

An X-ray Photoelectron Spectroscopic Study of Some Chromium–Oxygen Systems

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A series of pure and mixed chromium standards has been analysed by x-ray photoelectron spectroscopy in order to obtain a sufficiently homogeneous and self-consistent set of spectral parameters to be used in the resolution of complex spectra. Additional information was obtained about the stability of the various species under Ar ion bombardment. The results relevant to potassium chromate and dichromate, chromous acid, chromium (III) oxide, hydroxide and nitrate are described and compared critically with those in the published literature.

INTRODUCTION

A study¹⁻³ was initiated recently in order to characterize the corrosion behaviour of stainless steel under nitric acid vapour attack. Specimens of 304L austenitic stainless steel were seasoned for different periods of time in the vapour phase of aqueous, concentrated, boiling acid and analysed by x-ray photoelectron spectroscopy (XPS). Particular attention was paid to the identification of Cr(III) and Cr(VI) species since they are known to enhance the corrosion of some steels in nitric acid solutions.^{4,5} According to the latter studies, aimed at testing the corrosion behaviour of materials used in spent nuclear-fuel processing plants, several oxidizing ions (such as Ru(VIII), Rh(IV), I(VII), Ce(IV), V(V)) exhibit the same effect but in the former work,¹⁻³ performed under inactive experimental conditions, i.e. in the absence of the fuel, only Cr and Fe ions were present, with Cr ions producing the greater effects.

Unfortunately, despite the fact that many investigations have been aimed at the XPS characterization of various Cr compounds (see for example Refs 6-19), disagreement still exists about the relevant spectroscopic parameters.

In order to obtain a self-consistent set of spectroscopic data to be used in the resolution of complex Cr XPS spectra, e.g. relevant to the above mentioned steel specimens, a series of Cr standards was analysed. The results are described in this paper and compared with previous measurements.

EXPERIMENTAL

Cr(III) oxide (99.999%) and Cr metal (99.99%) were obtained from Ventron GmbH, Cr(III) hydroxide, Cr(III) nitrate, and chromous acid (chromium oxide hydroxide) from ICN Biomedicals Inc., and potassium dichromate and potassium chromate (reagent grade) from Carlo Erba.

Chemicals (pure or mixed) were pulverized in agate mortars and pressed to form thin pellets. They were mounted either by pressing into indium foil or by sticking on to a conducting adhesive-coated copper tape (3M, UK). Each powder specimen was analysed at least in duplicate. When necessary, specimens were sputtered with argon ions to test their stability or to remove possible surface impurities, and oxides in the case of the metal.

The spectrometers used in this work were a VG ESCALAB MK2 (Harwell) and a Leybold-Heraeus LHS10 (Bari). Most of the spectra were excited with unmonochromatized Al K α radiation (1486.6 eV), but a few were excited by unmonochromatized Mg K α radiation (1253.6 eV). Pressure in the analysis chamber was always lower than 5×10^{-9} mbar. Only when analysing chromium nitrate containing specimens did the pressure range between 10^{-7} and 10^{-8} mbar. The fixed analysis transmission (FAT) mode was always used for detailed spectra, at a pass energy of 50 eV.

Data analysis was performed with an in-house data processing program,²⁰ which allowed smoothing, satellite and structured background subtraction, resolution and synthesis of spectra, etc. to be carried out. Curve fitting was carried out by adding background and satellite contributions to the various bare doublets and then comparing the result with the raw data. The degree of fit was evaluated via the χ^2 test. Mixed Gaussian/Lorentzian sum functions were used to construct symmetric peak shapes. Asymmetric peak shapes (necessary to account only for Cr metal contributions, e.g. doublets 1 + 2 in Figs 2 and 9), were obtained by using different half-width at half-maximum (HWHM) values and different G/L mixing ratios on the left and right wings of the peaks. FW in Table 1 is the sum of the left and right HWHMs.

The increasing slope of the Shirley background at the highest kinetic energy (KE) values in some figures (see for example Figs 2 and 9) is due to the fact that the software allows the resulting background plus the satellite contributions²⁰ to be plotted. The KE values in the figures are not corrected for surface charging.

Table 1. Spectral parameters of some chromium standards

	Chromium 2p _{3/2} FW†	Chromium 2p _{1/2} FW†	R	Oxygen 1s FW	Notes‡	Ref.
K ₂ Cr ₂ O ₇	580.8	1.9			a Mg	6
	579.4	2.3		530.0	b* Al	7
	579.8				b Al	11
	579.4	1.9	2.4	529.8	b AlMg	tw
Na ₂ Cr ₂ O ₇	579.4	2.0		530.0	b* Al	7
K ₂ CrO ₄	579.6	1.8		530.0	b* Al	7
	579.7	1.7	2.1	530.2	b Al	tw
Na ₂ CrO ₄	579.8	2.0		530.3	b* Al	7
	580.5			531.1	b* AlMg	19
Cr ₂ O ₃	578.4	3.1			a Mg	6
	576.8	3.0		530.5	b* Al	7
	576.8			530.8	b Al	11
	576.52			529.98	c Al	12
	576.6			530.1	c Al	13
	576.8	3.2	3.4	530.4	d Al	14
	577.3				b* Al	15
	576.2				d Al	16
	577.2				d* Al	18
	576.6	3.2	3.5	530.1	b AlMg	tw
HCrO ₂	577.0			531.4	b Al	11
	576.9	3.0	3.3	531.2	b Al	tw
Cr(OH) ₃	577.03			530.85	c Al	12
	578.5			532.5	b* Al	15
	577.0	3.2	3.5	530.8	b Al	tw
Cr(NO ₃) ₃	577.3	3.1	3.3	532.1	b Al	tw
Cr metal	574.14				c Al	12
	574.2				c Al	13
	574.6				b* Al	15
	574.8				d* Al	18
	574.4				b* Al	19
	574.2	2.0	2.2	533.5	b AlMg	tw

tw = this work.

* The reference BE used by the authors is different from that used here (the BEs quoted in the table have been adjusted accordingly).

‡ The letters indicate that (a) the energy axis was not calibrated, (b) reference was to the Au 4f level (84.0 eV), (c) reference was to the Fermi level, and (d) reference was to the C 1s level (285.0 eV).

† Left and right G/L mixing ratio for symmetric peak shapes was 0.85 ± 0.10 . Right-hand G/L ratio for metallic peaks was 0.67 ± 0.8 ; left-hand G/L ratio for metallic peaks, zero. FW is the sum of left and right HWHMs.

The binding energies (BE) obtained in this work are referenced to the Au 4f_{7/2} level (84.0 eV). The experimental uncertainties in the table are assumed to be ± 0.1 eV on BE, $\pm 10\%$ on the spin-orbit area ratio (R) and ± 0.2 eV on FW values.

Sensitivity factors derived by Wagner *et al.*²¹ were used when comparing the results of applying the curve fitting procedure to the Cr 2p and O 1s regions from the same specimen, recorded by the LHS10 spectrometer, since it is known²² that the analyser transmission function in that system varies with the inverse of the photoelectron KE, i.e. has the same dependence as that used by Wagner *et al.* This limited quantification, used only as a check on the curve fitting, is not reported here.

X-ray diffraction measurements were performed by a Siemens D500 x-ray powder diffraction system in the Materials Characterization Service at Harwell.

RESULTS AND DISCUSSION

Cr metal

Cr metal sheets were sputtered with Ar ions at 5.0 kV until the O 1s signal was virtually absent. The parameters of the 'clean' metal are listed in Table 1. They are in good agreement with the data of Asami and Hashimoto¹² and of Allen *et al.*¹³

Cr metal + Cr(III) oxide

It is known¹³ that Cr surfaces are converted to Cr(III) oxide by exposure to molecular oxygen at high temperature (e.g. 600 K) for prolonged periods. Figure 1 reports some spectra from the Cr 2p region of clean Cr

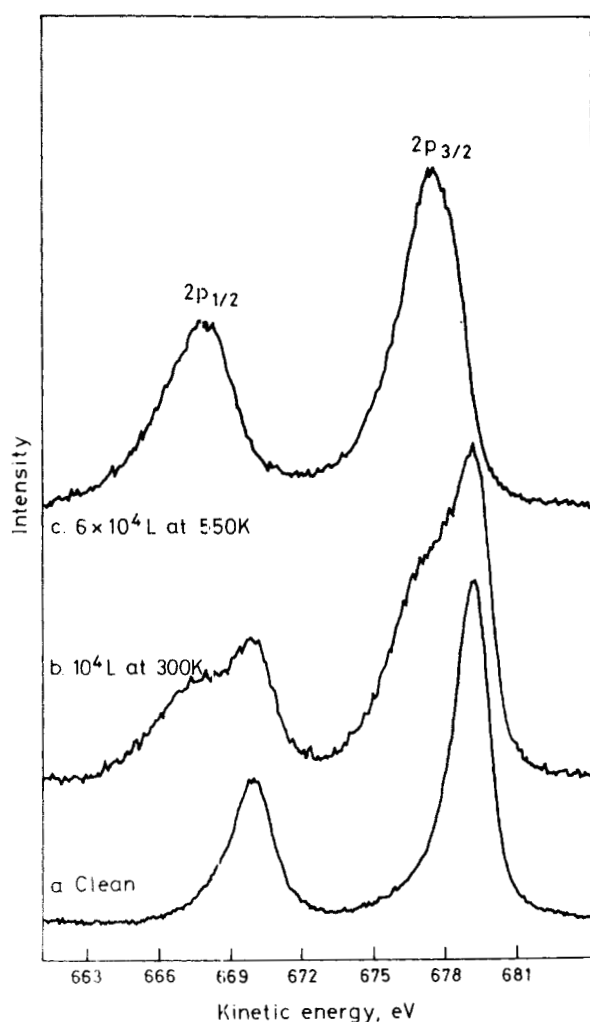


Figure 1. Mg K_{α} -excited spectra of the Cr 2p region of a Cr metal sheet exposed to different oxygen doses. (a) 0 L at room temperature (any initial trace of oxide was removed by sputtering with Ar ions); (b) 10^4 L at room temperature; (c) 6×10^4 L at 550 K.

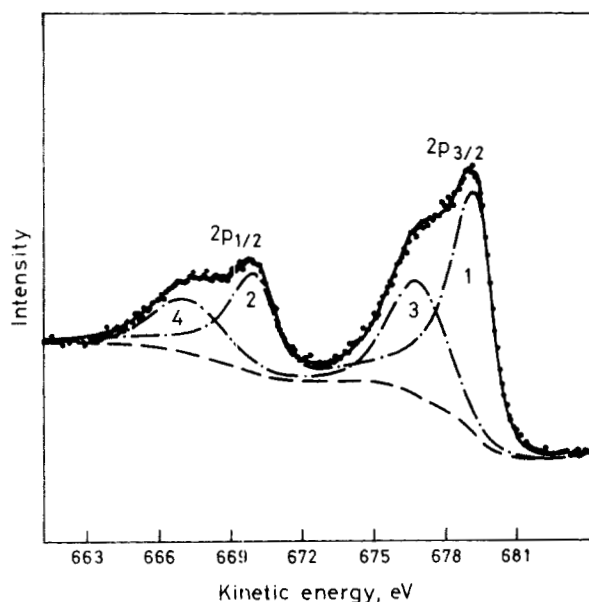


Figure 2. Resolution of spectrum b in Fig. 1. Doublets 1 + 2 and 3 + 4 arise from metallic Cr and Cr(III) oxide, respectively.

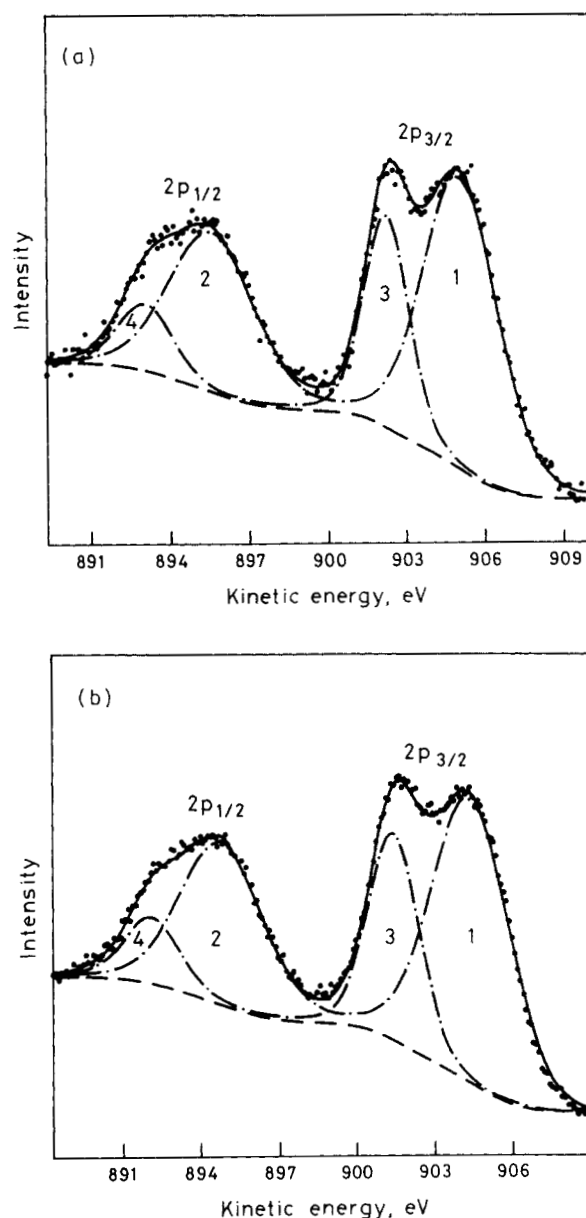


Figure 3. Al K_{α} -excited spectra of the Cr 2p region of a mixed Cr(III) oxide + potassium dichromate powder specimen (a) and of a potassium dichromate specimen sputtered with 3.0 kV argon ions for 10 s (b). Doublets 1 + 2; Cr(III) oxide; doublets 3 + 4; potassium dichromate.

metal sheet after exposure to dry molecular oxygen at different partial pressures in the temperature range 300–550 K (exposures are given in Langmuir* units).

The Cr(III)–Cr(0) chemical shift obtained by analysing these spectra (see an example in Fig. 2) is 2.4 eV and is in good agreement with the values previously reported.^{12,13,18} This chemical shift does not change appreciably under irradiation with flood electrons at 10 eV, as expected in the absence of any differential charging effect on the specimen surface.

The spectral parameters of Cr(III) oxide, obtained by analysing pure powder specimens, are reported in Table 1. The absolute BE values of the Cr $2p_{3/2}$ and 0 1s levels are in reasonable agreement with those previously reported.^{7,11–14} The spin-orbit area ratio (R) of

* 1 L = 10^{-6} Torr · s.

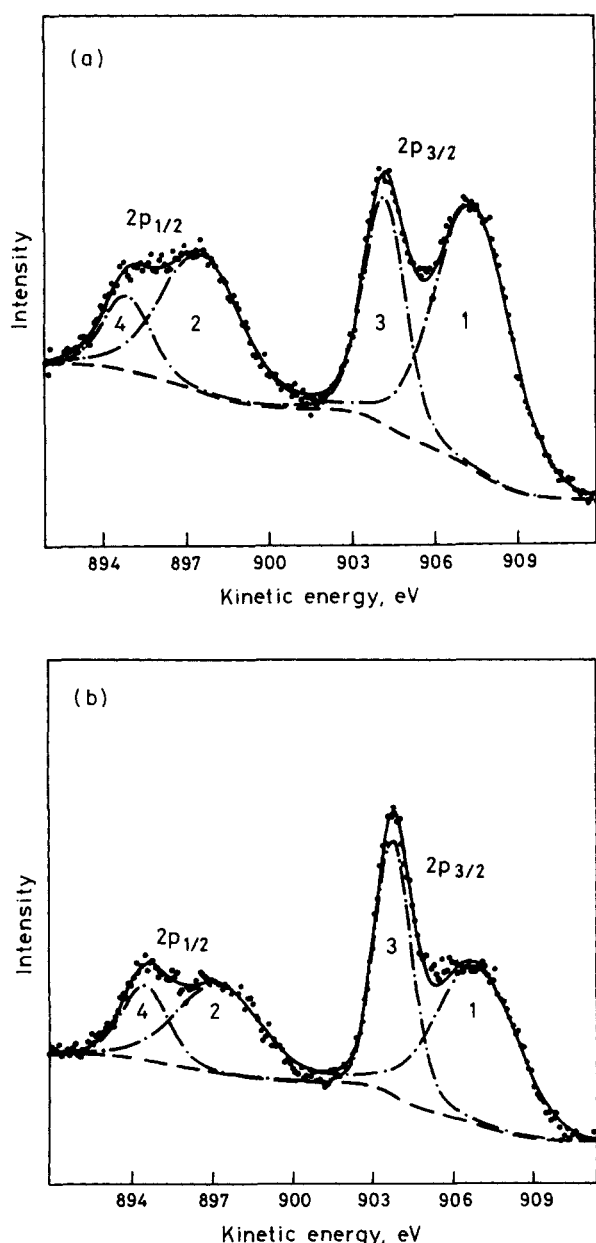


Figure 4. Al K_{α} -excited spectra of the Cr 2p region of a mixed Cr(III) oxide + potassium chromate powder specimen (a) and of a potassium chromate specimen sputtered with 3.0 kV argon ions for 10 s (b). Doublets 1 + 2; Cr(III) oxide: doublets 2 + 4; potassium chromate.

the Cr 2p level in Cr(III) oxide, as well as in all the Cr(III) species, is slightly lower than the theoretical value. The probable reason for this has been suggested by Ikemoto *et al.*,¹¹ that is, the $2p_{1/2}$ intensity is increased by the presence of a satellite associated with the $2p_{3/2}$. Cr(III) 2p spectra have strong shake-up structure at about 11 eV from the parent peak,^{11,14,15} whereas the spin-orbit splitting is ≈ 9.8 eV and thus comparable to the satellite separation.

According to the literature²³ no degradation is observed for Cr(III) oxide under Ar ion bombardment (at least up to 10 min at 5 kV). It is known,²⁴ however, that Cr(III) can be partly reduced to Cr(O) by sputtering with sufficiently high ion current density.

Potassium dichromate and chromate + Cr(III) oxide

The attribution of an absolute BE to the Cr $2p_{3/2}$ level in potassium dichromate was obtained by analysing a specimen prepared by mixing with Cr(III) oxide [see Fig. 3(a)]. To evaluate possible differential charging of the mixed powders, the specimen was also analysed both by operating the x-ray source at half-power, and by flooding the specimen with electrons at 10.0 eV, but even under these experimental conditions no appreciable variation of the chemical shift, 2.8 eV, could be observed. It was consequently assumed throughout this work that these mixed specimens are characterized by a practically homogeneous surface charge.

The spectral parameters obtained by analysing pure potassium dichromate are in good agreement with the values reported by Allen *et al.*⁷ The BE of the Cr $2p_{3/2}$ level in potassium chromate is 0.3 eV higher than in the dichromate (compare the peak positions in the dichromate + Cr(III) oxide and chromate + Cr(III) oxide mixed specimens reported in Figs 3(a) and 4(a)). This value is also in good agreement with those previously reported (0.2 and 0.4 eV for potassium and sodium dichromate, respectively: see Ref. 7 or Table 1).

The experimental spin-orbit area ratios (2.7 and 2.6, see Table 1), of the Cr(VI) 2p levels, obtained from spectra from the pure specimens, are higher than in theory. These values are comparable to those reported by Helmer⁶ and by Ikemoto *et al.*¹¹ for the spin-orbit intensity (i.e. peak height) ratio, 3.0, if it is remembered that the FW of the $2p_{1/2}$ peak is always slightly greater than that of the $2p_{3/2}$. No explanation of such an expected finding was put forward by those authors, and none is proffered here, nor for the unusually high ratio found also (Table 1) for Cr(O).

There is fairly good general agreement between the reported spin-orbit splittings and the FWs of the peaks, and those found here. Traces of Cr(III) always seemed to be present in the otherwise pure Cr(VI) specimens and could possibly be ascribed to the known¹⁰ reduction effects under x-ray irradiation.

The Cr 2p region from a potassium dichromate specimen sputtered for 10 s at 3.0 eV (compare Fig. 3) shows that Cr(VI) is reduced to Cr(III) oxide even under rather soft bombardment doses. As can be seen in Fig. 4, potassium chromate exhibits the same behaviour.

Cr(III) hydroxide + chromate

Figure 5 shows the Cr 2p region in the spectrum from a mixed chromate + hydroxide specimen. The BE of the Cr $2p_{3/2}$ level in the hydroxide is 2.7 eV lower than in the chromate. Chromium hydroxide parameters, obtained from the analysis of pure or mixed specimens, are reported in Table 1. They are in reasonable agreement with those of Ref. 12.

The chemical shift obtained between the Cr 2p levels in the Cr(III) oxide and hydroxide is 0.4 eV (see Table 1) which is in good agreement with that reported by Asami *et al.*¹²

No degradation could be found for chromium hydroxide under moderate ion bombardment doses (a few minutes at 3.0 kV).

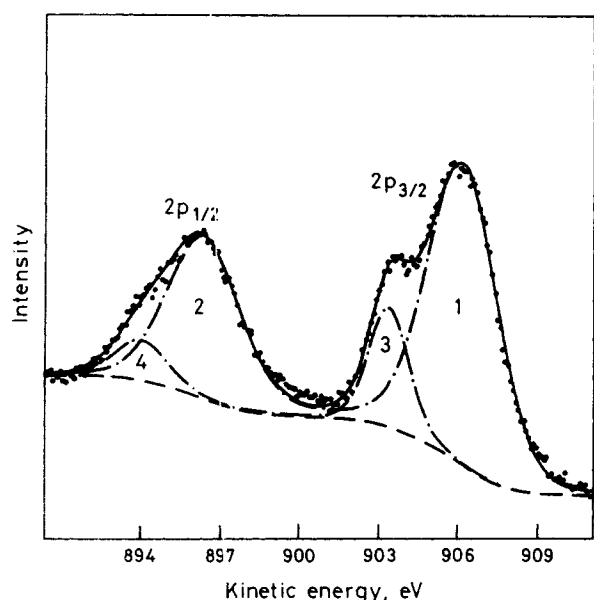


Figure 5. Al K_{α} -excited spectrum of the Cr 2p region of a potassium chromate + chromium hydroxide mixed specimen. Doublets 1 + 2 and 3 + 4 arise from hydroxide and chromate, respectively.

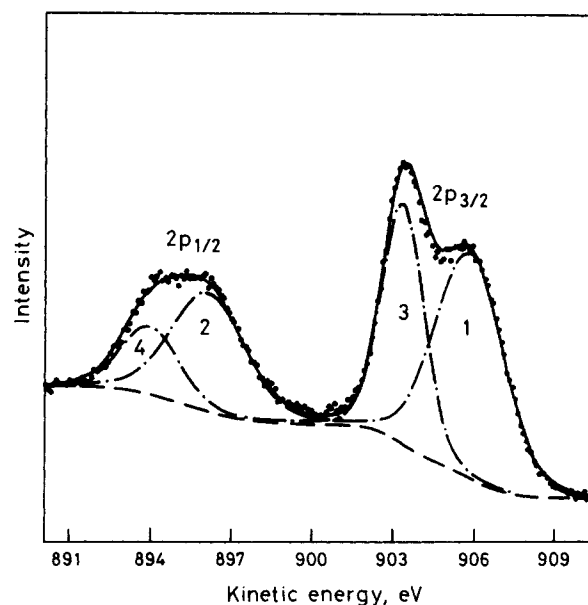


Figure 7. Al K_{α} -excited spectrum of the Cr 2p region of a mixed chromous acid + potassium dichromate specimen. Doublets 1 + 2 and 3 + 4 arise from the acid and dichromate, respectively.

Chromous acid (chromium oxide hydroxide) + dichromate

Since various chromium oxide hydroxides are known²⁵ the specimen was characterized by x-ray diffraction (see Fig. 6.) The results indicated that the compound was the hexagonal (rhombohedral) α form.²⁶

The Cr 2p region of a chromous acid + dichromate specimen is shown in Fig. 7. The parameters of the pure standard are listed in Table 1 and are in good agreement with those of Ref. 11. Chromous acid exhibits a

stability similar to that of Cr(III) oxide under Ar ion sputtering.

Cr(III) nitrate + dichromate

As far as we know no spectral information exists for Cr(III) nitrate. The analysed salt is likely to be the purple, monoclinic $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ but some uncertainty exists about the actual formula. This salt in fact melts at 333 K and decomposes above 373 K under ambient pressure. According to thermogravimetric

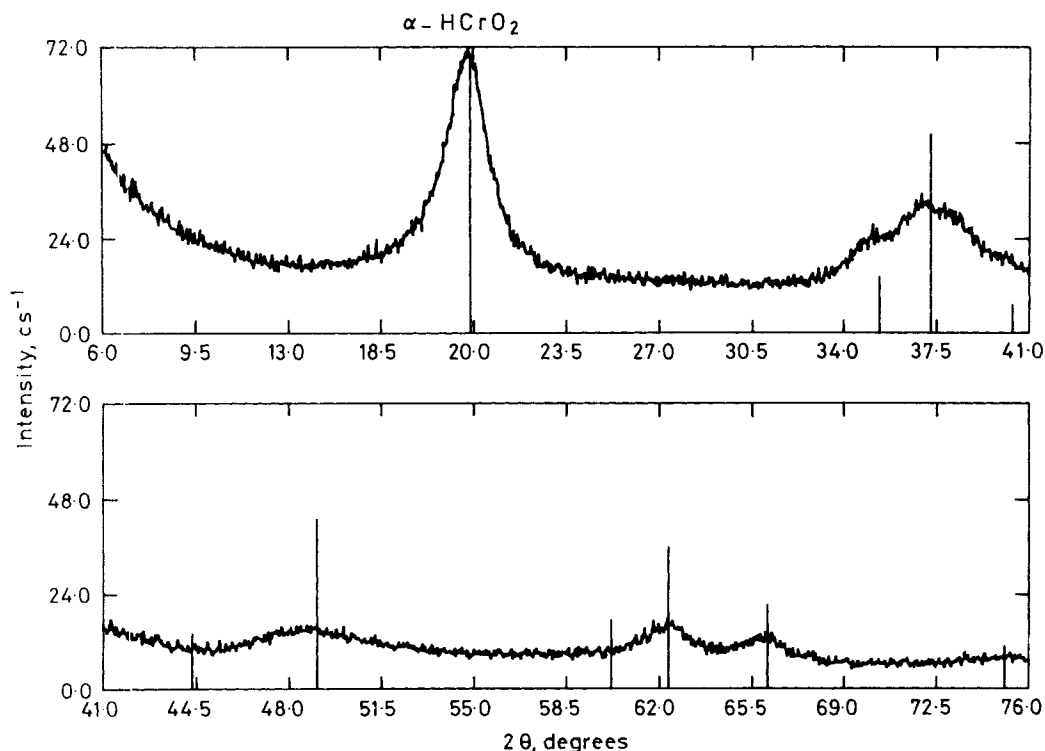


Figure 6. X-ray diffractogram of chromous acid. The diffraction pattern of the powder was excited by Cu K_{α} (1.5418 Å) radiation. The positions and intensities of lines from an $\alpha\text{-HCrO}_2$ standard are indicated.

analysis,²⁷ the salt can release water and reddish vapours upon heating, to give a green, basic oxynitrate. Unfortunately no information is available about its behaviour under ultra-high vacuum conditions. The rather high pressure in the analysis chamber in the course of the analysis of this compound (see the Experimental section) seems to suggest that there was some gaseous emission by the salt under UHV conditions.

Figure 8 reports the Cr 2p region of the salt mixed with potassium dichromate: the observed chemical shift of the Cr 2p_{3/2} level is 2.1 eV. The spectral parameters of chromium nitrate are reported in Table 1.

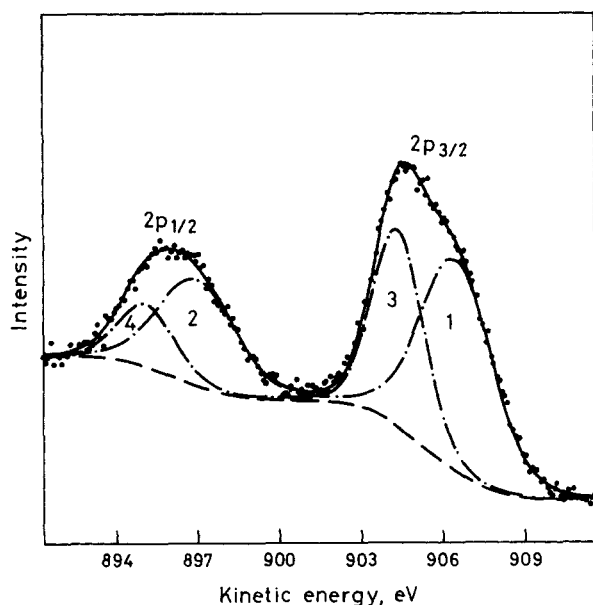


Figure 8. Al K_α-excited spectrum of the Cr 2p region of a mixed chromium nitrate (doublet 1 + 2) + potassium dichromate (doublet 3 + 4) specimen.

Cr(O) + Cr(III) + Cr(VI)

A specimen of Cr(O) + Cr(III) + Cr(VI), obtained by evaporating a droplet of a slightly acidic solution of potassium dichromate on a Cr metal sheet, was analysed with Mg K_α excitation. To compensate for possible surface charging the analysis was repeated with electron flooding at 10 eV (at two different current densities) and/or by mounting the specimen on an insulating Teflon holder. The results did not change appreciably thus indicating that the deposit was thin enough to avoid any differential charging.

An example of these spectra is given in Fig. 9. The fit to the data does not, of course, represent the 'perfect' solution but only the best one within the limits of the experimental procedure and of our present knowledge. As can be seen, an acceptable result requires the presence of Cr in at least four different chemical states. The right-hand doublet can be attributed to the metal. The doublet 2.4 eV to the left of the metal spectrum can be attributed to Cr(III) oxide. This could have been produced either by exposure of the clean Cr sheet to the atmosphere (when adding the dichromate solution) or by direct oxidation by the dichromate itself. The doublet 0.4 eV to the left of the oxide is attributed to Cr(III) hydroxide. The left-hand doublet is 2.5 eV distant from the Cr(III) oxide and is attributed to the dichromate. The Cr(VI)–Cr(III) oxide chemical shift is slightly lower than that previously observed by mixing potassium dichromate and Cr(III) oxide (i.e. 2.8 eV). The difference can perhaps be interpreted in terms of different lattice environments: the thickness of the specimen was much lower than in the case of the mixed powders (see earlier) and in this case the dichromate was present on a metal substrate together with oxyhydroxy-Cr(III) species (see Fig. 9).

The presence of Cr(V) or (IV) does not seem very likely. According to the literature the BEs of the Cr

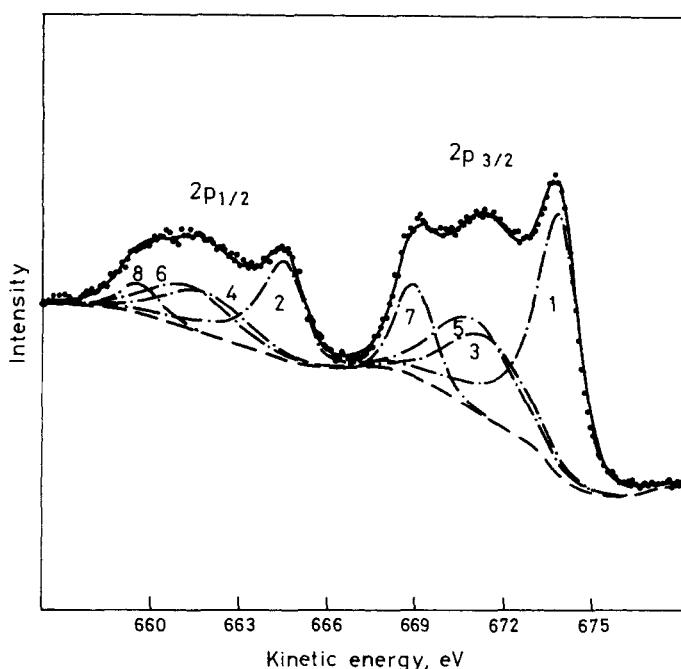


Figure 9. Mg K_α-excited spectrum of the Cr 2p region of a specimen prepared by evaporating an acidic solution of potassium dichromate on to a metallic Cr sheet supported by a teflon insulating holder. Doublet 1 + 2; Cr metal; doublet 3 + 4; Cr(III) oxide; doublet 5 + 6; Cr(III) hydroxide; doublet 7 + 8; potassium dichromate.

$2p_{3/2}$ level in Na_3CrO_4 and Na_4CrO_4 are 2.0 eV and 2.6 eV, respectively, lower than in sodium dichromate¹⁹ while in Cr(IV) oxide the BE is 3.5 eV lower than in potassium dichromate.¹¹ This means that Cr(IV) oxide exhibits an anomalous behaviour, having a BE 0.7 eV lower than in Cr(III) oxide.¹¹ On the other hand the presence of Cr(IV) oxide is very unlikely since, as far as we know, it can be obtained only by thermal decomposition processes at very high pressures (see for example Ref. 28).

CONCLUSIONS

An exhaustive comparison is not possible since none of the cited authors has reported data for all the standards analysed in this work. Nevertheless it is found that an overall general agreement exists between the spectroscopic parameters obtained here and those reported by

Allen *et al.*,^{7,13} Ikemoto *et al.*,¹¹ and Asami and Hashimoto.¹²

Even if the list of standards in Table 1 is far from being exhaustive, the set of experimental parameters collected here, measured in an internally self-consistent way, will allow better evaluation of the literature on Cr and provide useful information for the analysis of steels and other complex materials containing Cr in different states of oxidation.

Acknowledgements

This work was carried out with the financial assistance of the Ministero della Pubblica Istruzione (M.P.I. Rome, Italy), the British Council (Rome, Italy) and the Consiglio Nazionale delle Ricerche (C.N.R. Rome, Italy), and formed part of the UKAEA Underlying Research Programme. The authors are indebted to Dr L. S. Welch, Mr V. J. Moore and Mr R. A. Bartram, of the Surface Analysis Section at Harwell, for valuable assistance.

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