Al-2p photoemission study of alumina coatings formed on heat treated Al-containing alloys

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Fe-base alloys that contain Al develop a protective alumina layer when they are exposed to a high temperature treatment [1]. These Fe based alloys are among the metallic materials with the highest oxidation and corrosion resistance at elevated temperatures. The good resistance appears because alumina scales with excellent thermodynamic stability and very slow growth rates form during high temperature exposure. These Fe based alloys are thus widely used for high-temperature applications due to the combination of high temperature mechanical properties and superior oxidation resistance. Additionally, these alloys could also be suitable for room temperature applications due to the formation of the alumina layer on their surface after high temperature exposure. In the present work, two Fe-base alloys that contain Al have been investigated: the ODS-MA956 alloy and modified Fe_3Al. In both cases, an alumina layer develops upon heating under certain conditions [1,2]. The aim of this study was to evaluate the surface composition of these alloys by using synchrotron radiation and x-ray photoemission spectroscopy (XPS).

The MA 956 superalloy, with chemical composition Fe-20Cr-5Al-0.5Ti-0.5Y_2O_3 (wt %), was supplied by Inco Alloys International (Hereford, UK). Samples were abraded, polished, and ultrasonically cleaned in ethanol. At this stage, the material was annealed at 1100°C for four different exposure times, 3, 10, 50, and 100 hours. After heat treatment, the samples were removed from the furnace and air cooled. For the case of the modified Fe_3Al alloy, the chemical composition was 26.6% Al, 4.95% Cr, 0.08% Zr (at. %) and remainder Fe. The material was annealed at different temperatures between 500°C and 800°C to give rise to different states. Consequently, state-A samples were in form of disordered state, state-B material in recrystallized state, state-C samples had an imperfectly ordered B2 structure and state-D sample had an ordered DO_3 phase. Upon each annealing, and to eliminate remaining particles of contamination from heat treatments, samples were abraded, polished, and before testing, ultrasonically cleaned in alcohol.

XPS measurements were carried out at the TGM5 monochromator of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using undulator light, employing a VSW-ARIES electron spectrometer. The base pressure in the UHV-chamber during measurements was better than 2×10^{-10} mbar. Samples were cleaned by 1 min. Ar^+ bombardment at an ion energy of 3 keV.

Figures 1 and 2 show Al-*2p* photoemission (PE) spectra at a photon energy of 160 eV together with the results of a least-squares fit analysis for all samples. In all cases it was not possible to describe the broad spectral feature located at around 75 eV (and usually assigned to Al_2O_3) with a single Lorentz line. Instead, three Lorentz curves, corresponding to Al with different oxidation states, were used. A similar approach, using also three lines, has been made in a previous work on oxidized Al [3]. The same nomenclature was used in all spectra. The dashed subspectra represent the Al^{1+} component located at ≈ 73.75 eV. The dash-dotted curves represent the Al^{2+} component located at $\approx$ 74.5 eV. The dotted subspectra show the Al^{3+} component at $\approx$ 75.3 eV. The solid line subspectra represent to metallic aluminium. For the state-D of the Fe_3Al alloy it was necessary to use an additional Lorentz line at $\approx$ 76.10 eV (represented by a dash-double-dotted line) in order to be able to describe the spectrum. The existence of Al^{1+} and Al^{2+} oxidation states is probably related to the partially amorphous character of the surface layer, which involves a wide distribution of bond lengths and coordination numbers at atomic scale, making possible the existence of Al atoms with low oxidation states. The present interpretation of Al-2p spectra can explain some binding energy shifts observed in previous works of the oxidized Al component, which might be actually due to changes in the intensity ratios between the different oxidation states in non crystalline oxidized Al.

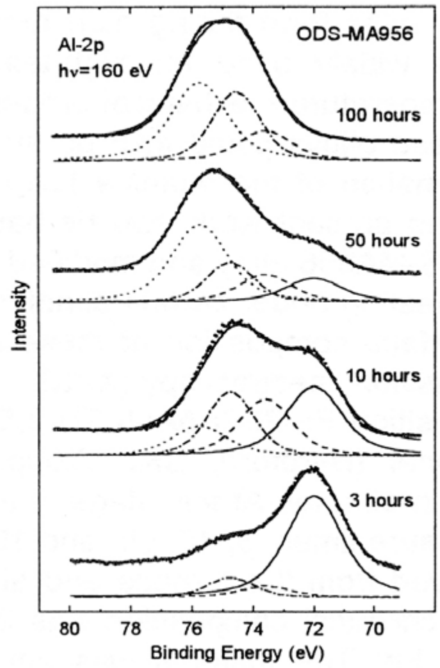

Figure 1: Al-*2p* photoemission spectra of the MA956 superalloy heated at diffferent temperatures. The solid lines through the data points represent the result of the least-square fits. The subspectra show different chemical states of aluminium.

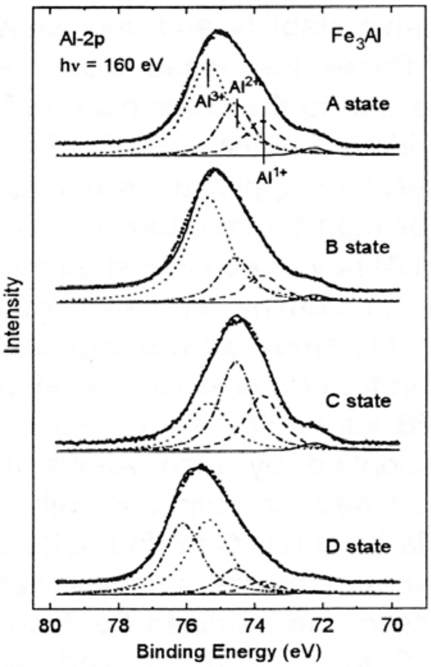

Figure 2: Al-*2p* photoemission spectra of the different heat-treated Fe-27%Al-5%Cr alloys. The solid lines through the data points represent the result of the least-square fits. The subspectra show different chemical states of aluminium.

In Figure 1, the emission corresponding to metallic Al is largest for the 3 hours-sample, decreasing when the exposure time is increased. It can be observed from this figure the existence of Al^{1+} and Al^{2+} components for all samples what indicates a partial amorphous character of the alumina surface layer. The Al^{3+} component is not present for the case of the 3 hours-sample indicating a high amorphous character of the oxide layer for this sample. This emission can be observed for the 10 hours-sample and becomes larger for the 50 hours-sample. This suggests a decrease of the amorphous character of the surface layer when increasing the time. Therefore, the photoemission data on these samples show that for short treatment times the non-oxidized aluminum state is the most important contribution. However, when the treatment time is increased, the non-oxidized state intensity decreases until it becomes negligible for larger treatment times.

As can be observed in Fig. 2, the ratio of the different Al oxidation components in the Fe_3Al samples is different for each state. The existence of Al^{1+} and Al^{2+} components observed for all samples indicates a partial amorphous character of the surface. The intensity of this Al^{3+} component with respect to Al^{2+} can serve as a measure of the amorphous character of the film: the higher the ratio between Al^{3+} and Al^{2+} components, the less amorphous the surface layer. Excluding state-C sample, which has a defect of Al atoms at the surface induced by the structure of the bulk, there seems to be a correlation between the amorphous character of the surface film and the structure of the bulk. State-A sample, which has a bulk disordered structure, has the lowest ratio between Al^{3+} and Al^{2+} components, i.e., it has the highest amorphous character. State-B sample, which corresponds to a recrystallized state, presents an intermediate behaviour. Finally, state-D sample with an ordered DO_3 bulk structure has the highest Al^{3+} component as compared to Al^{2+}. These results suggest that the order of the surface layer is directly related to the order of the bulk material. However, state-C sample does not follow this correlation because the defect of Al atoms in the bulk crystal structure induces a thinner passive layer.

In summary, the Al-2p photoemission study performed on the two Fe based alloys has shown the existence of different Al oxidation states in the surface layer. This result agrees with the previous finding of three different Al oxidation states [3]. The different ratio between the intensity of the Al^{3+} component to Al^{2+} can serve as a measure of the amorphous character of the surface film.

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