

Electrochemical behaviour of metal silicides in acidic and alkaline media

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The elaboration of new materials with high corrosion resistance is one of the actual problems of modern corrosion science. One of the most interesting objects is intermetallic compounds and metallides. These materials are widely used as the basis for new resistive alloys.

Complex investigation of electrochemical behavior (cathodic and anodic reactions) of iron group metal silicides in acidic and alkaline media has been done using electrochemical, analytical and structural methods. The influence of internal and external factors on the mechanism and the kinetics of anodic process have been explored in details. It has been shown that the mechanism of anodic dissolution of silicides in acids, alkaline electrolytes and also in fluoride containing solutions are significantly different. During anodic dissolution of silicides in acids metal atoms are ionized and they move into the solution. Initial dissolution rates of silicides with low silicon content (Co_2Si , etc.) are close to those of the pure metals. At the same time remaining silicon is oxidized on the surface forming hydrated SiO_2 layer, which thickness is determined by the amount of silicon in silicides. More compact and dense films on silicides with high Si amount (CoSi_2 , FeSi_2) serve as the reason of low anodic currents. In alkaline media silicon and SiO_2 are more soluble and the kinetics of silicides dissolution is determined by the formation of metal oxides and hydroxides on metal surface and these films are responsible for the passivation of silicides.

It has been determined that the corrosion rate of iron group metal silicides in acidic media is 2–6 times lower (as counted from anodic current density) than that of pure metals (M) and it depends on the ratio of amounts of M : Si in silicides. High corrosion resistance of silicides takes place because of high stability of covalent Me-Si bonds that is due to the great donor ability of Me-atoms. The last leads to the decrease of the probability of surface atoms removal from the metal matrix. Protective properties of surface SiO_2 layer must be taken into consideration also.

The electrochemical and corrosion behavior of compact and powder NiSi-electrodes as well as of pure Ni and Si in 0.1–5.0 N NaOH has been investigated using stationary and cyclic voltammetry. Main features of NiSi anodic dissolution have been determined. In spite of increasing dissolution of Si at high pH NiSi shows high resistance to anodic dissolution because of protective properties of surface $\text{Ni}(\text{OH})_2$. At high anodic potentials the reversible process $\text{Ni}(\text{OH})_2 \rightleftharpoons \text{NiOOH}$ takes place.

The influence of the ratio of components on the anodic behaviour of metal silicides in alkaline media has been investigated using Co_2Si , CoSi , CoSi_2 , $\text{CoSi}_2\text{-Si}$ (eutectic alloy) and pure Co and Si. It has been

shown that in spite of the less protective properties of SiO_2 , passivation of cobalt silicides takes place that is due to formation of cobalt hydroxide $\text{Co}(\text{OH})_2$. On the cyclic voltammogram of pure cobalt one can observe some peaks related to the reversible process: $\text{Co} \rightleftharpoons \text{Co}(\text{OH})_2 \rightleftharpoons \text{Co}_3\text{O}_4 \rightleftharpoons \text{CoOOH}$. The same process is observed on Co_2Si but with lower anodic currents. Anodic behaviour of iron silicides in alkaline media coincides mainly with that of cobalt and nickel silicides.

Cathodic behaviour of metal silicides in alkaline as well as in acidic media is determined mainly by metal component.