

**IN SITU XANES STUDY OF THE VALENCE STATE OF CHROMIUM
DURING ELECTROCHEMICAL POLARIZATION OF AlCr ALLOYS**

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The chemistry of chromium in the passive film on pure chromium and sputtered AlCr thin films has been studied *in situ* in an electrochemical cell under potential control using XANES. Depending on the rate of potential increase, the 6-valent chromium can dissolve from the alloy or be trapped in the passive film where it is electroactive *i.e.* the valence state can be reversibly switched between the 3- and 6-valent states by switching the applied potential. The kinetics of these processes were investigated.

INTRODUCTION

The chemistry of chromium in passive oxide films is of interest due to the corrosion resistance it imparts as an alloying element. The valence state is conventionally studied using techniques such as AES and XPS. However, some problems are encountered in the unambiguous identification of hexavalent chromium using these techniques, and in addition, as they use electrons as probes, measurements can only be carried out post-exposure in UHV. X-ray Absorption Spectroscopy (XAS) has recently been applied to the study of chromium in oxide films on metals (1-10). The detailed structure of the edge (X-ray Absorption Near Edge Structure, XANES) is particularly sensitive to the presence of 6-valent chromium due to the appearance of a sharp peak just below the edge. Furthermore, as XAS only uses x-rays, *in situ* measurements can be carried out in aqueous solution while the sample is under potential control.

The chemistry of chromium in oxide films on aluminum treated in chromate solution has been studied using XANES by a number of authors (1-4). Hawkins *et al.* (1) found 3-valent chromium in oxide films produced by anodizing aluminum in a borate buffer and then subsequently exposing these to a chromate solution. The thinner the film, the greater the proportion of 3-valent chromium. Chung *et al.* (2,3) investigated the chemistry of chromium in oxide films on aluminum formed by anodizing in a chromate solution. They also found both 3- and 6-valent chromium

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with the 6-valent chromium predominantly on the outside of the film. Wainright *et al.* (4) studied the sealing in dichromate solution of aluminum which had previously been anodized in sulfuric acid. The chromium co-ordination in the oxide film most closely resembled that in chromate.

In the present study, XANES was used to study chromium in the passive oxide film on AlCr alloys. Thus chromium is introduced into the film from the metal rather than from the solution side of the interface. Previous *ex situ* glancing incident angle XANES experiments (5) have shown that at and above 0.7V(MSE), both 3- and 6-valent chromium is found in the passive film, with the 6-valent chromium predominantly in the outer part of the film.

We have recently demonstrated the feasibility of measuring the valence state of chromium *in situ* during electrochemical polarization using XANES (6). In the present paper, we demonstrate the effect of the rate of potential increase on the behavior of chromium in the passive oxide film on AlCr alloys. Measurements were made while the samples were exposed to bulk solution and under electrochemical control.

EXPERIMENTAL

The cell design (which has been described previously (6)) was based on that used by Kerkar *et al.* (7) for EXAFS measurements. The working electrode is a thin metal film deposited on thin plastic which is the window of the electrochemical cell. The incident x-ray beam and resulting fluorescent x-rays pass through the thin plastic. The metal is in contact with bulk solution (0.5M H_3BO_3 + 0.05M $Na_2B_4O_7$). The cell also contains a reference electrode and a platinum wire counter electrode. Potentials are quoted with respect to the mercurous sulfate reference electrode (MSE, 0.64V(SHE)).

The samples used were pure chromium and AlCr alloys in the form of sputtered films 20-40Å thick. Thin films were used so that most or all of the alloy is oxidized when the passive layer is formed, minimizing the signal from metallic chromium in the underlying alloy. The films were deposited on thin Mylar (~6µm) which had previously been sputter-coated with 100Å of Ta (for electrical contact).

Measurements were made at Beamline X19A at the National Synchrotron Light Source at Brookhaven National Laboratory. Monochromatic x-rays were incident at ~45° to the back of the electrode surface and Cr $K\alpha$ radiation was detected through the back of the electrode with a 13 element solid state detector placed at 90° to the incident x-rays. Such an energy-discriminating detector is required in order to detect the small chromium fluorescence signal against the high background of incident radiation scattered by the cell, especially by the solution.

Many spectra were collected with coarse energy steps and short counting time per point in order to minimize the total spectrum collection time (spectra took 3 minutes to complete). This enabled time-dependent changes in the sample surface to be monitored. Higher quality spectra were obtained by using smaller energy steps and increasing the counting time.

RESULTS

Previous work (6) showed that following a potential step from open circuit to +2V, 6-valent chromium was trapped in the passive film of an AlCr alloy. This chromium is electroactive and can be reduced to the 3-valent state by stepping the potential to -1.5V. These data are reproduced in Fig. 1 (6). Together with the data from the passive films (solid lines), edges of standard compounds characteristic of the different valent states of chromium are shown as broken lines. Chromium metal (edge (a)) has the lowest edge position. (The chromium K edge position, 5989eV is calibrated at the position of the maximum slope on the first part of the edge.) Edge (b) shows 6-valent chromium (K_2CrO_4) which has an edge at a higher energy than chromium metal and has a very sharp peak below the edge at 5993eV. This pre-edge peak is associated with the tetrahedral co-ordination found for 6-valent chromium compounds (11) and is a very useful fingerprint for the presence of Cr(VI) as it can be seen even in the presence of a substantial amount of chromium in other valence states because they contribute little or nothing to the spectrum below the edge. It can also provide semi-quantitative information on the amount of Cr(VI) present: the ratio of the pre-edge peak height to the edge height approximates to the ratio of Cr(VI) to the total chromium present (10). Edge (c) shows 3-valent chromium (Cr_2O_3). The edge position is midway between those of Cr(0) and Cr(VI) and no pre-edge features are present.

Fig. 2 shows an experiment similar to that shown in Fig. 1 using pure chromium. At open circuit (a), the x-ray absorption edge is characteristic of chromium metal (see Fig. 1(a)). The passive oxide film, presumably 3-valent chromium, is so thin that the signal due to it is not detectable in the signal from the underlying 40Å of chromium. As the potential was stepped to +1.5V, a rapid 3-minute spectrum was initiated (b). By the time the energy had reached the edge position (~1 minute), the chromium was present in the 6-valent state (as indicated by the pre-edge peak, *c.f.* Fig. 1(b)), and a substantial proportion of the chromium had dissolved. The observation that the pre-edge peak appears to be higher than the edge (which is not the case for 6-valent chromium standard compounds) is due to the fact that the chromium was continuously and rapidly dissolving so more was present in the middle of the spectrum than at the end. By the time a second spectrum was completed, 6 minutes after the potential step, little chromium is detectable above the background noise.

The critical potential for the onset of transpassive dissolution of pure chromium was determined by stepping the potential in 100mV steps from the open circuit potential and initiating a rapid (3-minute) spectrum at the beginning of each potential step. The results are shown in Fig. 3 where it can be seen that the K edge remains the same as chromium metal from open circuit to +0.1V. At +0.2V, the 6-valent chromium pre-edge peak appears and loss of chromium is visible as a decrease in the height of the edge.

The previous experiment was repeated for AlCr alloys with a number of different chromium contents. Fig. 4 shows an alloy 20Å thick containing 22% chromium. The potential was stepped from open circuit to -0.7V and then incremented in 100mV steps to +0.7V. At each potential, a 3-minute edge spectrum was obtained and the current flowing was measured at the end of the spectrum prior to the next potential step. Selected spectra are shown in Fig. 4 where they are labelled with the potential during the spectrum. At open circuit, the chromium is in the metallic form. The spectra from -0.7V to -0.3V show metallic chromium. Around -0.2V there is a transition 3-valent chromium which persists until 0.1V. At +0.2V, the characteristic 6-valent pre-edge peak appears and dissolution is significant, as is apparent from the lower edge height. The currents measured at the end of each spectrum are shown in Fig. 5. The current reaches a maximum at 0.2V coinciding with the appearance of Cr(VI) and significant dissolution. The current at the end of the previous step is significantly raised indicating that a small amount of oxidation may begin at 0.1V. Identical behavior is found for Al-12%Cr (Fig. 6), Al-43%Cr (not shown) and Al-53%Cr (Fig. 7). In the latter case, some underlying metallic Cr can be seen up to 0.3V.

It thus appears, from a comparison of Figs. 1 and 4, that during slow polarization of AlCr alloys through +0.2V, chromium can dissolve via formation of chromate whereas if the potential is stepped to a high value (+2V), the chromate is trapped in the film and does not dissolve. The question then arises as to whether trapping 6-valent chromium in the passive film at high potential will prevent its dissolution if the potential is subsequently slowly raised through the critical potential of 0.2V. The results of this experiment, carried out on a 40Å Al-12%Cr alloy, are shown in Fig. 8. Edge (a) was taken 20 minutes after the potential was stepped to 2V. The pre-edge peak indicates the presence of some 6-valent chromium in the film. This was then reduced to the 3-valent state by stepping the potential down to -1.5V (edge (b)). The potential was then stepped to -0.5V and increased by 100mV at 3-minute intervals during which edges were measured. At +0.7V, the x-ray beam went down, so the potential was maintained at that value for 2 hours. From +0.8V, the potential was increased in 200mV steps up to 2V. Selected edges are shown in Fig. 8. As the potential was increased through the critical value for dissolution of 0.2V, no 6-valent chromium peak is apparent and the edge height remains constant so no dissolution is taking place. The pre-edge peak only appears after the sample

has been held at +0.7V for 2 hours. Even in the presence of the pre-edge peak, the edge height remains constant so no significant dissolution is taking place.

Because edges can be measured relatively rapidly (in 3 minutes), it is possible to study the kinetics of processes that take place over a sufficiently long timescale. Figs. 9 to 12 show a sequence of experiments which demonstrate this, carried out on 40Å of Al-12Cr. The potential of a fresh sample (with chromium in the metallic state, first edge, Fig. 9) was stepped to 2V. Starting simultaneously with the potential step, a series of 3 3-minute edges were collected (Fig. 9). The first of these shows that the chromium has been immediately oxidized to the 3-valent state. A small and rather noisy shoulder at the beginning of the edge may indicate that there is still some remaining metallic chromium. However, none of them show any sign of 6-valent chromium. The characteristic pre-edge peak only appears during a more detailed spectrum which was initiated 9 minutes after the original potential step and took 32 minutes to complete. The height of the pre-edge peak (and thus the proportion of 6-valent chromium) continues to increase and is significantly higher in another detailed spectrum which was collected between 50 and 77 minutes after the potential step.

The last edge on Fig. 9 is reproduced at the top of Fig. 10. After this edge was collected, the potential was stepped down to -1.5V and another series of 3 3-minute spectra were collected. These all show a 3-valent edge with perhaps a very small and noisy pre-edge peak indicating some small amount of residual 6-valent chromium. No pre-edge peak is present in the slower, detailed spectrum which was subsequently taken (the last edge on Fig. 10). This indicates that the reduction of 6 to 3-valent chromium is more rapid than the initial oxidation process.

The last edge on Fig. 10 is reproduced at the top of Fig. 11. The 3-valent chromium was then oxidized to the 6-valent state by stepping the potential back to +2V. The 3 3-minute spectra collected immediately after the potential step show a small and increasing pre-edge peak. Comparison of Figs. 9 and 11 indicate that the second oxidation process takes place more rapidly than the first one.

The last edge on Fig. 11 is reproduced at the top of Fig. 12. The potential was stepped from +2V down to -1.6V in 200mV intervals. The pre-edge peak only begins to disappear at -1.4V indicating that a large overpotential is required for the reduction process.

DISCUSSION

Polarizing pure chromium above 0.2V results in its rapid dissolution as chromate ions. Polarization of AlCr alloys also causes oxidation of chromium to the 6-valent state. However, whether or not it dissolves depends on the potential

treatment: stepping the potential to a high value (2V) traps the 6-valent chromium in the film without allowing any of it to dissolve, whereas stepping through the critical potential of 0.2V using 3-minute 100mV steps results in dissolution of the 6-valent chromium as it is formed. This behavior was found for AlCr alloys of different chromium contents ranging from 12 to 53%.

Once chromium is trapped in the oxide film by stepping the potential to 2V, it is electroactive *i.e.* can be switched between the 3- and 6-valent states by switching the potential between -1.5V and +2V. Furthermore, the chromium will then not dissolve from the oxide if the potential is stepped through the critical potential of 0.2V using 3-minute 100mV steps.

Stepping the potential directly to +2V from open circuit causes immediate oxidation of the chromium from the metallic state to the 3-valent state. Only then does it slowly transform over a period of an hour to the 6-valent state. This provides a possible explanation as to how the 6-valent chromium becomes trapped in the film. The 3-valent state is insoluble so the film is formed without dissolution and with chromium present throughout the film. Subsequently-formed 6-valent chromium within the film does not dissolve. One might speculate that during slower polarization in 100mV steps, chromate is formed on the surface in contact with the electrolyte and can more readily dissolve. The aluminum oxide still forms but chromate can dissolve from the film due to solution percolating into the film through flaws left by chromium dissolution. It is known that once 6-valent chromium begins to form, it will be present closer to the surface than the remaining 3-valent chromium. This was determined in previous *ex situ* glancing incident XANES measurements (5) for samples polarized to 2V. However, the question remains unanswered as to how the 6-valent chromium is prevented from dissolving from the thick film.

It is interesting to note that the presence of 3-valent chromium, even at very high potentials, is found on anodizing aluminum in the presence of chromate (2,3). In this case, the 6-valent chromium is also found predominantly at or near the surface of the oxide.

It is known from *ex situ* Auger LVV measurements (12) that the 6-valent chromium in the oxide film is not identical to chromate ions. A difference was found between the behavior of 6-valent chromium in the passive film on AlCr alloys formed by potential steps and that of chromate adsorbed onto a anodized aluminum surface. The adsorbed chromate gave an LVV Auger peak and was susceptible to photoreduction to 3-valent chromium in the incident x-ray beam, whereas the 6-valent chromium in the passive film gave no Auger LVV signal and was considerably less susceptible to photoreduction. This was interpreted in terms of stronger overlap between the oxygen atoms tetrahedrally surrounding the chromium atoms and

adjacent aluminum atoms for the case of the passive film. It was assumed that the adsorbed chromate on the anodized aluminum behaved more as discrete chromate ions. 6-valent chromium tetrahedrally-surrounded by oxygen atoms which have a strong chemical interaction with adjacent aluminum atoms might be expected to be more resistant to dissolution than discrete chromate ions. However, this approach does not address the critical question as to why the behavior is different during the two different potential treatments.

It was also observed that the formation of 6-valent chromium was more rapid during the second oxidation to 2V than during the first. The oxidation of 3-valent chromium to the 6-valent state requires a change from octahedral to tetrahedral coordination as well as the change in the charge on the chromium atom. It may be that this is accommodated by the movement of protons and vacancies within the film as well as electron transfer to the metal and that the first oxidation step is diffusion-limited whereas for subsequent steps they remain close to the chromium atoms which are changing valency.

CONCLUSIONS

- 1 Above 0.2V, pure chromium dissolves rapidly as Cr(VI) in a borate buffer solution.
- 2 During slow potentiodynamic sweeps, Cr in AlCr alloys dissolves as Cr(VI) above 0.2V.
- 3 Pulsing AlCr alloys to 2V initially incorporates 3-valent Cr in the film. This gradually transforms to the 6-valent state which is trapped in the film and does not dissolve. This Cr can be reversibly cycled between the 3- and 6-valent states by switching the potential between -1.5V and +2V. Once a film has been formed a 2V, slow potential sweeps through 0.2V no longer result in dissolution.

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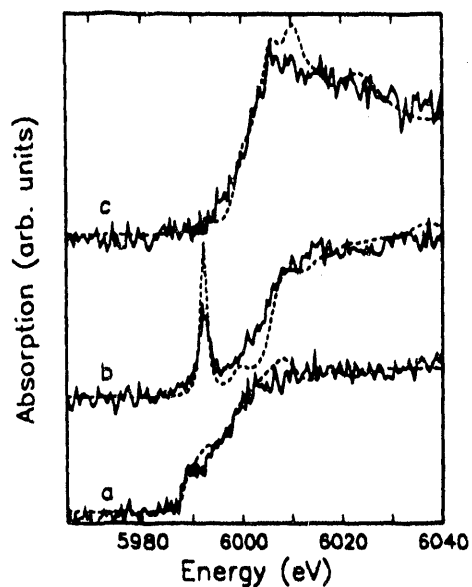


Fig. 1 *In situ* XANES measurement of the Cr K edge of a 20Å Al-12%Cr film in a borate buffer solution (a) at open circuit, (b) after 7 minutes at 2V(MSE), (c) after 6 minutes at -1.5V(MSE) (solid lines). The broken lines show standard compounds measured in transmission: (a) Cr (b) K_2CrO_4 , and (c) Cr_2O_3 (6).

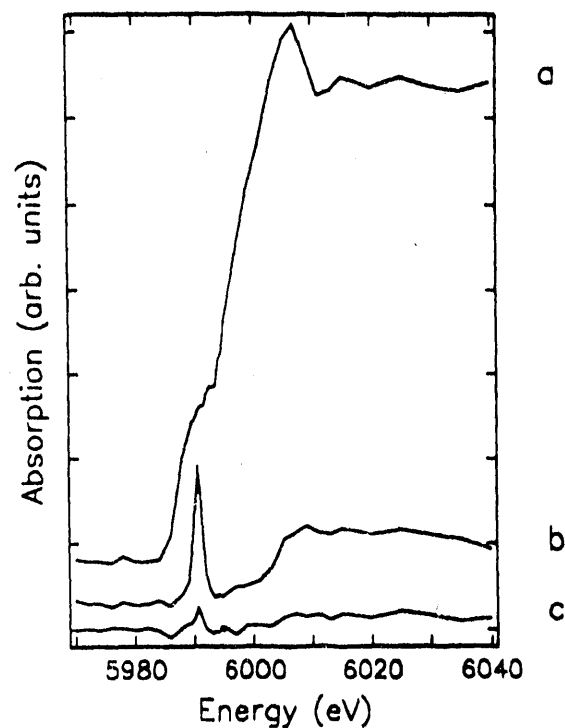


Fig. 2 Cr K edge for a 40Å film of pure chromium (a) at open circuit and (b) 0-3 minutes and (c) 3-6 minutes after stepping the potential to +1.5V(MSE).

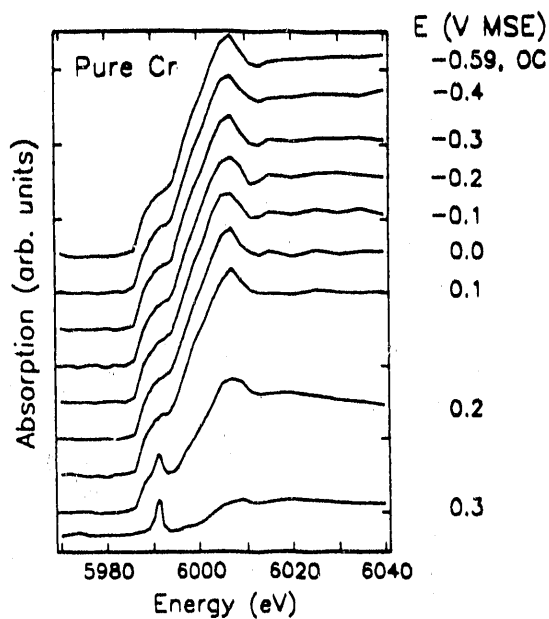


Fig. 3 Cr K edge for pure chromium at open circuit and during stepwise anodic polarization in a borate buffer. The potential was incremented to the potential indicated at the beginning of each 3-minute energy spectrum.

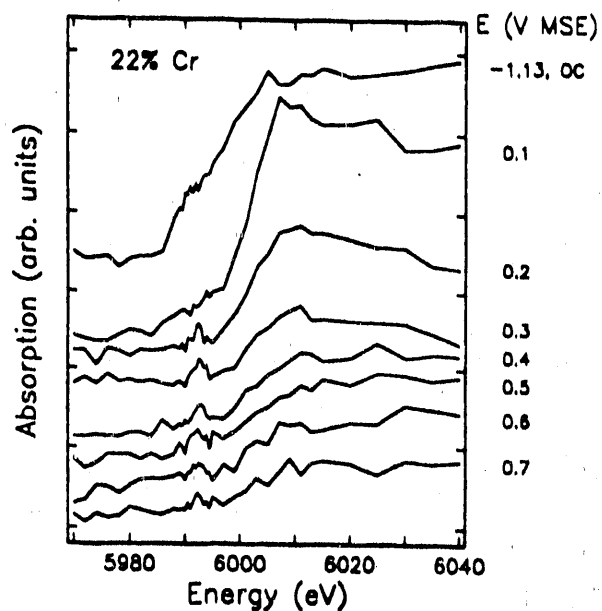


Fig. 4 Cr K edge for a 20Å Al-22%Cr alloy polarized in a borate buffer solution at the potentials indicated. The potential sequence is described in the text. Each spectrum took 3 minutes.

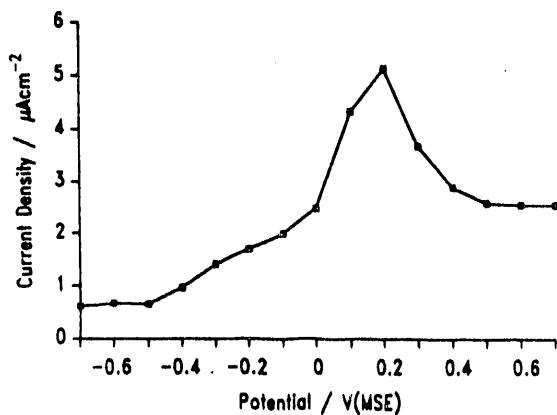


Fig. 5 Current densities flowing after 3 minutes at each potential for the sample shown in Fig. 4.

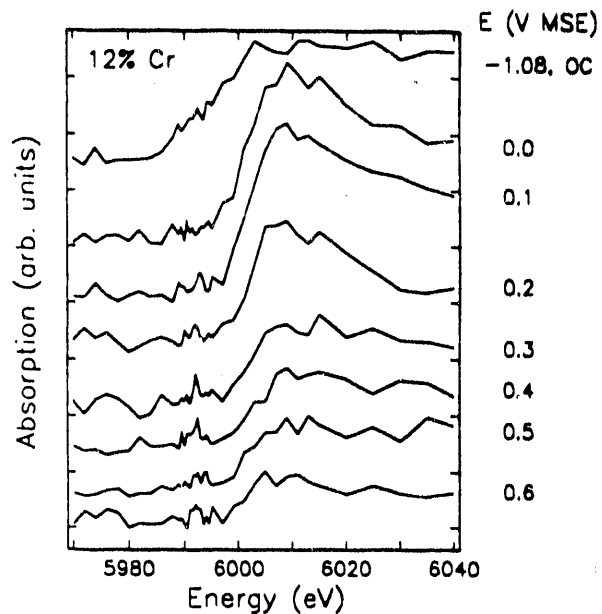


Fig. 6 Cr K edge for Al-12%Cr (20Å) at the potentials shown during stepwise polarization from open circuit.

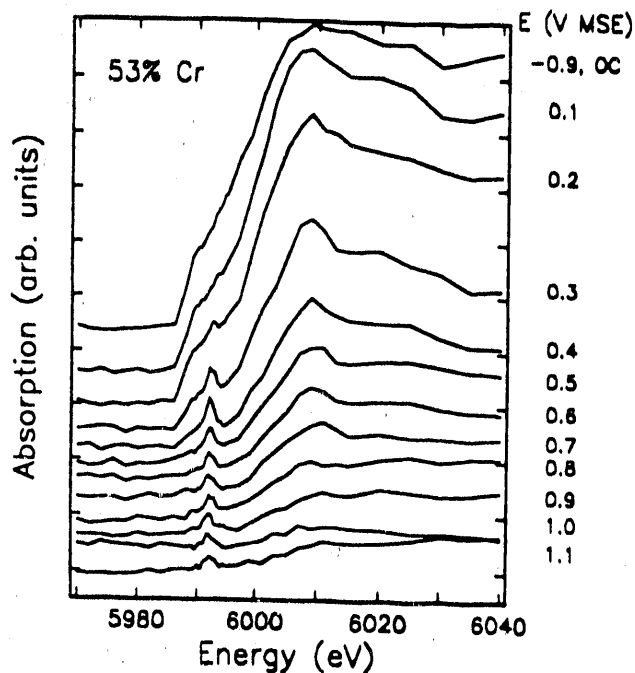


Fig. 7 Cr K edge for Al-53%Cr (20Å) at the potentials shown during stepwise polarization from open circuit.

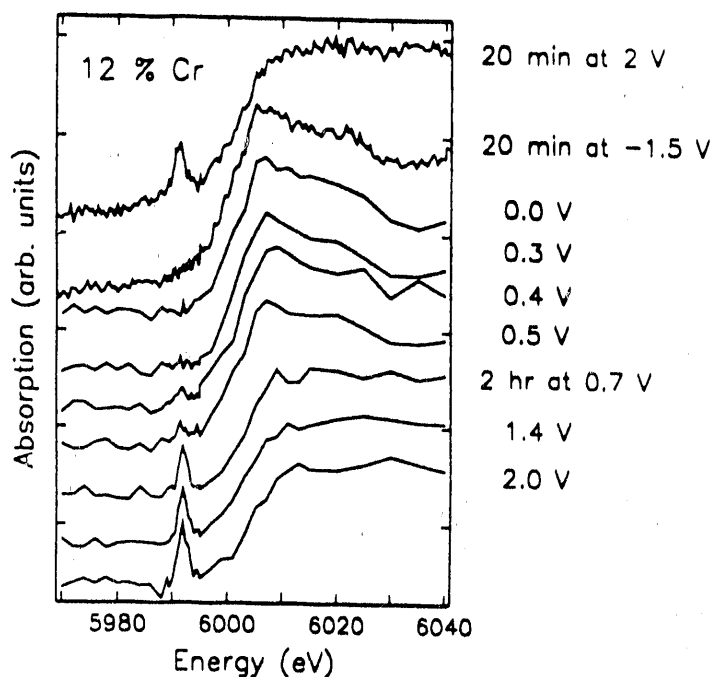


Fig. 8 Cr K edge for Al-12%Cr alloy which has been polarized at +2V(MSE), then polarized at -1.5V(MSE) and then stepped at 100mV intervals from -0.5V(MSE) to +0.7V(MSE) where the potential was maintained for 2 hours and then stepped in 200mV intervals from +0.8V(MSE) to 2V(MSE). Edges are shown for selected potentials.

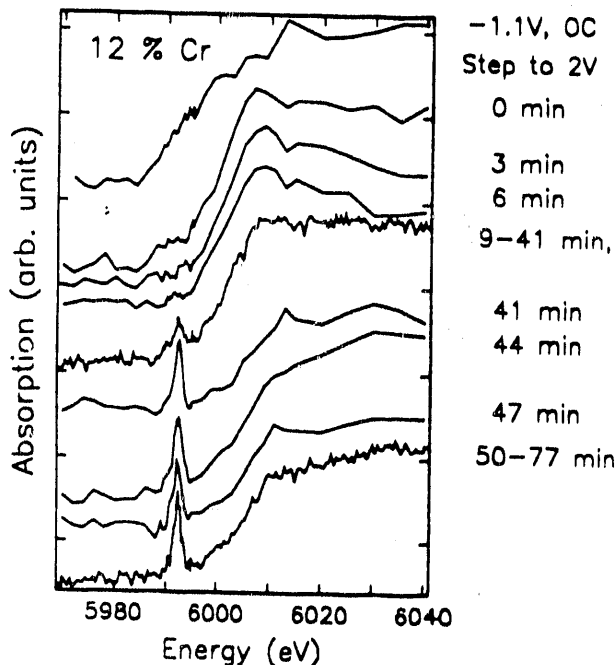


Fig. 9 Cr K edge for Al-12%Cr alloy. The potential was stepped from open circuit to 2V(MSE) and edges were collected at the times indicated.

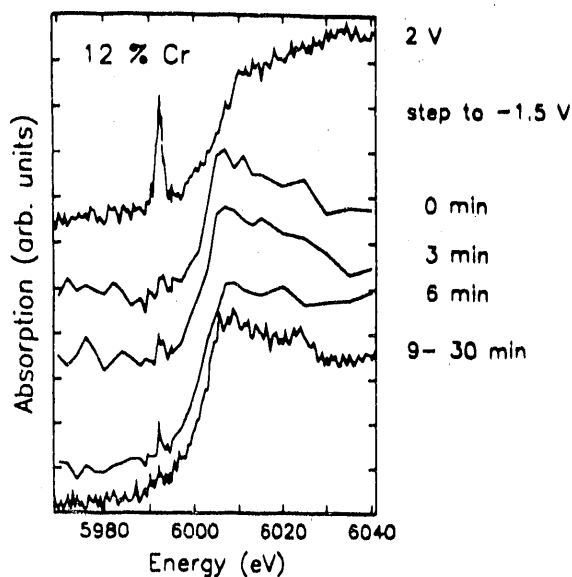


Fig. 10 Continuation of the experiment shown in Fig. 9. The last edge of Fig. 9 has been replotted as the first of Fig. 10. The potential was stepped from +2V(MSE) to -1.5V(MSE) and edges were collected at the times indicated.

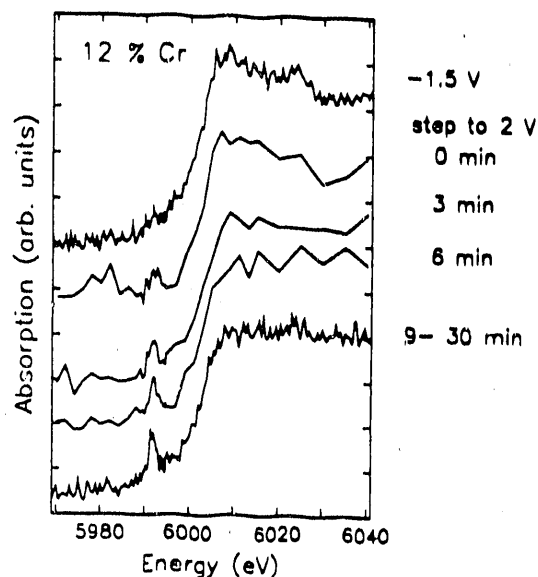


Fig. 11 Continuation of the experiment shown in Figs. 9 and 10. The last edge of Fig. 10 has been replotted as the first of Fig. 11. The potential was stepped from -1.5V(MSE) to +2V(MSE) and edges were collected at the times indicated.

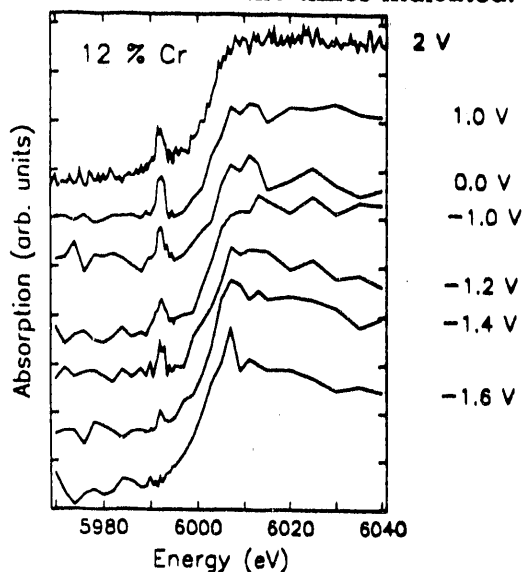


Fig. 12 Continuation of the experiment shown in Figs. 9-11. The last edge of Fig. 11 has been replotted as the first of Fig. 12. The potential was stepped from +2V(MSE) down to -1.6V(MSE) in 200mV intervals.

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