EFFECT OF WATER ON THE ANODIC BEHAVIOR OF CHROMIUM IN METHANOL SOLUTIONS OF HYDROGEN CHLORIDE

(UDC 620.193.2)

Ya. M. Kolotyrkin and G. G. Kossyi

L. Ya. Karpov Scientific-Research Physicochemical Institute

Translated from Zashchita Metallov, Vol. 1, No. 3,
pp.272-276, May-June, 1965
Original article submitted January 19, 1965

In investigating the mechanism of dissolution and passivation of metals, study of the effect of the solution composition of these processes is extensively used. Most investigations of this type have been carried out in relatively weak (0.1-5 N) aqueous solutions of electrolytes. It is obvious that the presence of excess free water in these solutions makes it difficult to determine the role of molecules of water itself in the processes under investigation.

To solve this problem it may be advantageous to use nonaqueous solutions. The necessity for a detailed investigation of the electrochemical behavior of metals in nonaqueous solutions has already been pointed out [1]. However, until very recently little attention has been paid to the study of such solutions, despite the fact that investigations of this type are not only of theoretical interest but also of practical importance for dealing with metal corrosion problems in organic media.

To obtain data on the effect of water on the passivation process we studied the behavior of chromium during anodic polarization in solutions of an inorganic electrolyte (HCl) in an organic solvent (methanol) in the presence of various quantities of water. Methanol solutions of hydrogen chloride have a high electrical conductivity.* This facilitates experimental procedure because, among others, it is not necessary to take into consideration the potential drop due to resistance.

The measurements were made on clamped electrodes from cast and rolled chromium of 99.9% purity with an active surface of 0.12 cm^2 in a cell made of glass and polyethylene. The solutions were prepared by saturating methanol of the "chemical purity" grade (with a water content of 0.05%) with dry gaseous hydrogen chloride (these solutions will subsequently be referred to as nonaqueous). The electrode potential was changed in 50-mV steps from negative to positive values by means of a valve potentiostat. In most cases the potential was maintained for 1 min, which gave a mean rate of potential change of 3 V/h. All the experiments were carried out without agitation, at room temperature. The potentials were measured against a saturated aqueous calomel electrode and converted to the normal hydrogen electrode scale.†

Figure 1 shows quasi-potentiostatic anodic polarization curves for chromium in 1 N solutions of HCl in methanol. It can be seen that water additions do not influence the kinetics of active dissolution, which are characterized at all the water concentrations by the same straight line with a slope of about 120 mV. Similar results were obtained in 0.5 and 0.1 N HCl (Fig. 2). This independence clearly demonstrates that the dissolution of chromium in the active condition proceeds without the participation of water molecules. A decrease in the HCl concentration

*The high electrical conductivity of such solutions is due to the anomalously high mobility of the methoxonium ion $CH_3OH_2^+$; the case is analogous to that of acid aqueous solutions, in which a high electrical conductivity is caused by the anomalous mobility of the hydroxonium ion H_3O^+.

†Since the energy of solvation of most ions changes only little on transition from water to methanol [2], it can be assumed that these corrections will not be large. This is confirmed by the fact that the active dissolution kinetics is found to be independent of the quantity of water added. Otherwise it would have to be assumed that the errors introduced by the presence of an interphase potential are fully compensated at all water concentrations by the reverse influence of water on the position of the active dissolution zone, which is unlikely.

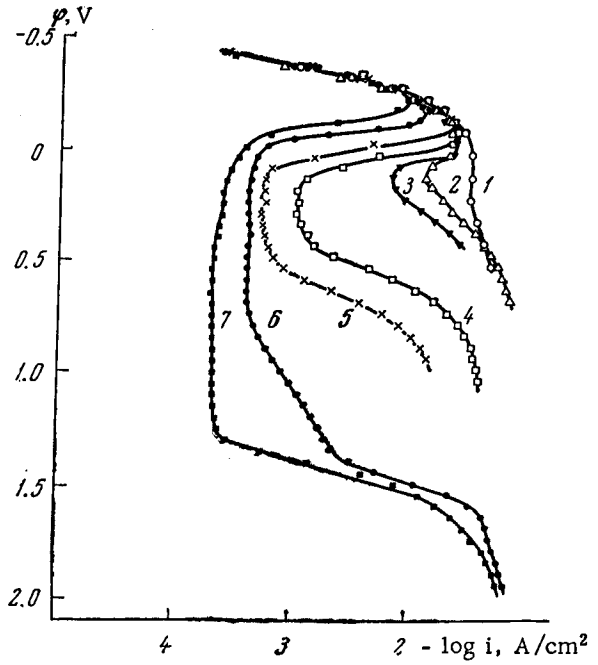

Fig. 1. Anodic polarization curves of Cr in 1 N HCl solutions in methanol with various water additions (%): 1) 0; 2) 1; 3) 2; 4) 3; 5) 4; 6) 5; 7) 10.

from 1 to 0.5 N (curves 5, 1, 2, and 3, Fig. 2) does not affect the active dissolution of chromium. On the other hand, transition from 0.5 to 0.1 N HCl is accompanied by a noticeable inhibition of the process, which manifests itself in a displacement of the straight line toward more positive potentials (Fig. 2). Special experiments have shown that a change in acidity at constant Cl' ion concentration (curve 4, Fig. 2) has little influence on the kinetics of active dissolution. Thus, the observed inhibition is associated with a decrease in the Cl' ion concentration and can be explained by the direct participation of these ions in the dissolution of chromium.

Although water has no appreciable influence in the active dissolution region, it substantially affects the potentiostatic curves at more positive potentials. It can be seen from Figs. 1 and 2 that in nonaqueous solutions the curves have no falling section, and only a limiting current is observed, which is probably associated with the effect of moisture traces. When water is introduced, a drop in the current can be observed on the curves after reaching a certain potential φ_p, which is characteristic of the passivation process. An increase in the water concentration from 1 to 10% is accompanied by easier passivation, which manifests itself in a displacement of φ_p by approximately 250 mV toward more negative values and a reduction of the critical passivation current by about two-thirds. At the same time the rate of dissolution of chromium in the passive state decreases even more (from $1.6 \cdot 10^{-2}$ to $2.3 \cdot 10^{-3}$ A/cm^2), which indicates a deeper passivation of the metal in solutions with higher water concentrations. In less concentrated HCl solutions the passivating properties of water are even more pronounced. Thus, the rate of dissolution in the passive state at a potential of + 0.1 V in solutions with 1% H_2O decreases, compared with the nonaqueous solution, by about 50% in 1 N HCl (curves 1 and 2, Fig. 1) and by a factor of 70 in 0.1 N HCl (curves 1' and 2', Fig. 2), while in solutions with 3% H_2O the respective values are 30 and 350. Furthermore, a decrease in the HCl content at a constant H_2O concentration or an increase in the H_2O concentration at a constant HCl content widens the zone of potentials corresponding to a stable passive state. These results show, in the authors' opinion, that under the conditions investigated water molecules may act as passivating particles. (Only particles which participate in the passivation reaction are under consideration.)

In the solutions studied, the passive state of chromium at sufficiently high positive potentials may be disturbed not only because of overpassivation (curve 7, Fig. 1), but also as a result of activation of the passive surface by chlorine ions. In some cases (curves 4, 5, and 6 in Fig. 1 and curves 3, 2', and 3' in Fig. 2) this activation has a local character and leads to pitting.* As in the case of Zr [13], Fe [14], and Fe–Cr alloys [5], studied earlier in our laboratory, as well as Mg [6] and Al [7], the activation of chromium occurs only after the attainment of a certain critical potential φ_{cr} which is more positive than the passivation potential φ_p.† In the same way as during the activation of the above metals in aqueous solutions, φ_{cr} of passive chromium in aqueous methanol solution shifts toward the negative values with increasing Cl' ion concentration. However, in the solutions investigated φ_{cr} is also found to depend on the water concentration, which is expressed in a shift of φ_{cr} in the positive direction with increasing water concentration. This dependence is linear over a wide range of potentials, and the slope of the φ_{cr}

*Pitting was also observed during the anodic polarization of titanium in methanol solutions of NaBr [8] and HCl [9] which contained small quantities of water.

†It must be borne in mind that, owing to nonsteady-state conditions, the φ_{cr} values obtained are shifted toward more positive potentials.

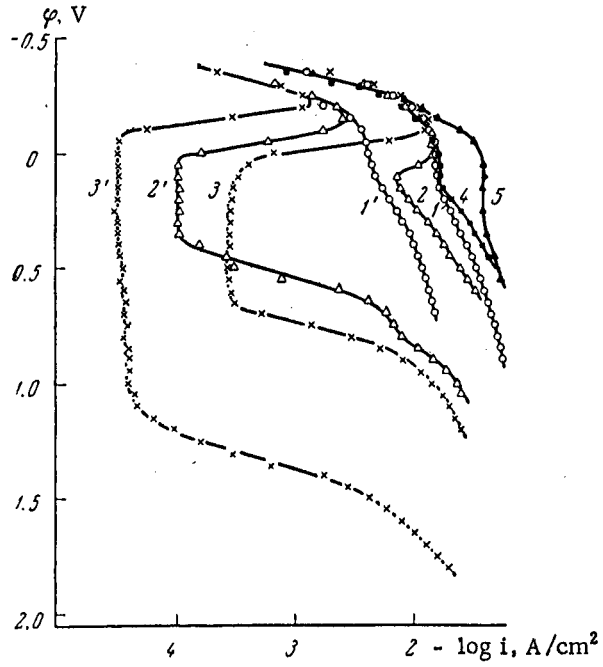

Fig. 2. Anodic polarization curves of Cr in solutions: 0.5 N HCl (curves 1-3); 0.1 N HCl (curves 1'-3'); 0.1 N HCl + 0.9 N LiCl (curve 4), and 1 HCl (curve 5) in methanol with various water additions (%): 1, 1', 4, 5) 2; 2') 1; 3, 3') 3.

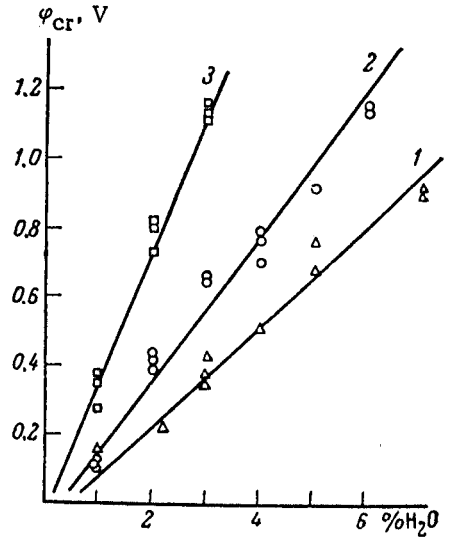

Fig. 3. Dependence of φ_{cr} of Cr on the amount of water in HCl solutions: 1) 1 N; 2) 0.5 N; 3) 0.1 N.

vs % H_2O lines increases with decreasing HCl concentration (Fig. 3). The results obtained explain the absence of activation of chromium by halide ions in aqueous solutions, observed in [5]. Indeed, as can be seen from Fig. 3, as the water concentration increases beyond a certain limit, equal to 3.5% for 0.1 N HCl and 9% for 1 N HCl, φ_{cr} shifts toward values which are more positive than the overpassivation potential. In such a case, with aqueous solutions, no pitting is observed on chromium.

A comparison of data for the cast and rolled electrodes shows that the φ vs log i curves for the two types of electrode are practically identical but the shape of the pits differs considerably. In 1 N HCl with 3% H_2O the pits on undeformed chromium have a square cross section, while on rolled metal under the same conditions the pits are irregularly shaped (Fig. 4). However, as the water content increases to 5%, the pits on both types of electrode assume the usual circular shape. These data apparently indicate that, at small quantities of passivating water, activation develops in a definite crystallographic direction. At higher water concentrations the shape of the pits no longer depends on the structure of the metal.

According to the electrochemical activation theory [3] the migratory supply of activator anions causes their concentration at individual sections of the metal surface to increase above a certain critical value, and this produces a localization and stabilization of pits. In pits operating under steady-state conditions this concentration remains constant because of hydrolysis of the corresponding halide complexes. It also follows from the results obtained that, in addition to the above cause of pitting corrosion in aqueous solutions, it is also necessary to take into consideration the decrease in the concentration of free water at the surface, as the water is combined as a result of hydration of dissolution products in the pits. This in turn must lead to a further facilitation of activation and an even greater localization of pitting corrosion.

The results obtained demonstrate conclusively that the passivation of chromium in acid solutions is associated with its reaction with water molecules. The first stage of such reaction is obviously the adsorption of water molecules, which begins at potentials slightly more negative than φ_p and results in Cl' ions being driven out from the surface. Beginning from a certain critical degree of filling of the surface, the attainment of which is facilitated at higher water concentration and lower Cl' ion concentration, a drop in the current is observed with increasing potential. It is quite probable that a further increase of potential will lead to additional adsorption of water and a change in the nature of the bond between the surface chromium atoms and oxygen. To explain the results obtained for chromium, it is also necessary to assume that the affinity of chromium toward the oxygen of water and toward chlo-

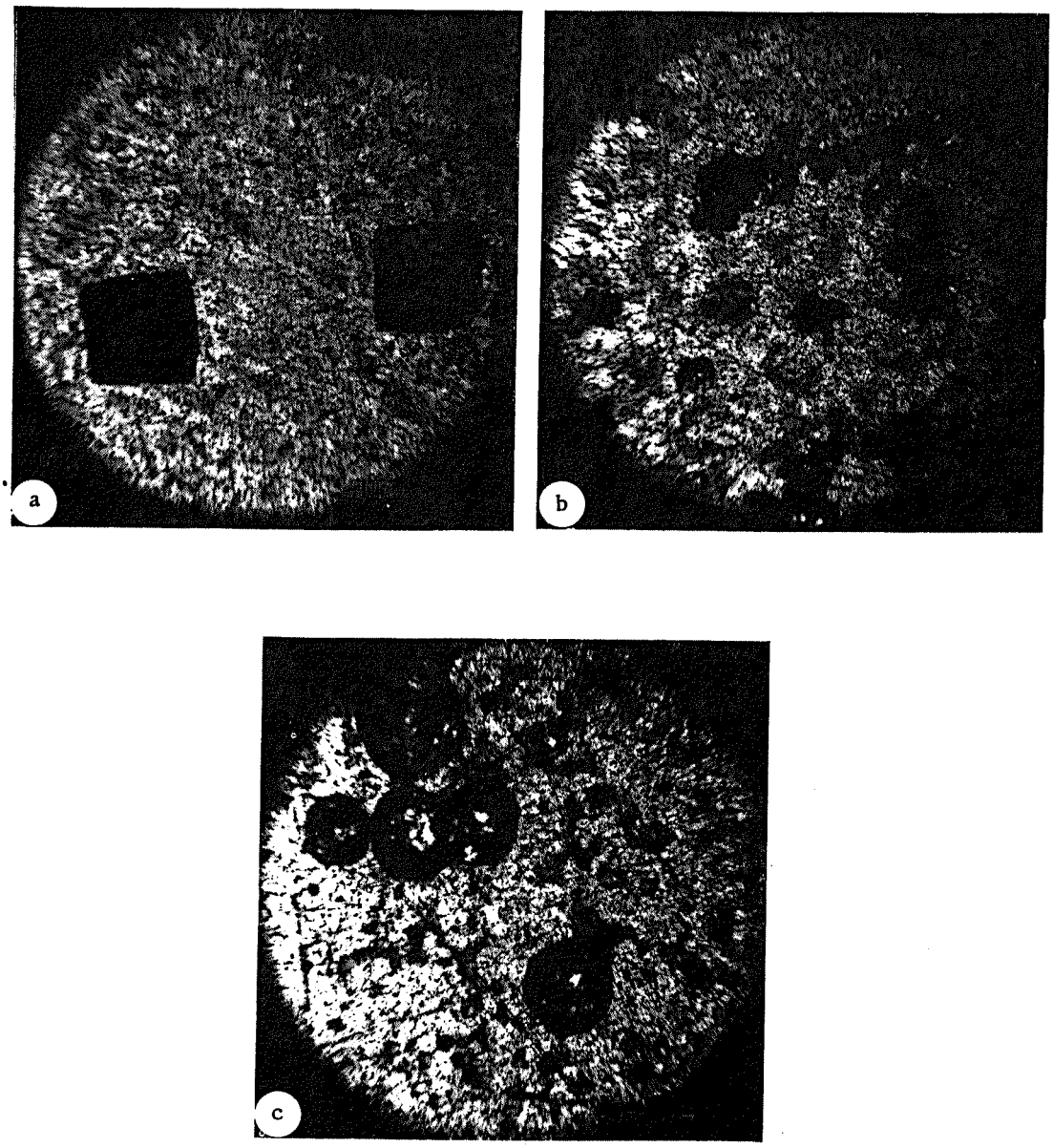

Fig. 4. Photomicrographs of pits on chromium, produced in different solutions (× 100): a) 1 N HCl + 3% H_2O, cast Cr; b) 1 N HCl + 3% H_2O, rolled Cr; c) 1 N HCl + 5% H_2O, cast Cr.

rine ions depends on potential in such a way that, beginning from a certain potential, the chlorine ions may in turn displace the passivating oxygen and activate the surface. It is obvious that in this case activation will be facilitated by increased concentration of chlorine ions and decreased amounts of passivating water.

LITERATURE CITED

1. T. P. Hoar, "Anodic behavior of metals," in book: Contemporary Problems in Electrochemistry (editor J. Bocriss) [Russian translation] Moscow, (1962), p. 284.
2. N. A. Izmailov, Electrochemistry of Solutions [in Russian] Khar'kov Univ., Khar'kov (1959).
3. Ya. M. Kolotyrkin and V. A. Gil'man, Dokl. Akad. Nauk SSSR, 137, 641 (1961).
4. Ya. M. Kolotyrkin and L. I. Freiman, Dokl. Akad. Nauk SSSR (1965 in press)
5. Ya. M. Kolotyrkin, G. V. Golovina, and G. M. Florianovich, Dokl. Akad. Nauk SSSR, 148, 1106 (1963).
6. D. V. Kokoulina and B. N. Kabanova, Dokl. Akad. Nauk SSSR, 112, 692 (1957).

7. N. D. Tomashov and V. N. Modestova, Tr. Inst. Fiz. Khim. Akad. Nauk SSSR, No. 2; Investigation of Metal Corrosion [in Russian], No. 1 (1951), p. 42.
8. N. D. Tomashov, R. M. Al'tovskii, and V. V. Vladimirov, Collection: Corrosion and Protection of Construction Materials [in Russian], Mashgiz, Moscow (1961), p. 164.
9. A. I. Tsinman, E. P. Kovsman, and V. S. Kuzub, Ukr. Khim. Zh. (1965 in press).

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.**
