CONNEXION BETWEEN HYPERSTRUCTURE
AND ELECTROCHEMICAL PROPERTIES OF ALLOYS

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The influence of hyperstructures in binary Ni—Fe and Ni—Co alloys on their electrochemical properties was studied. One of suitable electrochemical parameters for determining the structural changes is the depassivation potential. Its course shows that the resistance of the alloys against pitting corrosion rises in the region of formation of hyperstructures.

The structure of metals and alloys and their electrochemical properties show a correlation. It is known that electrochemical dissolution under defined conditions can be made use of in the separation of individual phases. Electrochemical methods can be, however, applied even in the study of less profound changes than the phase transformations. Uhlig[1] pointed out the relation between the rate of corrosion of alloys and their electronic structure. The possibility of studying the magnetic changes in alloys from the course of polarization curves was proved recently[2,3]. Lattice defects on the metal surface can be made visible by the method of electrochemical etching[4,5]. Our aim was to use the kinetics of electrochemical dissolution of alloys in studying the formation of hyperstructures.

EXPERIMENTAL

The rate of electrochemical dissolution was studied with Ni—Fe alloys prepared from iron and nickel of 99·99% purity and with Ni—Co alloys prepared from 99·995% Ni and 99·95% Co. Measurements were performed with hardened (heated for 1 h at 1100°C and cooled with water) and quenched (heated for 100 h at 700°C) samples which were embedded in an epoxy resin; their surface area after grinding was about 0·5 cm². The kinetics of dissolution of the samples was determined from the polarization curves recorded potentiodynamically with a rate of potential change of 17 mV/s. The electrolyte was 0·2M-KCl saturated with air. Potentials are given against S.C.E. at (22 ± 1)°C. Depassivation potentials were measured at a current density of 5 mA/cm².

RESULTS AND DISCUSSION

The relation between the structure and electrochemical properties of metals and alloys can be studied by measuring, *e.g.*, the corrosion potential, current density

in the active state, critical passivation current density, current density in the passive state, passivation potential, transpassivation potentials or the current maximum in the transpassive region. The choice depends largely on the course of the polarization curve of the alloy. During polarization of the Ni—Fe and Ni—Co alloys in 0·2M-KCl the current density after exceeding the depassivation potential increases considerably with a simultaneous appearance of an uneven corrosion of the sample and formation of pits. The corrosion is caused by a point attack due to chloride ions in the solution. Since in our case the depassivation potential was most easily measurable and well reproducible it was used to indicate structural changes in the alloys. It turned out that its values depend on the composition and heat treatment of the alloy sample, other conditions (electrolyte composition, temperature and rate of potential change) being constant. The smallest values of the depassivation potential were measured on pure iron and cobalt. The presence of nickel in low concentrations causes a significant increase of the depassivation potential; at higher concentrations the course of the depassivation potential is more complicated and considerably different with hardened and quenched samples.

The difference of the depassivation potentials on quenched and hardened samples $(E_{Dq} - E_{Dh})$ as a function of the nickel content in the alloy is shown in Fig. 1. With the Ni—Fe alloys, this dependence has two maximums at 60 and 75% Ni. With the Ni—Co alloy the curve has only one maximum at 75% Ni. The differences in depassivation potentials on hardened and quenched samples can be caused by changes in the grain size, changes in the lattice defectivity and in the structure. It was found microscopically that the heat treatment was in most cases substantially without influence on the grain size. E.g., the mean grain size of the Ni—Fe alloy was in the case of hardened samples 0·30, 0·12, 0·15, 0·20, 0·50−0·60 mm, and with the corresponding quenched samples 0·30, 0·13, 0·25, 0·15 and 1·10−1·60 mm, respectively.
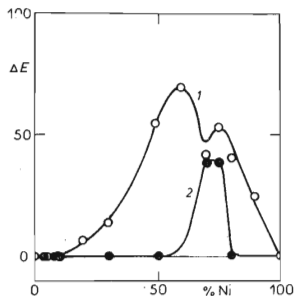

Fig. 1

Dependence of the Difference of Depassivation Potentials of Quenched and Hardened Samples, $\Delta E = E_{Dq} - E_{Dh}$ (in mV), on Alloy Composition

1 Ni—Fe, *2* Ni—Co. Electrolyte 0·2M-KCl.

Hence, only the last sample showed a pronounced change in the grain size. This was, however, not manifested by a conspicuous change of the depassivation potential. Equal values of E_{Dh} and E_{Dq} with many samples are an evidence that even a decrease in the lattice defectivity does not influence substantially the depassivation potential. It is therefore probable that the observed differences are a result of structural changes occurring at a certain composition of the alloy.

The maximum at 75% Ni in the Ni—Fe samples is in good agreement with the assumed formation of a hyperstructure[6] Ni_3Fe and is apparently connected with a decrease in the activity of the alloy components. This causes an increase of the activation enthalpy of metal dissolution, and thus the resistivity of the sample against the agressive influence of chloride ions increases.

The rate of dissolution can be decreased by changes in the electronic structure. The electron configuration of nickel is in the last levels according to Mott[7] $(3d)^{9\cdot6}$ $(4s)^{0\cdot6}$, which corresponds to the existence of three structures, $(3d)^{10}$ $(4s)^0$, $(3d)^9$ $(4s)^1$ and $(3d)^8$ $(4s)^2$. The last one is present in the alloy in the lowest concentration but is most suitable for the dissolution of nickel from the energetic point of view since its electronic structure is closest to that of the Ni^{2+} ion, $(3d)^8$. In contrast to this, the first two structures must change their configuration during the dissolution of nickel. In the region of hyperstructures, the relative content of different electronic structures is obviously different as a result of a strong interaction of Fe and Ni atoms, and changes so that the ionization of nickel is connected with a higher activation enthalpy and therefore proceeds more slowly. It should be also considered that the electrode can be oxidized only during strong adsorption of chloride ions, which can also depend to some extent on the electronic structure of the alloy. The reason for the changes at about 60% Ni content remains hitherto unclear.

With the Ni—Co alloy, the maximum on the curve has obviously a similar reason as with Ni—Fe. The existence of a hyperstructure in this alloy was not proved with certainty but several authors observed discontinuities at 75% Ni in the dependence of physical and chemical properties on concentration[8-11]. In accord with them, also electrochemical measurements revealed a marked difference in depassivation potentials in the region of the supposed hyperstructure Ni_3Co. The increased resistance against pitting is again due to changes in the chemical bond, which is stronger in the hyperstructures than in alloys of another composition.

It is further obvious from the results of measurement that the depassivation potentials exert a discontinuity in 0·2M-KCl in the region of hyperstructures but not in the region of phase transformations which proceed in the alloys under study. The influence of phase transformations (e.g. $\alpha \rightarrow \gamma$ in a Ni—Fe alloy) on the polarization curves can be observed with the use of other electrolytes, e.g. 0·05M-KCl + + 0·5M-NaNO$_3$. In this case, however, the depassivation potentials at higher nickel contents have a complicated course caused by competitive adsorption of NO_3^- and Cl^- ions and are therefore not suitable for following the structural changes of alloys

rich in nickel. It follows that the choice of a suitable electrolyte is of basic importance for the described method of measurement. It is necessary to choose such a medium, where the rate-determining step of the electrochemical dissolution is splitting of the metallic bond, and where the following reactions do not influence substantially the dissolution of the alloy.

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