

Research on the oxidation of iron-chromium alloys by means of x-ray electron spectroscopy (ESCA) and Auger electron spectroscopy (AES) [1, 2] has shown that the compositions of the surface in the near-surface layer depend on temperature and pressure and may differ significantly from the bulk composition.

Our aim is to ascertain the dependences of the composition of an Fe-Al alloy surface on temperature and p_{O_2} . This alloy belongs to the class with limited solubility (up to 18 at.%) [3], whereas Fe and Cr form a continuous series of solid solutions [3]. As in the case of Cr, the electron affinity of Al is much greater than that of Fe; therefore, the laws of oxidation, ascertained for both alloys, give us a fairly reliable picture of the influence of temperature and p_{O_2} on the segregation of the alloy component during oxidation of iron-based alloys.

EXPERIMENTAL

We made the alloy Fe+2% Al in an electron-beam furnace with repeated remelting; the impurity content was less than $10^{-3}\%$. The ESCA spectra were obtained by means of a Vacuum Generators ESCA-3 spectrometer equipped with a high-vacuum preliminary treatment chamber (PTC), in which the specimen was etched by an Ar^+ ion beam to purify the surface or obtain the depthwise concentration profile of the elements and phases. The specimens were heated and oxidized both in the PTC and in the spectrometer itself, according to the p_{O_2} . The purity of the oxygen introduced was monitored with a quadrupole mass spectrometer fixed to the PTC. The residual gas pressure was $(2-5) \cdot 10^{-10}$ torr. The ESCA spectra were accumulated and processed by means of a PDP-8 minicomputer.

To investigate the kinetics of the possible change in composition of the alloy surface, the specimen was etched with an Ar^+ ion beam (5 keV, $5 \cdot 10^{-5}$ A/cm²) in the PTC at 450°; then after attaining the ratios of the integral intensities of the lines $Fe2p_{3/2}/O1s = 50$ [4], the specimen was transferred to the spectrometer chamber at the same temperature. The specimen was kept at $p_{O_2} = 2 \cdot 10^{-8}$ torr. The surface composition was estimated from the change in the integral intensities of the lines $Al2p$, $Fe3p$, $Fe2p_{3/2}$, and $O1s$.

DISCUSSION OF RESULTS

In the calculation of the atomic ratios we used the integral ratios of the electron lines $Al2p/Fe3p$ and $O1s/Fe2p_{3/2}$, with similar bond energies E_b , to avoid additional errors due to the dependence of the mean free path of the electron on its kinetic energy. It will be seen from Fig. 1 that with an increase in time the amount increases threefold, despite the fact that after heating and etching with Ar^+ ions the surface concentration of aluminum (~ 7 at.%) was somewhat higher than the bulk concentration. The great width of the $Al2p$ peak of the alloy surface after ion etching indicates that $\sim 50\%$ of the aluminum was oxidized. An increase in the ion etching time did not reduce the ratio O/Al below 0.5-0.6.

Note that the ionization cross section σ of the $O1s$ level, taken from [5], leads to exaggeratedly high values of O/Al . As shown by our experiments on Al_2O_3 heated in a high vacuum at 500°, the ratio O/Al is also too high and corresponds to ~ 2.2 , despite the fact that the $O1s$ peak of the electrons is a distinct singlet without any lines which could make a contribution to the overall integral intensity of the $O1s$ peak as a result of adsorbed oxygen-containing particles.* On this basis we can assume that the ratio $\sigma[O1s]/\sigma[Al2p] = 3.5$, not 2.7-2.8, as follows from [5]. We used our value of the ratio $\sigma[O1s]/\sigma[Al2p]$ to calculate

*Similar data were obtained in [6].

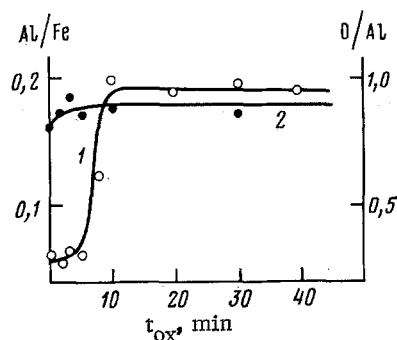


Fig. 1. Atomic ratios Al/Fe (1) and O/Al (2) vs oxidation time (t_{ox}) (450°C, $p_{O_2} = 1 \cdot 10^{-8}$ torr).

the atomic ratios O/Al. The ratio Al/O = 0.8-1.0 changes very little during the course of an experiment; its value was calculated from the ratio of the intensities of the corresponding electron lines, taking account of σ .

The maximal Al concentration in the near-surface layer, calculated with allowance for σ for the lines Al2p and Fe3p and corresponding to the plateau on the graph of Al/Fe vs t for $t \geq 10$ min, is 22 at.%. This is somewhat higher than the limit of solubility of Al in Fe [3], but it must be borne in mind that this value is averaged for a layer thickness of ~ 12 monolayers (according to the calculated [7] mean free path of the electron, λ). The presence of 1-2 monolayers of aluminum oxide on the surface reduces the aluminum concentration in the near-surface layer to 17-18 at.%, i.e., below the solubility limit of Al in Fe.

Under the experimental conditions the degree of oxidation of all the Fe atoms is 0, because the E_b of the $Fe2p_{3/2}$ electrons corresponds to 706.7 ± 0.2 eV [4]. This indicates that all the oxygen on the surface and in the near-surface layer is combined with Al. This is confirmed by the fact that E_b (O1s) = 531.0 ± 0.2 eV, corresponding to oxygen combined in the aluminum oxide lattice [8].

Summing up the foregoing, we can assume that residence of the specimen at $p_{O_2} = 2 \cdot 10^{-8}$ torr for 10 min* (or more) leads to formation on the surface of a static structure, which is a thin (1-2 monolayers) film of Al_2O_3 . Beneath this film the concentration of Al, both oxidized and unoxidized, is higher than the bulk concentration. The maximal Al concentration does not exceed the limit of existence of the solid solution.

The surface structure obtained has very high protective properties; this was verified by the following experiment. The specimen was cooled to -20°C and air was introduced at a pressure of 1 atm. After 25 h in air the atomic ratio Al/Fe increased by $\sim 80\%$, although the atomic ratio Al/O did not change and was ~ 1.5 , indicating that to a depth of 12 monolayers all the Al was oxidized. The absence of any changes in the line $Fe2p_{3/2}$ (Fig. 2, spectrum 1) (i.e., $E_b = 706.7 \pm 0.2$ eV and the line intensity is practically constant) clearly indicates the absence of oxidation of iron. After brief (~ 20 sec) bombardment of the specimen surface with Ar^+ ions to an Al concentration of ~ 7 at.%, oxidation at $p_{O_2} = 2 \cdot 10^{-6}$ torr for 0.5 h shifted the level of $Fe2p_{3/2}$ (cf. spectrum 2) to the level $E_b = 710.6$ eV, indicating complete oxidation of Fe to a depth of 8 monolayers (on the basis of the λ for $Fe2p$ electrons [7] for Fe_3O_4 [4]).

To ascertain the laws of oxidation of the alloy at p_{O_2} values at which the diffusion current of aluminum is insufficient to combine all the oxygen on the surface, we performed experiments on oxidation of the alloys at $p_{O_2} = 3 \cdot 10^{-6}$ torr for 30 min† at 450 and 200°C. After oxidation by etching with Ar^+ ions the oxide formed was subjected to layerwise analysis to obtain the distribution profile of the elements and phases over the oxide thickness. Figure 3a-b plots the atomic ratios of the elements, Al/Fe and O/Fe, vs the etching time, not the thickness, to avoid the error due to the inexact values of the atomization coefficients of the corresponding phases. The approximate atomization rate under the selected

*An exposure of 12 L (langmuir = $1 \cdot 10^{-6}$ torr/sec).

†The additional experiments showed that this period was sufficient to attain steady oxidation conditions.