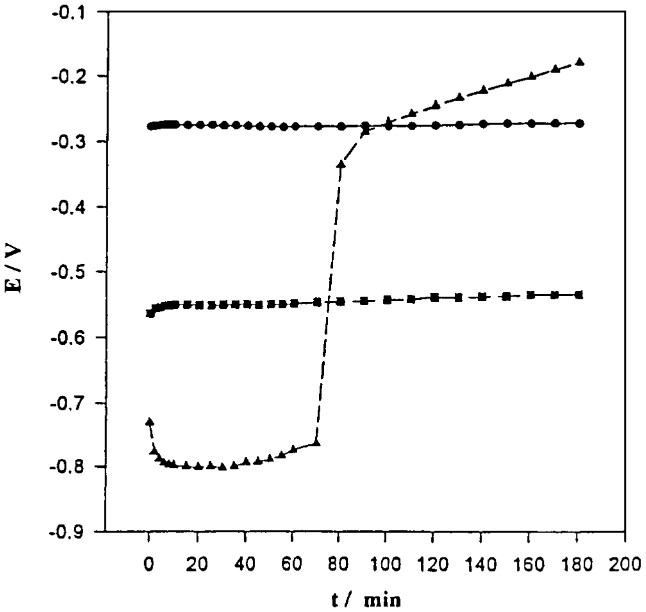

Fig. 1. Variation of the cobalt electrode potential with time in naturally aerated solutions of different pH. Key for pH: (●) 1(HCl), (■) 7(phosphate) and (▲) 13(NaOH).

previously [6, 32]. The steady state potential behaviour of cobalt in these solutions is very similar to that in HCl solution but it acquires more negative values. The values of E_{ss}, recorded after three hours of electrode immersion in 0.1 M H_2SO_4 and 0.48 M H_3PO_4 at pH 1 are included in Table 2. The effect of halide ions and the oxidizing properties of the ambient electrolyte on the electrochemical behaviour of the metal is the subject of extensive investigations [33].

In the pH range 6 < pH < 10, the steady state potential of the cobalt electrode remains approximately the same, which indicates that the metal is covered with a passive layer which inhibits the corrosion process as confirmed by corrosion rate measurements. In more basic solutions, the steady state potential becomes more positive which indicates continuous passivation of the metal surface. The jump in the steady state potential to more positive values after a long time of electrode immersion in basic solution indicates a remarkable change in the structure of the passive film. The recorded values of the steady state potential of the cobalt electrode in aqueous solutions at different pH are presented in Table 2.

of Figure 2 is equal to −33 mV per pH unit. A value of about −30 mV $(\text{decade})^{-1}$ for the slope β suggests that the corrosion process of Co in acidic solutions up to pH 6 is a two electron transfer electrochemical process [31] which can be represented by

$$Co \rightarrow Co^{2+} + 2\,e^- \qquad (2)$$

The use of oxidizing acids like H_2SO_4 or H_3PO_4 instead of HCl for preparation of the acidic solutions at pH 1 has lead to higher corrosion rates as reported

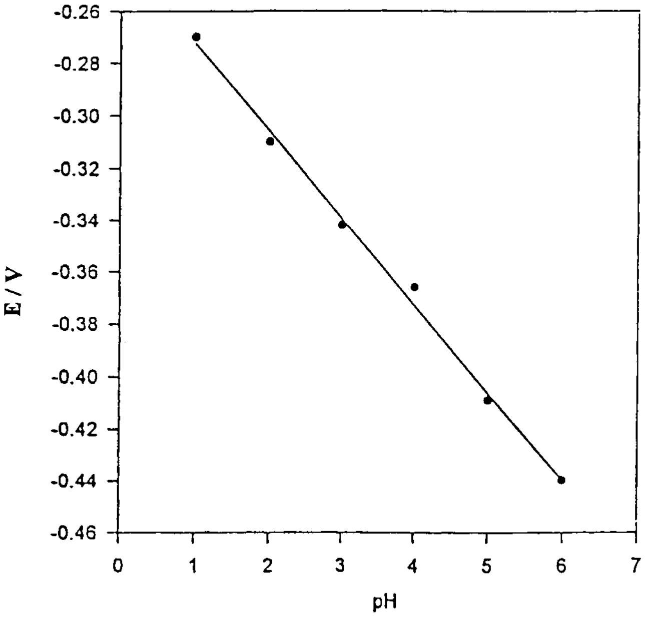

Fig. 2. Steady state potential (E_{ss}) against pH for the cobalt electrode in naturally aerated buffer solutions.

3.2. *Effect of oxygen on the steady state potential*

The steady-state potential of cobalt in naturally aerated, oxygen saturated and oxygen-free acidic, neutral and basic solutions was investigated. Deaeration of the test electrolyte was carried out by bubbling pure nitrogen or hydrogen for at least 20 min prior to the electrode immersion and during the whole time of the experiment. Oxygen saturation was done by bubbling pure oxygen following the same procedure. The results of these measurements are presented in Figure 3. It is clear that the open-circuit potential of cobalt becomes more positive when the solution contains oxygen, especially in neutral and basic media. This positive shift can be

Table 2. Steady state potential of cobalt in solutions of pH 1 to 13 as measured after 3 h of electrode immersion

pH	E_{ss}/mV
1 (HCl)	−270
1 (H_2SO_4)	−377
1 (H_3PO_4)	−409
2	−310
3	−342
4	−366
5	−409
6	−440
7 (phosphate)	−537
7 (biphthalate)	−484
8	−534
9	−552
10	−501
11*	−312
12*	−211
13*	−111

*After 5 h

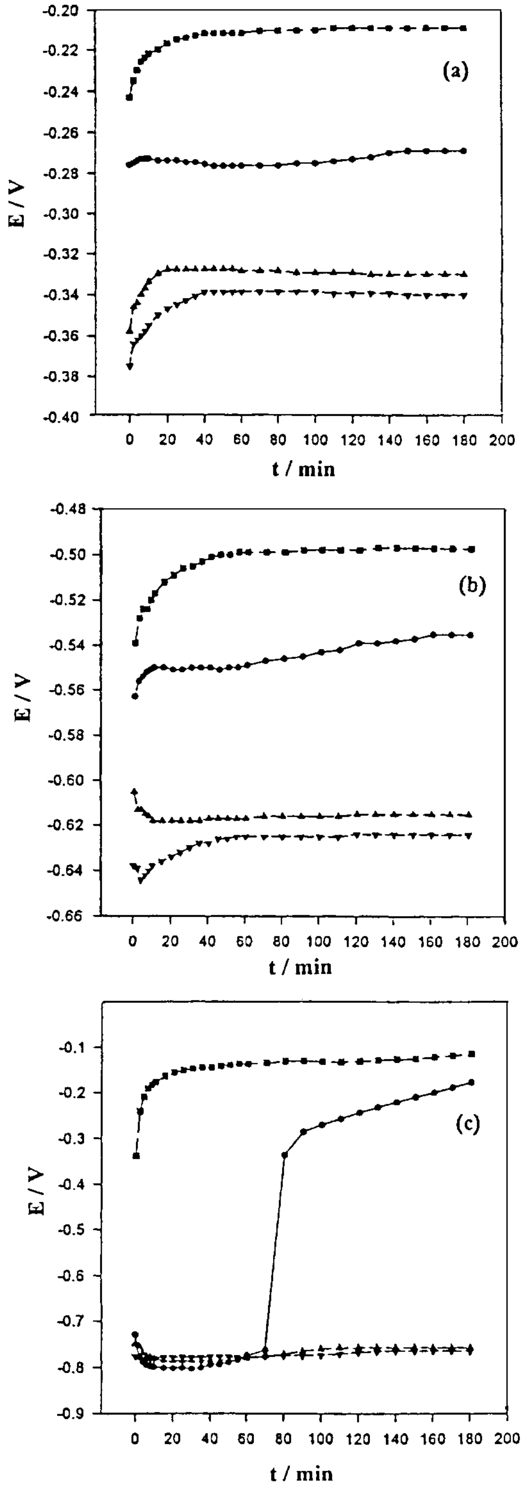

Fig. 3. Effect of the prevailing gas on the electrode potential of cobalt in solutions of different pH. (a) pH 1(HCl), (b) pH 7(phosphate) (c) pH 13(NaOH). Key: (●) naturally aerated, (■) O_2 gas, (▲) N_2 gas and (▼) H_2 gas.

attributed to the change in the cathodic counter part of the corrosion reaction to oxygen reduction.

The presence of oxygen in the solution affects the nature of the barrier layer and its stability [34, 35]. On the one hand, in acidic and neutral solutions the positive shift is in the range of 150 and 100 mV, respectively. In basic solutions, on the other hand, the electrode potential is very sensitive to the presence of oxygen. In oxygen saturated solutions, the potential jumps quickly to the steady state which corresponds to the second step recorded after long times of electrode immersion in naturally aerated basic solutions (about −111 mV). In oxygen free basic solutions, the electrode potential has a more negative value (about −800 mV), which corresponds to the first arrest recorded in the naturally aerated solutions. This means that the presence of oxygen enhances barrier film formation and increases electrode passivity. Especially in basic solutions, the use of either N_2 or H_2 for solution deaeration did not show a significant effect. This implies that the cathodic part of the corrosion reaction is independent of hydrogen. The corrosion reaction is controlled by oxygen reduction and the exchange current density of the H_2/H^+ reaction on Co is insignificant [36].

3.3. *Potentiodynamic and EIS measurements*

Typical potentiodynamic polarization curves of Co in acidic, neutral and basic solutions are presented in Figure 4. In neutral solutions, a passivation behaviour can be observed in which the electrode is anodically polarized to more positive potential whereas the value of the corresponding current remains limited. In both acidic and basic solutions such a limiting condition was not recorded. In solutions of oxidizing acids at pH 1, higher rates of corrosion were recorded. Also, the use of phosphate buffer for neutral solutions at pH 7 leads to higher rates of corrosion [33].

Electrochemical impedance spectroscopy has shown that the behaviour of cobalt in acidic solutions is typical for a corroding transition metal [29]. The impedance spectra of the metal recorded in solutions at pH 1 and different intervals of electrode immersion in the test solution are presented as Bode plots in Figure 5. In neutral solutions, the phase maximum acquires lower values and shifted towards lower frequencies (Figure 6). In basic solutions, the impedance spectrum of the metal depends on the time of immersion in the test solution (Figure 7). It is clear that the spectrum recorded at less than 1 h of electrode immersion in the test solution, which corresponds to the first steady state in the open-circuit potential behaviour (Figure 1), is very similar to that obtained in neutral solutions and the corrosion resistance of the metal at this stage is about the same. As the time of electrode immersion in the test solution increases, the spectrum changes and a flattening in the frequency-phase plot is recorded. The flattening of the frequency-phase plot and the broadness of the phase maximum are characteristic for passivated transition metals as was recorded previously for different valve metals [29, 31, 37]. The corrosion parameters of cobalt in the different solutions were calculated as reported previously [37] and are presented in Table 3.

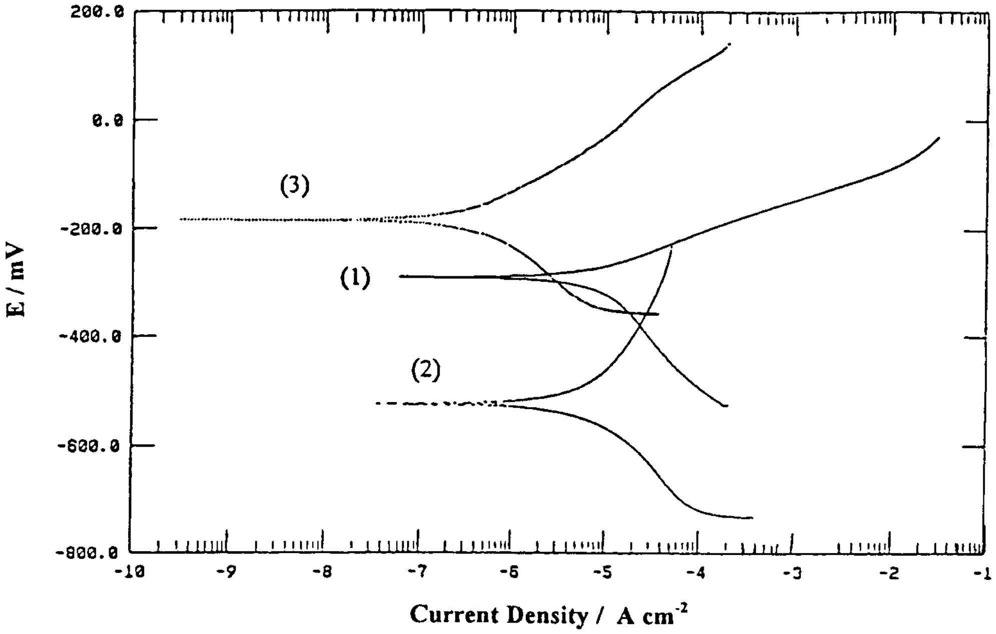

Fig. 4. Potentiodynamic polarization curves of the cobalt electrode in pH 1(HCl) (1), pH 7(biphthalate) (2) and pH 13(NaOH) (3) solutions after 180 min of electrode immersion.

3.4. *Spectroscopic investigation of the cobalt surface in different solutions*

The corrosion and passivation phenomena occurring at the electrode/electrolyte interface in different solutions were investigated by examination of the metal surface using XPS and SEM. Figure 8(a) presents the XP spectrum of a mechanically polished cobalt surface. This shows the cobalt peaks (Co 2s1 at 927.1 eV, Co 2p1 at 796.6 eV, Co 2p3 at 780.4 eV and the cobalt Auger peak Co LM2 at 714.0 eV), clear oxygen peak (O 1s at 532.7 eV) and a small carbon peak (C 1s at 286.6 eV, as a residual of the vapour of the oil pumps). The spectrum of the mechanically polished surface shown in Figure 8(a) is identical with the XP spectrum of pure CoO (Figure 8(b)) which confirms that the cobalt surface is covered by a native oxide film. The presence of such an oxide film was also confirmed by surface sputtering with argon ion bombardment [38]. After surface sputtering, the oxy-

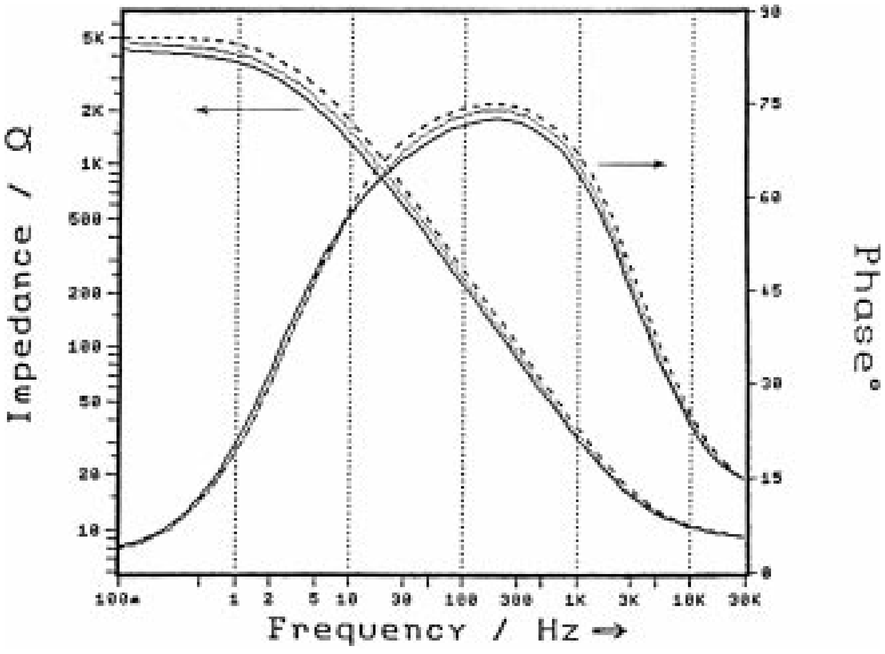

Fig. 5. Bode plots of cobalt after different time intervals of electrode immersion in solutions at pH 1(HCl). Interval: (—) 15 min, (···) 30 min and (----) 180 min.

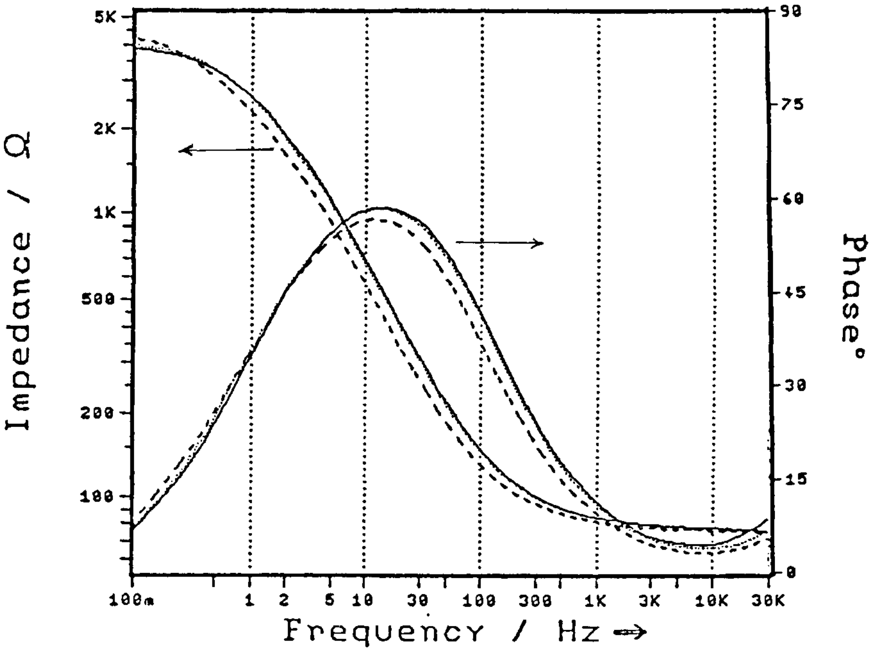

Fig. 6. Bode plots of cobalt after different time intervals of electrode immersion in solutions at pH 7(phosphate). Interval: (—) 15 min, (···) 30 min and (----) 180 min.

gen and cobalt peaks were shifted toward lower binding energy values, where those of Co match the standard peaks of metallic cobalt (Co 2p1 at 795.0 eV and Co 2p3 at 777.0 eV) [39]. Beside the shift towards lower binding energy values, the oxygen peak diminishes, whereas the cobalt peaks increase on surface sputtering. This means that the oxide film is removed gradually as the sputtering time increases (5 min surface sputtering by argon ion bombardment removes 1 nm thickness [28, 38]). The depth profiling results of the cobalt and oxygen peaks are presented in Figure 9 (a) and (b), respectively.

The XP spectrum of cobalt in acidic solution at pH 1 is presented in Figure 10(a). Beside the carbon, cobalt and oxygen peaks two small chlorine XP peaks were recorded (Cl 2p3 at 199.5 eV and Cl 2s at 268.6 eV). The chlorine peaks are due to the chloride ions which are the main constituents of the electrolyte. These ions seem to be adsorbed on the electrode

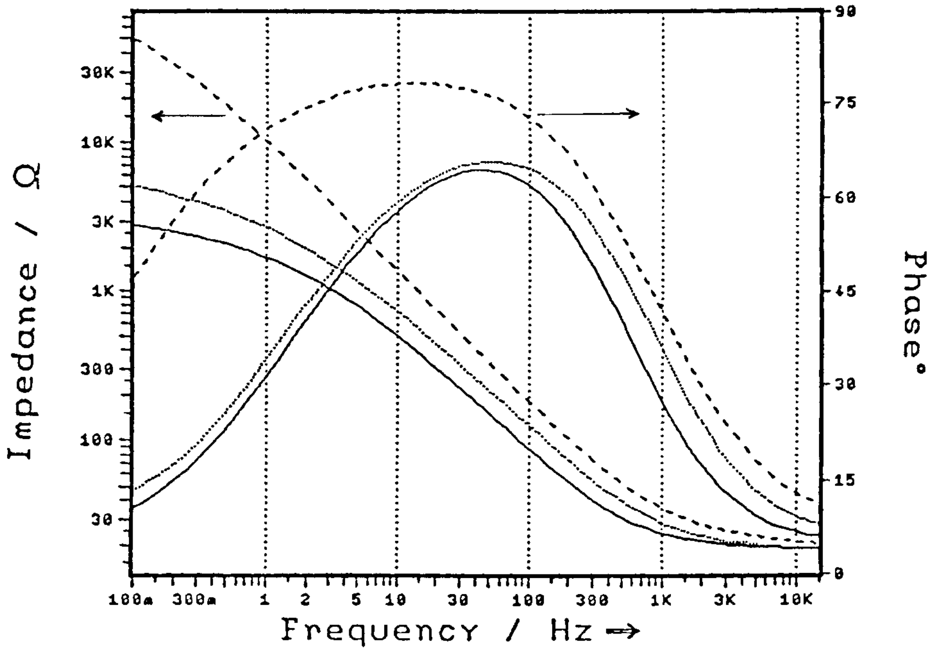

Fig. 7. Bode plots of cobalt after different time intervals of electrode immersion in solutions at pH 13(NaOH). Interval: (—) 15 min, (···) 30 min and (----) 180 min.

Table 3. Corrosion parameters of cobalt in naturally aerated aqueous solutions of different pH as calculated from the polarization data recorded after 3 h of electrode immersion in each solution

pH	R_p/kΩ cm^2	E_{corr}/mV	i_{corr}/μA cm^{-2}
1 (H_3PO_4)	0.11	−398	176
1 (H_2SO_4)	0.72	−359	21.5
1 (HCl)	1.79	−292	8.60
7 (phosphate)	1.47	−572	15.9
7 (biphthalate)	3.88	−524	4.25
13*	16.54	−185	0.34

*After 5 h

surface [9, 11], since they are removed together with the oxygen peaks after surface sputtering by argon ion bombardment for 2 min only. This confirms that the native passive film formed on cobalt is unstable in acidic solutions. It undergoes continuous dissolution and hence higher rates of corrosion are recorded. The XP spectra of the cobalt surface after immersion in neutral (pH 7) and basic (pH 13) solutions show intensive oxygen peaks which increase on etching the surface by argon ion bombardment. The spectra in both cases are presented in Figure 10 (b) and (c), respectively. An example of the depth profiling of the oxygen peak in these solutions is presented in Fig-

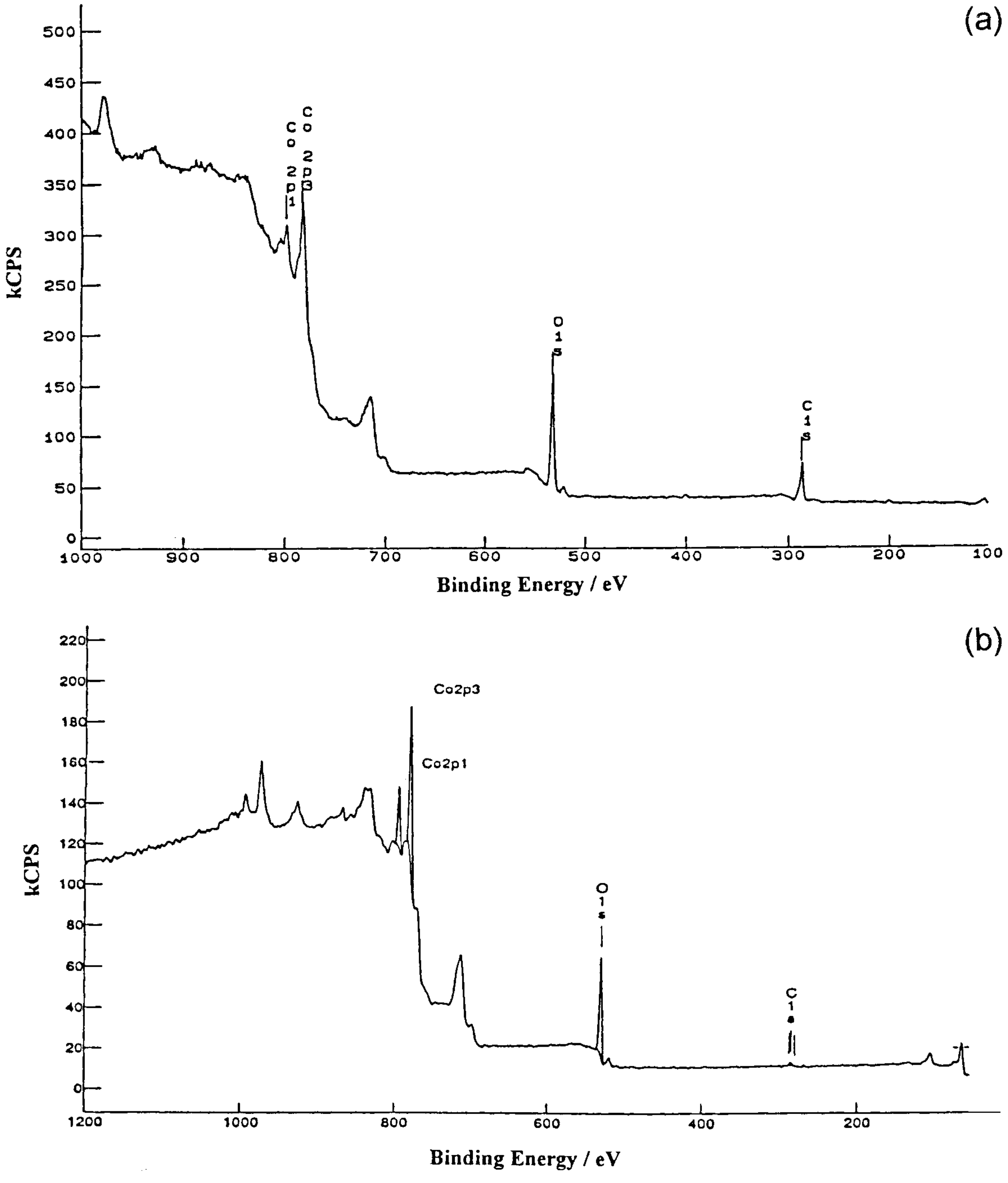

Fig. 8. (a) XP survey spectra of mechanically polished cobalt surface. (b) XP survey spectra of pure CoO.

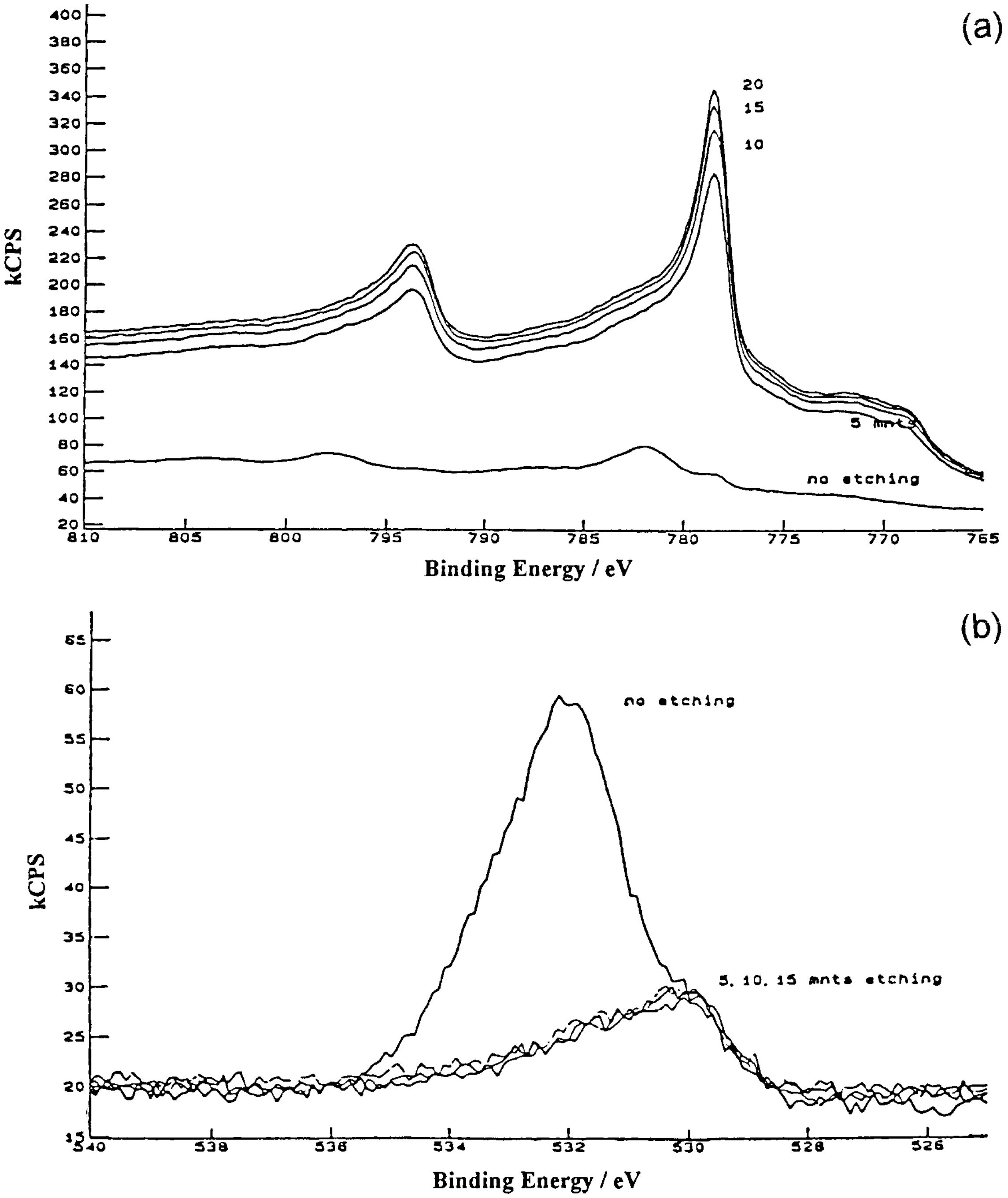

Fig. 9. Depth profiling experiments of the cobalt peaks (a) and the oxygen peak (b) after different intervals of sputtering by argon ion bombardment.

ure 11. The results of these XPS experiments indicate that the cobalt surface is always covered with a native oxide film which is unstable in acidic solution. In neutral or basic solutions thicker barrier film is formed on the metal surface which most probably consist of two layers, as can be seen from the splitting of the oxygen XP peak recorded after sputtering of the metal surface by argon ion bombardment [39].

The scanning electron microscopy indicates that the immersion of cobalt in neutral or basic solutions leads to the formation of a smooth surface which is responsible for the low rates of corrosion in these media. Electrodes immersed in chloride containing acidic solution acquire pitted surfaces which was not observed after immersion in chloride free solutions of the same pH [40].

4. Discussion

Like many other transition metals, cobalt is covered by a native barrier film which consists mainly of CoO or hydrated oxide $CoO.H_2O$ [32]. In acidic solutions, the passive film is unstable and hence higher rates of

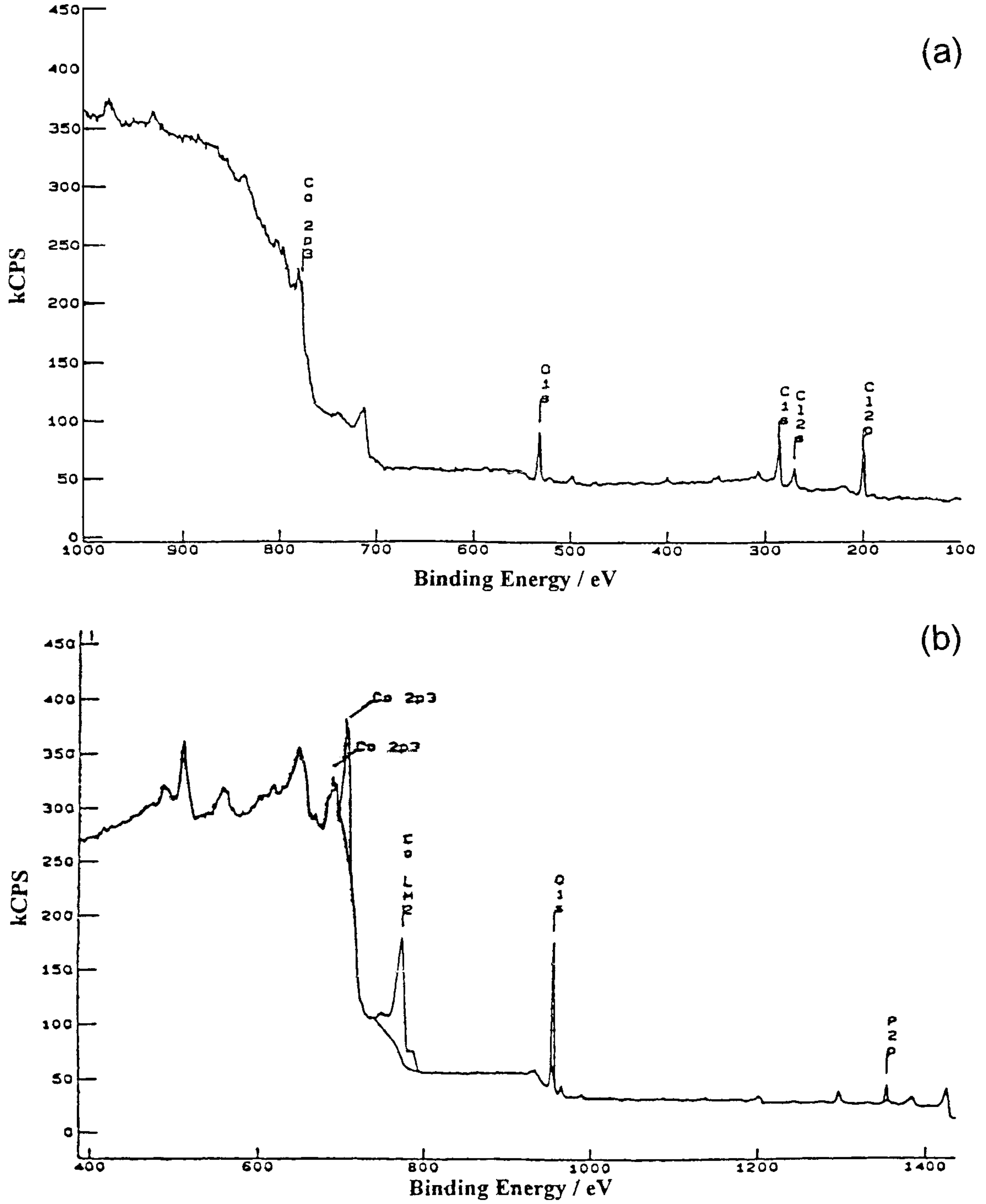

Fig. 10 (a) XP survey spectra of cobalt surface after 180 min of electrode immersion in acidic solution at pH 1(HCl). (b) XP survey spectra of cobalt surface after 180 min of electrode immersion in neutral solution at pH 7(phosphate). (c) XP survey spectra of cobalt surface after 180 min of electrode immersion in basic solution at pH 13(NaOH).

corrosion were recorded. The slope of the E_{ss} against pH relation in these solutions (pH 1 to 6) suggests that the corrosion process is a two electron transfer process preceded by pure chemical dissolution of the native barrier film according to the following equations:

$$\mathrm{CoO} + 2\,\mathrm{H}^+ \rightarrow \mathrm{Co}^{2+} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{Co(OH)_2} + 2\,\mathrm{H}^+ \rightarrow \mathrm{Co}^{2+} + 2\,\mathrm{H_2O} \tag{4}$$

The passivation of the cobalt surface and its reactivation in acidic solutions was observed previously during potentiodynamic current–potential investigations of cobalt rotating disc electrodes [5]. The activation and passivation of the electrode surface are due to simultaneous processes controlled by the electrode potential

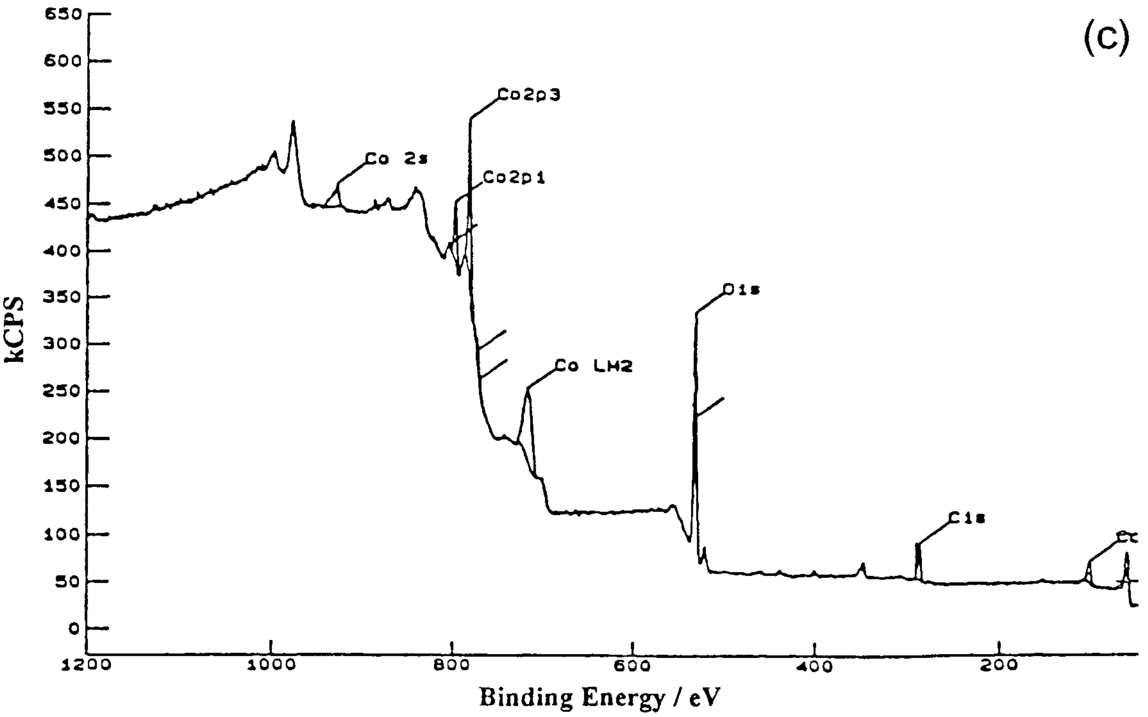

Fig. 10.

and its polarization condition [41]. The passivation of the electrode involves water molecules which are adsorbed on the electrode surface according to the following equations:

$$Co(H_2O)_{ads} \rightarrow CoOH + H^+ + e^- \quad (5)$$

$$CoOH + H_2O \rightarrow Co(OH)_2 + H^+ + e^- \quad (6)$$

$$Co(OH)_2 \rightarrow CoO + H_2O \quad (7)$$

Such passivation reactions are enhanced by both the positive potential and the solution pH. In neutral and

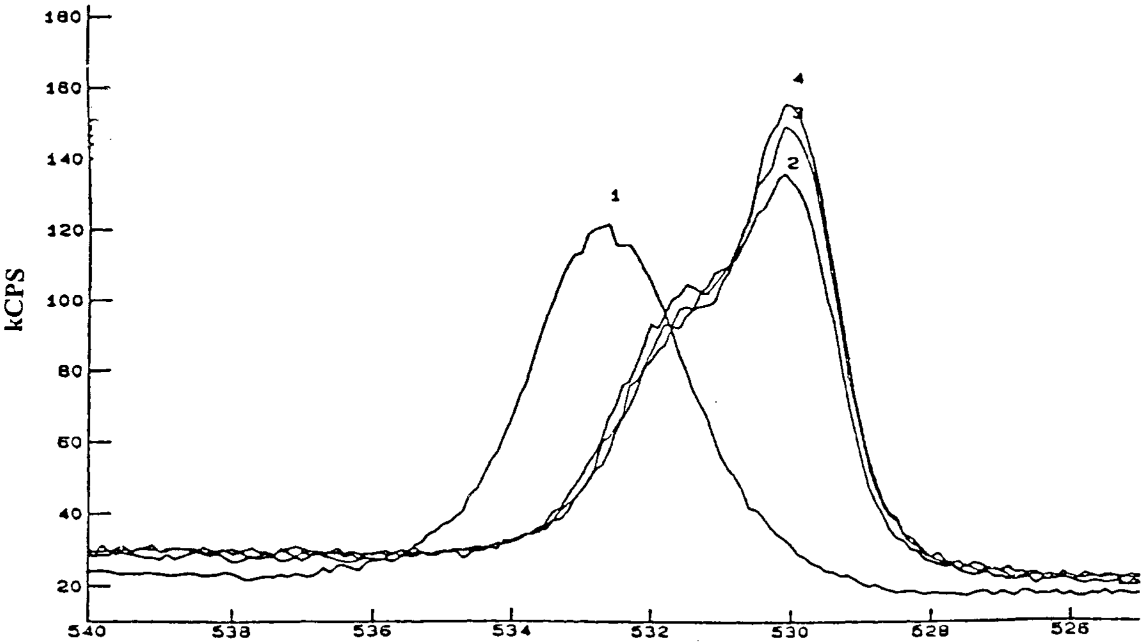

Fig. 11. Depth profiling results of the oxygen peak of Figure 10(c): (1) without etching; (2) after 5 min etching by argon ion bombardment; (3) after 10 min etching by argon ion bombardment; and (4) after 15 min etching by argon ion bombardment.

basic solutions stabilization of the passive film occurs, whereas in acidic solution reactivation of the passive film takes place.

The presence and thickening of the passive film, occurring in neutral or basic solutions, which are confirmed by XPS, can be attributed to the formation of a duplex film on the electrode surface according to different mechanisms involving chemical and electrochemical steps:

$$Co + H_2O \rightarrow Co(H_2O)_{ads} \qquad (8)$$

$$Co(H_2O)_{ads} \rightarrow Co(OH)^+ + H^+ + 2\,e^- \qquad (9)$$

The sequence of the reactions depends on the pH of the solution:
In acidic solutions

$$CoOH^+ + H^+ \rightarrow Co^{2+} + H_2O \qquad (10)$$

and continuous dissolution of cobalt or its passive film takes place, which explains the high rates of corrosion recorded.
In neutral solutions

$$Co(OH)^+ + H_2O \rightarrow Co(OH)_2 + H^+ \qquad (11)$$

$$Co(OH)_2 \rightarrow CoO + H_2O \qquad (12)$$

In this case the passive film is stabilized and a decrease in the rate of corrosion of the metal is recorded.
In basic solutions

$$CoOH^+ + OH^- \rightarrow Co(OH)_2 \qquad (13)$$

$$Co(OH)_2 + OH^- \rightarrow CoOOH + H_2O + 2\,e^- \qquad (14)$$

$$3\,CoO + 2\,OH^- \rightarrow Co_3O_4 + H_2O + 2\,e^- \qquad (15)$$

The formation of either CoOOH or Co_3O_4 increases the stability of the passive film and can be present as a second layer on the top of the native CoO passive film. The formation of $Co(OH)_2$ on the cobalt surface in basic solutions was confirmed by Bewick et al. by *in situ* IR spectroscopic investigations of the anodic oxide film on cobalt [42]. These authors have identified peaks corresponding to the oxidation of $Co(OH)_2$ into Co(III). This explains the change in the characteristics of the passive film recorded by the electrochemical experiments and the XPS measurements in basic solutions.

5. Conclusions

Cobalt is always covered by a native passive film which consists mainly of CoO or $CoO.H_2O$. The passive film is unstable in acidic solutions. In neutral solutions stabilization of CoO takes place and in basic solution the $Co(OH)_2$ passive film undergoes further oxidation to Co(III) compound (CoOOH and/or Co_3O_4), depending on the electrode potential and the pH of the solution.

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