

RELATIONSHIP BETWEEN THE ELECTROCHEMICAL PROPERTIES AND ELECTRONIC STRUCTURE AND STRUCTURAL INHOMOGENEITY OF HIGH-CHROMIUM ALLOYS

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Binary Cr-Fe solid solutions, while being annealed at temperature near 750 K, can finally decompose into α' - and α -phases containing 80% and 20% Cr, respectively [1]. It is related with the change of electronic structure during long-term annealing [2]. The purpose of this work is study the effect of Cr-Fe alloys decomposition on their electrochemical and corrosion behaviour in aqueous electrolyte solution.

Cast model alloys containing 17 to 95 at.% Cr and commercially manufactured alloys containing 16 to 60 wt % Cr and 2 to 5 % Al were studied. The as-cast model alloys were homogeneous solid solutions. All as-cast alloys under study were subjected to annealing on special regime to cause their decomposition. The structure and electronic structure of alloys were studied by electron microscopy and X-ray photoelectron spectroscopy, respectively. Electrochemical tests were performed by potentiostatic and voltammetric methods (0.5 V/s) in 0.5 M H₂SO₄ solution at 298 K.

The voltammetric curves of model binary Cr-Fe alloys exhibit either two or three active anodic peaks, depending on whether an alloy is as-cast or annealed, respectively. Curves with two anodic peaks were recorded on as-cast solid solutions containing 17, 26, 48, 55, 71, 77.6, 81, 86.4, and 95 % Cr. Curves of this type are characteristic of typical homogeneous solid solutions [3]; their first peak ($-0.52 \text{ V} > E > -0.35 \text{ V}$) describes selective dissolution of Cr, while the second peak ($E > -0.05 \text{ V}$) relates to the dissolution of Fe-enriched surface layer formed during the former stage. Three-maxima curves were recorded on annealed alloys containing 80.3, 82.3, 83.2, and 92.3 % Cr. The first anodic peak of the curves of longheated alloys located in active dissolution range of Cr, approximates the first anodic peak of voltammetric curve of an 80Cr-20Fe homogeneous solid solution, and, hence, supposedly reflects selective dissolution of Cr from α' - phase of the same chemical composition formed during the long-term annealing of solid solution. The second (additional) anodic peak arises within potential range $-0.35 \text{ V} > E > -0.05 \text{ V}$. Its location coincides with the first anodic peak of voltammetric curve of 20Cr-80Fe homogeneous solid solution. Hence, this peak is obviously related to selective Cr dissolution from α -phase of the same chemical composition. The third anodic peak ($E > -0.05 \text{ V}$) on the long-annealed binary alloys coincides with the second peak of voltammetric curve of homogeneous solid solution and, hence, relates to the dissolution of the already discussed Fe-enriched surface layer. Thus, quick voltammograms discussed indirectly prove that Cr-Fe alloys with more than 70%Cr decompose into Cr-rich α' -phase and Fe-rich α -phase during their long-term annealing near 773. Additional

peak in the active dissolution region and higher passivation current density, i_p , in passive range point on decrease of passivability of long-annealed alloys.

In the case of decomposition of solid solutions containing less than 60% Cr by the nucleation mechanism the microareas enriched in Cr (α' -phase) and depleted of it (α -phase) grow significantly larger than during spinodal decomposition and, hence, significantly affect the mechanical properties of the alloys. The hardness and wear resistance of commercial alloys containing 27-60 wt %Cr and 2-5 %Al increase noticeably after their long-term annealing on special regime. Electrochemical and corrosion properties of commercial alloys are also enhanced by the annealing. Presence of Cr-rich α' -phase improves their passivability. Namely, in 0.5 M H₂SO₄ solution the foregoing alloys passivate much more readily after their long-term annealing at 773 K than in an as-cast state. Most profoundly, this effect looks on Cr60Al2 alloy. After special tests this alloy spontaneously passivates in the same solution.

Thus, anodic behaviour of Cr-Fe alloys in aqueous electrolyte solutions depends on their electronic structure and structural state. Decomposition of model alloys, containing more than 70 %Cr, is accompanied by difficulties in their passivation because of presence of Fe-rich α -phase. The long-term annealing of commercial alloys containing 27-60 wt %Cr and 2-5 %Al on the same regime results in their decomposition by the nucleation mechanism into larger α' - and α - phases, but increases electrochemical properties and corrosion resistance as well as the hardness and wear resistance of the alloys because of presence of Cr-rich α' -phase.

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