Passivity of Nickel Alloys with Iron and Chromium in

Alkaline Solutions

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PASSIVITY OF NICKEL ALLOYS WITH IRON

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The high stability of nickel operating as an anode in suf-
ficiently concentrated alkali solutions permits its isolation from
among other technical metals and its consideration on the same level
with noble metals such as platinum. In this connection it appeared
of interest to ascertain whether anodic stability of nickel in
alkali solutions is retained by its alloys with other metals, par-
ticularly with iron and chromium.

Numerous studies have been devoted to problems pertaining
to passivity of iron and its alloys with chromium and nickel (1 - 9).
Anodic behavior of nickel in alkali was the subject matter of our
previous publications (10, 11).

The present paper is devoted to the study of anodic beha-
vior of various alloys of nickel with iron and chromium in alka-
line solutions. The investigation was conducted in o.1 and 5.0
N solutions of chemically pure potassium hydroxide at 80 degrees
Centigrade, using the method of recording the polarization curves.
Measurement methods were the same as thosed used previously (10,
11). The anodes used in the investigation comprised various iron-
chromium-nickel and iron-nickel alloys. In the graphs, anodic po-
tentials are given in comparison with a normal hydrogen electrode.

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TABLE I

Anode material	Nickel	Chromium	Iron	Manganese	Silicon	Sulfur	Phosphorus	Carbon	Aluminum
				(i n p e r c e n t)					
EI — 334	76.9	20.1	1.94	0.88	0.56	0.01	0.02	0.13	0.06
EKhN — 60	57.74	16.17	23.74	0.97	1.20	0.013	0.020	0.45	—
EYa — 3S	25.10	18.70	53.12	0.51	2.16	0.010	0.018	0.38	—
EYa — 1	8.45	17.42	72.19	0.35	0.72	0.012	0.018	0.14	—
ST — 20	0.10	0.16	98.85	0.47	0.16	0.035	0.016	0.11	—
Chromium	—	97.81	1.74	—	0.58	—	0.06	0.04	—

Iron-Chromium-Nickel Alloys

Studies were conducted using four alloys similar in their
chromium content and differing in nickel content. Composition
of the materials studied is given in Table I. The results obtained
are shown in figures 1 and 2. From examination of these drawings
it can be seen that anodes EYa-1, EYa-3S, and EKhN-60 display ana-
logous behavior. The polarization curves reflect the pronounced
correlation between alkali concentration and the behavior of these
anodes. While in a 0.1 N solution the anodes rapidly acquire pas-
sivity, in a 5N solution they retain their activity up to a cer-
tain current density. Three sharply-differentiated portions ap-
pear in the polarization curves. The first corresponds to the
process of dissolution of the metal, the second to its passivity
stage, and the third reflects evolution of oxygen. Examination
of the curves shows that the limiting current density of passage
of metal into solution in 5N KOH decreases with increasing nickel
content of the alloy (Table II).

Figure 1. Electrolyte 0.1N KOH saturated with air. t = 80 de-
grees Centigrade. I, nickel; II, EYa-1; III, EYa-3S; IV, EI-334;
V, EKhN-60; VI, chromium; VII, steel-20. (below horizontal axis,
"Potential")

Figure 2. Electrolyte 5N KOH, saturated with air. t = 80 de-
grees Centigrade. I, nickel; II, EYa-1; III, EYa-3S; IV, EI-334;
V, EKhN-60; VI, chromium; VII, steel-20. (below horizontal axis
"Potential")

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TABLE II

Anode material	Current density at the moment of becoming passive in 5N, KOH A/cm^2
EYa-1	$1.5 \cdot 10^{-4}$
EYa-38	$2.3 \cdot 10^{-5}$
EKhN-60	$7.5 \cdot 10^{-6}$
EI-334	$3.1 \cdot 10^{-6}$
ST-20	$2.3 \cdot 10^{-5}$

Behavior of a EI-334 anode is somewhat different. It must be noted that EI-334 is essentially of chromium-nickel alloy since its iron content does not exceed 2 percent. However, although this alloy contains about 77 percent of nickel, at the beginning of polarization passage of metal into solution is observed.

In order to elucidate the question as to what component is responsible for the instability of the alloys, polarization curves were recorded for ordinary carbon steel 20 and chromium in addition to those for pure nickel and the alloys.

In its behavior on anodic polarization it differs sharply from the other anodes which were studied. Chromium polarization curves in 0.1N as well as in 5N solution extend almost vertically, with little change of potential. Direct and reverse progressions of the curve almost coincide completely. Such a progression of the curve indicates a very small polarization of the electrode: chromium passes into solution almost quantitatively.

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In 0.1N alkali, all the anodes with the exception of chromium are very similar. In 5N alkali, scattering of the curves is observed at the beginning of polarization; this characterizes the dissimilar behavior of the anodes under these conditions. The same drawing clearly shows that none of the alloys, with the exception of EI-334, approximates in its behavior that of nickel. It must also be noted that in the case of steel-20, anode overvoltage of oxygen evolution is higher than in the case of all other metals.

In view of the fact that the effect of iron and chromium in a triple alloy can be concealed by various contents of nickel, it appeared expedient to determine separately the effect of various amounts of nickel present in an alloy on the stability of the latter by testing it in alloys with iron.

Iron-Nickel Alloys

Iron-nickel alloys EN-5, EN-25, and EN-46 were used as anodes. Their composition is given in Table III.

Results obtained using iron-nickel alloys are shown in the composite graphs of figures 3 and 4. From the progression of the curves and the data of Table IV, it can be seen that iron-nickel alloy anodes also acquire passivity more readily in 0.1N alkali solution than in 5N solution. The nature of the curves and their mutual positions indicate a similarity of the various anodes in P.1N alkali, with respect to one another and with nickel. However, beginning with a current density of the of $2.5 \cdot 10^{-3}$ amperes per square centimeter, the EN-5 anode becomes unstable and undergoes

TABLE III

Anode material	Nickel	Chromium	Iron	Manganese	Silicon	Sulfur	Phosphorus	Aluminium
			(i n p e r c e n t)					
EN–46	46.57	—	52.75	6.34	0.43	—	—	0.02
EN–25	25.0	3.0	71.65	0.40	0.25	—	—	0.3
EN–5	4.63	0.06	94.18	0.41	0.23	0.016	0.018	0.15

deterioration with formation of localized centers of corrosion.

Figure 3. Electrolyte, 0.1N KOH, saturated with air. t = 80 degrees Centigrade. I, nickel; II, EN-46; III, EN-25; IV, EN-5; V, steel-20. (below horizontal axis, "Potential")

Figure 4. Electrolyte 5N KOH, saturated with air. t = 80 degrees Centigrade. I, nickel; II, EN-46; III, EN-25; IV, EN-5; V, steel-20.

TABLE IV

Anode material	Current density at the moment of becoming passive in 5N KOH A/cm^2
EN-5	$7.2 \cdot 10^{-6}$
EN-25	$1.5 \cdot 10^{-6}$
EN-46	$0.98 \cdot 10^{-6}$

The curves obtained for the nickel-containing alloys in 5N solution present an entirely different appearance. On following the progression of the curves obtained for the electrodes beginning with that of iron and up to that of nickel, in Figure 4, the beneficial effect of nickel in the alloys becomes clearly apparent.

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Potential of the EN-5 anode, as this can be seen in Figure
4, shifts abruptly towards the more positive values, and the na-
ture of the polarization curve indicates a more readily-attainable
passivity in the case of EN-5 anode in comparison with that of
iron. The EN-25 anode, as can be seen from the progression of
the polarization curve, approximates fairly closely that of nickel,
even though for current densities up to $1.5 \cdot 10^{-6}$ amperes per
square centimeter there apparently takes place a dissolution of
the metal. Most similar to nickel is, naturally, the anode made
of EN-46. Beginning with a current density of $1.0 \cdot 10^{-6}$ amperes
per square centimeter, the EN-46 acquires passivity. At high cur-
rent densities all three anodes retain their stability in 5N al-
kali solution.

The analogy in anodic behavior between alloy EN-46 and nic-
kel is confirmed also by the fact that inclination angles of the
portion of the curve corresponding to the process of oxygen libera-
tion on the EN-46 anode approximate very closely the inclination
angles of the curve for nickel. This makes it necessary to assume
that the mechanism of oxygen liberation on nickel and on an anode
made from EN-46 is analogous.

CONCLUSIONS

1. A study was made of iron-chromium-nickel alloy anodes
in 0.1N and 5N solutions of caustic potash at 80 degrees Centi-
grade. On the basis of the obtained data it has been established
that iron-chromium-nickel austenitic steels are unstable at the
anode in concentrated alkali at 80 degrees Centigrade. The cause

of the instability is chromium, which in a pure state quantitatively passes into solution on anodic polarization in alkaline solutions.

2. Chromium, which causes the passivity of stainless steels in oxidative media, drastically decreases their passivity in alkalies.

3. A study was made of iron-nickel steels at the anode in 0.1N and 5N solutions of caustic potash at 80 degrees Centigrade.

The capability of acquairing passivity in alkaline solutions is imparted also to its alloys with iron. An addition of 5 percent nickel (alloy EN-5) produces a beneficial effect on iron even though this alloy is not completely stable at high current densities in a dilute solution. Alloys containing 25 and 46 percent of nickel approximate nickel by their stability in alkaline solutions.

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