THE ELECTROCHEMICAL PHASE ANALYSIS OF HIGH-CARBON STEELS

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The process of anodic dissolution of high-carbon steels has been investigated, and a relation has been established between the phase composition of the deposit and the electrolyte composition, the pH, and the current density. Conditions have been selected for the isolation of austenite from hardened steel grade 120G2.

Phases of hardened steel, isolated electrolytically in the form of powders, are free from stresses of the first and second order. The investigation of these powders makes it possible to obtain new data on the role of stress in processes of phase transition. The problem of the electrochemical separation of austenite and martensite is complicated by the metastability of both these phases and the similarity in the values of their dissolution potentials.

Arbuzov [1] and Zelenova [2] showed that, with the anodic dissolution of samples of hardened high-carbon steels in aqueous solutions of potassium chloride and citric acid, or of hydrochloric acid, at low current densities, the residual austenite dissolved and the deposit contained crystals of martensite.

Popova [3] and Zelenova [2] considered that the presence of a carbide phase in the steel was a necessary condition for the isolation of austenite. Klyachko and Mal'tseva [4] investigated the conditions for the anodic dissolution of austenitic-martensitic steels and proposed a method for the isolation of austenite from subeutectic steels after intermediate transformation. These authors [4] found that they could not isolate austenite from hardened high-carbon steels, having an austenitic-martensitic structure, with any of the electrolytes they used.

In the present work we investigated the dissolution of these steels and selected conditions for the isolation of austenite.

The various structural components of alloys give different types of anodic polarization curves. Changes in the electrolyte composition, the pH of the medium, and the current density can be used to select conditions for the selective dissolution of one phase or another, while the other phase remains on the sample as a powder.

We investigated steel grade 120G2, containing 1.25% C, 2.65% Mn, and 0.2% Si. The samples were 10 mm in diameter and 70 mm long, and were quenched from 1150°C in water. After thermal treatment the steel had a two-phase austenite-martensite structure.

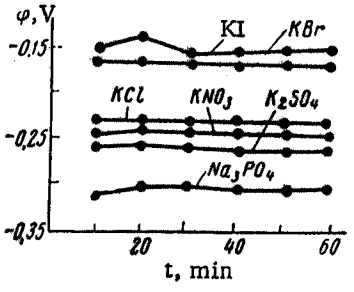

Fig. 1. Potential-time curves, recorded with electrolytes 1 to 6, at 0.02 A/cm², pH 3, and t = 20°C.

Polarization curves and potential-time curves were recorded during the process of electrolysis. The potentials were measured with an R300 potentiometer, by a compensation method, and were recalculated referred to a normal hydrogen electrode. The reference electrode was a saturated calomel half-element. A connecting bridge, filled with electrolyte, made it possible to measure the anode potential directly. The phase composition of the deposit was determined by x-ray diffraction (FeK_α radiation, camera diameter 57.3 mm).

The Effect of Electrolyte Composition. In selecting electrolytes we started from the basis that the nature and charge of the anion [5] had a definite influence on the process of anodic dissolution. As electrolytes we selected N aqueous solutions of the salts KCl, KBr, KI, KNO_3, K_2SO_4, Na_3PO_4, with 0.5% of citric acid added as a complexing agent; these were

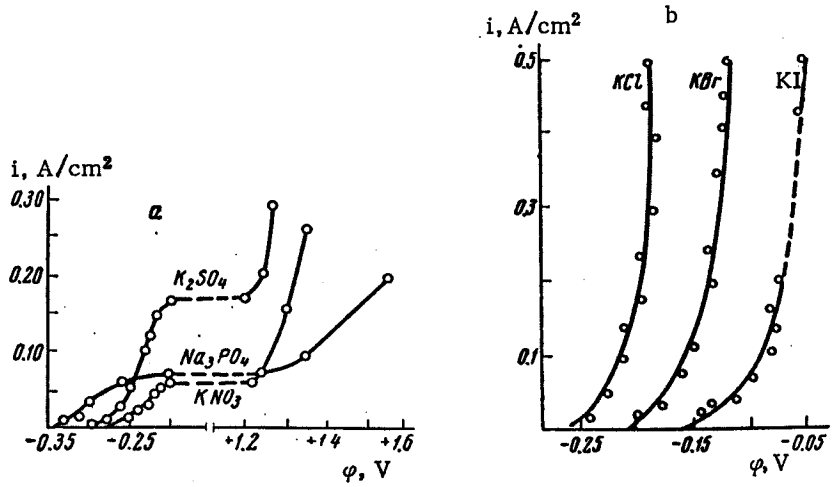

Fig. 2. Polarization curves, recorded at pH = 3 and t = 20°C.

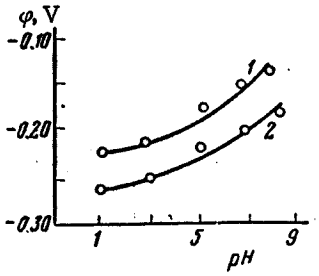

Fig. 3. Relation between dissolution potential and the pH of the medium, with N KCl as electrolyte and t = 20°C: 1) 0.2 A/cm²; 2) 0.02 A/cm².

electrolytes 1 to 6 respectively. Dissolution was carried out at a current density of 0.02 A/cm², pH 2.5 to 3, and t = 20°C. The greatest polarization of the sample was achieved with univalent anions, the least with trivalent anions (Fig. 1). Our results agreed well with previous data [4]. The deposit, isolated with potassium chloride as electrolyte, contained crystals of martensite. With the other electrolytes, used under the same conditions, both phases dissolved and the residue contained only amorphous carbon.

The Effect of Current Density. It has been established that, in order to separate phases which are similar in electrochemical properties, a considerable degree of polarization of the metal is required [4 to 6]. This can be achieved by increasing the anodic current density. With electrolytes 4 to 6, at relatively low current densities, there was an abrupt shift in potential in the positive direction, and full passivation of the anode took place (Fig. 2a). With potassium iodide as electrolyte, at a current density of 0.2 to 0.3 A/cm², a periodic variation in potential was observed, i.e., the metal was passified locally. With electrolytes containing chloride and bromide ion, when the current density was raised to 0.5 A/cm², the dissolution potential shifted in the positive direction. The sample dissolved, but both phases went into solution in spite of the considerable polarization of the anode (Fig. 2b). The deposit, isolated with electrolyte 2, at a current density of 0.2 to 0.4 A/cm², contained traces of austenite.

Thus, the degree of polarization which could be achieved by changing the electrolyte composition and the current density was insufficient for the isolation of austenite.

The Effect of the pH of the Medium. The dissolution potential of pure iron, at constant current density, is shifted in a positive direction by increasing the pH of the electrolyte. This can be attributed to activated adsorption

Recommended Conditions for Electrolysis

Electrolyte composition*	pH of medium	Current density, A/cm²	Anode potential, V	Phase composition of deposit
N KCl	3	0,02	—0,23	Martensite
The same	8	0,2	—0,12	Austenite
N KCl + 0.04 N KNO_2	2	0,2	—0,11	»
N KBr	8	0,3	—0,03	»

*All the electrolytes contained 0.5% of citric acid.

of OH^- ions (or oxygen) on the metal surface [7, 8]. In our experiments the pH was altered in the range 2 to 9, in the anode space only, by addition of drops of aqueous ammonia. With electrolytes 4 to 6, at pH 7 to 8 and a current density of 0.02 A/cm^2, the potential for oxygen evolution was established at the anode and the metal became passive. In the presence of iodide ion, at pH 7 to 8 and a current density of 0.02 A/cm^2, the sample dissolved extremely slowly (under a metallic film). Dissolution of metal increased when the current density was increased to 0.3 A/cm^2.

The deposit, isolated at a current density of 0.3 A/cm^2 and an anode potential of 0.05 V, contained austenite. Under these conditions dissolution took place under a metallic film, the sample corroded, and crumbling of the metal was possible. Dissolution also took place under a metallic film with potassium bromide as electrolyte, a low current density, and pH 7 to 8. However, the film vanished if the current density was increased to 0.3 A/cm^2, and uniform dissolution of the anode began.

The deposit, isolated under these conditions at −0.03 V, contained austenite. In the presence of chloride ion, at pH 7 to 8, the metal was found to be in an active state when the current density was varied in the range 0.02 to 0.5 A/cm^2.

Figure 3 shows that the greatest polarization of the anode, in the presence of chloride ion, was achieved at a current density of 0.2 A/cm^2 and pH 7 to 8. Under these electrolysis conditions, a potential of −0.12 V was established at the anode, the martensitic phase dissolved, and the austenite remained on the sample in the form of a powder. The best results, according to x-ray analysis, were obtained with a potassium chloride electrolyte under the following conditions: current density 0.2 A/cm^2; pH = 8; t = 20°C; anode potential −0.12 V.

The Effect of a Passifier. A potential shift in the positive direction can be achieved by adding a passifying agent to the electrolyte [9, 10]. We used potassium nitrite as a passifier. With an electrolyte of N KCl + 0.04 N KNO_2, at a current density of 0.2 to 0.4 A/cm^2 and pH = 2, a potential of −0.11 V was established on the sample, and the deposit contained austenite.

Thus austenite can be isolated, with electrolytes containing chloride or bromide ion, under conditions of considerable anodic polarization, which can be achieved by increasing the current density and the pH of the medium, and also by introducing a passifying agent into the electrolyte (see table).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
