INFLUENCE OF THE STRUCTURE OF ELECTROLYTIC COBALT AND INSERTION OF CHLORIDE IONS INTO A DEPOSIT OF IT UPON THE ELECTROCHEMICAL PROPERTIES AND CORROSION IN SULFURIC ACID SOLUTION

(UDC 541.138 : 541.135.8-183:546)

Z. A. Iofa and Wei Pao-ming

M. V. Lomonosov Moscow State University
Translated from Élektrokhimiya, Vol. 2, No. 7,
pp. 755-759, July, 1966
Original article submitted July 7, 1965
Revised October 22, 1965

It was demonstrated that α-Co with hexagonal structure possesses a lower overvoltage in the discharging of hydrogen ions and the ionization of cobalt and lower corrosion resistance in acid solutions in comparison with β-Co with cubic structure. It was also shown that α-Co produced by electrolysis from a solution of the chloride possesses a higher overvoltage of the indicated reaction and greater corrosion resistance than α-Co precipitated from cobalt sulfate.

In a number of studies the relationship of the electrochemical properties of metals to their crystallographic structure is discussed. In [1] it was shown that the rate of the electrochemical reactions, for example, of discharging of hydrogen ions on individual facets of a single crystal of Cu, Co, and others possesses varied values. In [2-3] it was shown that the rate of dissolution of the facet (321) of iron in acid solution is twice as high as that of the facet (100). This difference is associated with the density of packing of the metal ions on the surface of individual crystal facets. It has been established in a number of studies that the electrochemical properties and rate of corrosion of a polycrystalline metal produced by electrolysis, for example, chromium [4], manganese [5], or cobalt [6], depends substantially upon their structure and modification. Of the two existing modifications of cobalt, the hexagonal α-modification, stable at low temperatures, differs from the cubic β-Co [7] in a lower value of the hydrogen overvoltage and a greater rate of self-dissolution (in 1 N H_2SO_4 for α-Co, $i_c = 3.3 \cdot 10^{-3}$, while for β-Co, $i_c = 7.3 \cdot 10^{-5}$ A/cm^2 [6]).
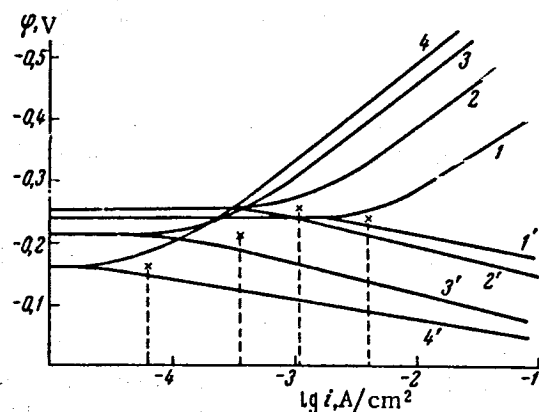
The structure and modification of Co, produced by electrolysis, depend upon the pH and temperature [9]. At pH < 2, β-Co of the surface modification, fine-crystalline and dense, is obtained. At pH > 4, α-Co with hexagonal structure is obtained in the form of larger crystals with well-expressed facets [10, 11]. The addition of KI to the electrolytic bath leads to a change in the orientation of the cobalt crystals deposited and to more dispersed deposits, possessing a substantially higher hydrogen overvoltage [8-10].

In this work, α-Co of the hexagonal modification was produced according to the method described in [9-10], however, without the addition of KCl, from a bath with composition: 500 g/liter $CoSO_4 \cdot 7H_2O$ + 45 g/liter H_3BO_3, pH ~ 5 (NH_4OH is added), $i_k = 0.015$ A/cm^2, t = 60°C, with mixing for five hours on a copper plate. The cubic modification of β-Co was produced from the same solution, but twice as dilute (H_2SO_4 is added to pH = 1.3-1.9), t = 20°C, $i_k = 0.1$ A/cm^2. X-ray diffraction study, conducted by L. M. Kovba (at the x-ray laboratory of the Chemical Faculty of Moscow State University) indicated that the lines of β-Co are not contained in the x-ray diffraction pattern of α-Co. The x-ray diffraction pattern of β-Co indicates a small content of α-Co.

Figure 1 presents the curves of cathodic and anodic polarization of α- and β-Co that we recorded in a solution of 1 N H_2SO_4. The electrodes were polished before the experiment with fine glass powder, and in certain cases were calcined in an atmosphere of hydrogen at 600°C.

TABLE 1

	φ_k	φ_a	b_k	b_a	φ_c	$- \lg i_o$
α-Co	−280	−215	120	45	−242	2,32
β-Co	−462	−105	150	30	−160	3,96
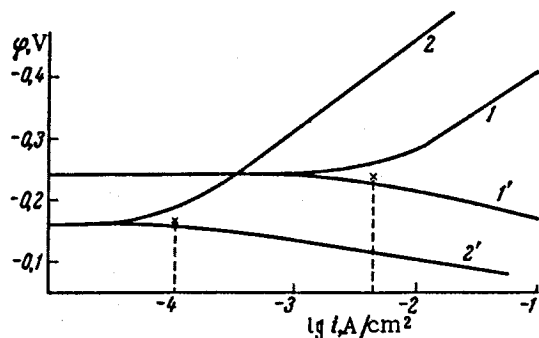
Fig 1. Curves of the cathodic and anodic polarization of cobalt in 1 N H_2SO_4: 1,1') α-Co, 2,2') β-Co.

Fig. 2. Polarization curves: 1,1') for α-Co (obtained from a sulfate bath), taken in 1 N H_2SO_4; 2,2') for the same α-Co in 1 N H_2SO_4 + 0.1 N KCl, 3,3') taken in 1 N H_2SO_4 for α-Co produced from a sulfate bath with an addition of 50 g/liter KCl; 4,4') for α-Co ("Gipronikel'"), produced by electrolysis from $CoCl_2$ solution.

Table 1 presents the values of the cathodic (φ_k) and anodic (φ_a) potentials at $i = 10^{-2}$ A/cm², the values of constants b_k and b_a, as well as the stationary potential (φ_c) in mV and the logarithms of the rate of self-dissolution for both modifications of cobalt in 1 N H_2SO_4 solution.

From the data of Fig. 1 and Table 1, it follows that the hydrogen overvoltage on α-Co is 180 mV lower and the rate of self-dissolution is 44 times higher than for β-Co. This result agrees with the data of [6].

It is interesting that the same modification, for example, α-Co, possesses different properties depending upon the conditions of its production. We investigated the properties of cobalt [12] produced from cobaltous chloride, provided us by the Gipronikel' Institute. X-ray diffraction study revealed its hexagonal structure and α-modification. The polarization curves for this cobalt are cited in Fig. 2 (curve 4). Comparison with the data for α-Co, which we obtained from a sulfate bath, indicate their substantial difference (see curves 1 and 4, Fig. 2, and the data of Tables 1 and 2). This difference is evidently due to the fact that in the deposition of cobalt from the chloride, chloride ions were inserted into the deposit, as occurred in [9-10] with iodide ions in the case of the deposition of Co from a sulfate bath to which the salt KI was added. To verify this hypothesis, we deposited Co from a sulfate bath to which 50 g/liter KCl was added. In this case we actually obtained α-Co possessing properties approaching the properties of the metal produced from a chloride bath, which is evident from curves 3 and 4 of Fig. 2 and the data of Table 2.

In recording the polarization curves for "sulfate" α-Co in 1 N H_2SO_4 solution, to which 0.1 N KCl was added, an increased overvoltage of the electrochemical reaction is also observed (see curve 2 of Fig. 2); however, it is lower than for cobaltous chloride when the curves are recorded in a pure solution of acid. Thus, the chloride ions, inserted into the electrolytic deposit, exert a greater influence upon the electrochemical properties of cobalt than when they are absorbed from solution. They are firmly retained in it: calcination at 650°C in an atmosphere of hydrogen for 10 h did not lead to their complete removal from the surface layer of metal, since the hydrogen overvoltage after calcination was lowered by only 20-30 mV, and the overvoltage of the anodic process by 15-20 mV.

Figure 3 presents polarization curves illustrating the effect of an addition of KI to a solution of 1 N H_2SO_4 in the case of "sulfate" and "chloride" α-Co. From the curves it is evident that the adsorption of I^- ions leads to an additional increase in the overvoltage of the cathodic and anodic reactions, which is substantially greater in the case of "sulfate" cobalt. However, in the case of "chloride" cobalt it still remains higher ($\varphi_k = -0.517$ V at $i = 10^{-2}$ A/cm²) than in the case of "sulfate" cobalt ($\varphi_k = -0.450$ V).

TABLE 2

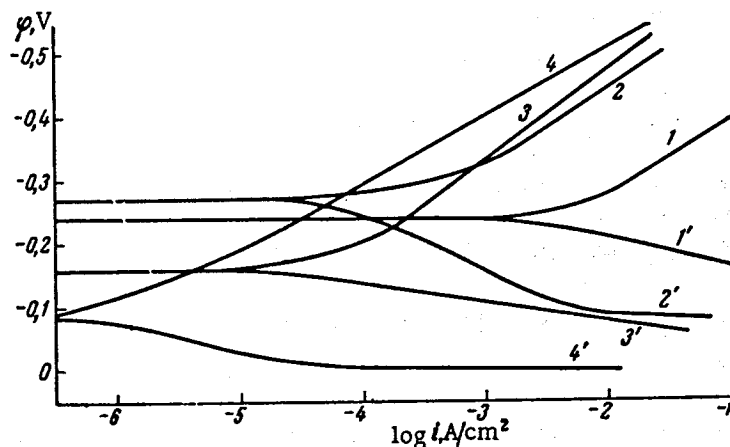| Nature of bath	Solution for polarization	$i = 10^{-2}\,A/cm^2$		$-\lg i_c$
		φ_k	φ_a	
Sulfate	1 N H$_2$SO$_4$	−280	−215	2,32
Chloride	1 N H$_2$SO$_4$	−480	−80	4,20
Sulfate + 50 g/liter KCl	1 N H$_2$SO$_4$	−450	−120	3,68
Sulfate	1 N H$_2$SO$_4$ +0,1 N KCl	−385	—	(2,96)

Fig. 3. Polarization curves in 1 N H$_2$SO$_4$: 1,1') for α-Co, produced from a sulfate bath; 2,2') the same, but with an addition of 0.001 N KI; 3,3') for α-Co, produced from a chloride bath; 4,4') the same, but with an addition of 0.001 N KI.

The effects from the addition of tetrabutylammonium (TBA) cations are also distinguished. From the polarization curves of Fig. 4, it is evident that the effect of an increase in the hydrogen overvoltage in the case of sulfate cobalt is greater ($\Delta\varphi_k$ = 105 mV) than for chloride cobalt ($\Delta\varphi_k$ = 15 mV). However, the cathode potential in the second case remains higher (490 mV) than in the first case (385 mV at i = 0.01 A/cm^2), and correspondingly, the rate of self-dissolution is lower (log i_c = − 4.25 instead of log i_c = − 2.98).

Neutral molecules of hexyl alcohol are very weakly associated and give a small effect both in the case of sulfate cobalt and in the case of chloride cobalt ($\Delta\varphi_k$ is equal to 30 and 20 mV, respectively).

It might have been assumed that the lower overvoltage of the cathodic and anodic reactions and the lower corrosion resistance of "sulfate" cobalt in comparison with "chloride" cobalt are associated with "insertion" of SO$_4^{-2}$ ions or their reduction products, for example, HS$^-$ ions, which activate these reactions, as is probably, the case for iron electrolyte in its production from sulfate baths. However, it has been shown [12] that the stimulating effect of adsorbed HS$^-$ in the case of cobalt is substantially weaker than in the case of iron. In addition, the fact that KI added to the solution from which cobalt is deposited leads to even higher values of the overvoltage and in the case of the addition of KCl, as well as the fact that the calcination of "chloride" cobalt in an atmosphere of hydrogen leads to a decrease in the overvoltage, is evidence that the high values of the overvoltage in "chloride" cobalt during the occurrence of the indicated electrochemical reactions upon it are due to adsorption and insertion of Cl$^-$ ions into its deposit. These ions passivate the cobalt with respect to these reactions, just as in the adsorption of halide anions from a solution of acid upon its surface [12].

Thus, it may be considered proven that the great corrosion resistance of electrolytic "Gipronikel" cobalt, which represents the hexagonal-modification, is associated with the insertion of Cl$^-$ ions during its electrolytic refinement in chloride baths.
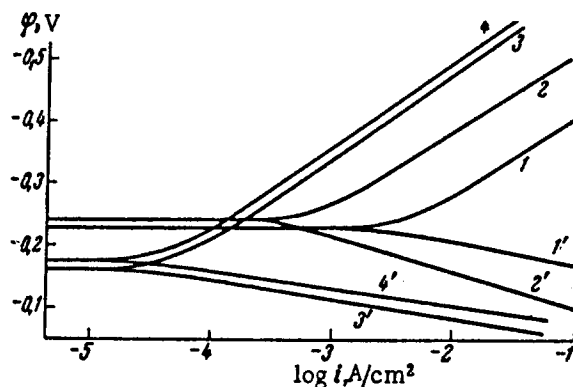
Fig. 4. Polarization curves for α-Co in 1 N H_2SO_4:
1,1') for cobalt produced from a sulfate bath; 2,2') the
same, but with an addition of 0.001 N TBA; 3,3') for
α-Co produced from a chloride bath; 4,4') the same,
but with an addition of 0.001 N TBA.

The question of the mechanism of the inhibiting effect of halide ions on the electrochemical reactions (discharging of hydrogen ions and ionization of the metal), as well as their influence on the adsorption of cations of organic bases in the case of iron and other metals has been repeatedly considered [13-15]. The stronger the bond of the chemisorbed halide ions to the metal atoms, which depends upon the nature of the metal and the nature of the anion, the more strongly they decelerate the indicated reactions. Cobalt evidently is first in this respect [12].

In the case of the cathodic deposition of cobalt from baths containing halide anions (Cl⁻, Br⁻, I⁻), the latter are adsorbed on the most active freshly formed portions of the crystals, and in contrast to their surface adsorption, penetrate the entire thickness of the metal. Therefore, their action is more pronounced, especially in the case of anodic reaction of ionization of the metal, in comparison with the adsorption of the same anions on its surface.

LITERATURE CITED

1. G. S. Vozdvizhenskii, Dokl. AN SSSR, 59, 9 (1948); M. Stroumanis, Nature, 124, 3115 (1929); H. Londheiser and A. Gwathmey, Trans. Electrochem. Soc., 91, 95 (1947); G. S. Vozdvizhenskii, V. A. Dmitriev, and E. V. Rzhevskaya, Zh. Fiz. Khimii, 29, 280 (1955); R. Piontelli and B. Peraldo, Atti Acad. naz. Lincei Rend., Sci., 32, 827 (1962); Ref. Zh. Khim., 22.6.504 (1963).
2. W. Buck and H. Landheiser, Electrochem. Soc., 104, 474 (1957).
3. T. Hurlen, Acta chim. scand., 14, 1533 (1960).
4. St. Christov and N. Pangarov, Z. Elektrochem., 61, 113 (1957).
5. O. Popova and K. Gorbunova, Zh. Fiz. Khimii, 32, 2020 (1958).
6. N. Pangarov, Zv. Mutaftschriev, and St. Raschkov, Compt. Rend. l' Acad. Bulgar Sci., 13, 705 (1960).
7. M. P. Slavinskii, Physicochemical Properties of the Elements [in Russian], Metallurgizdat, Moscow (1952).
8. St. Rashkov and V. Mircheva, Bolg. AN Izv. Inst. Fiz. Khim., 2, 116 (1962).
9. N. Pangarov and St. Rashkov, Dokl. Bolg. AN, 13, 555 (1960).
10. N. A. Balashova and St. Rashkov, Dokl. AN SSSR, 152, 896 (1963).
11. N. Pangarov and St. Rashkov, Izv. Inst. Fiz. Khim., Bolg. AN, 1, 69 (1960).
12. Z. A. Iofa and Wei Pao-ming, Zh. Fiz. Khimii, 36, 2558 (1962); 37, 2300 (1963).
13. Ya. M. Kolotyrkin and N. Ya. Buné, Zh. Fiz. Khimii, 29, 455 (1955).
14. Z. A. Iofa and V. A. Makarova, Élektrokhimiya, 1, 230 (1965).
15. É. I. Mikhailova and Z. A. Iofa, Élektrokhimiya, 1, 107 (1965).