X-RAY PHOTOELECTRON SPECTROSCOPY STUFY IN THE ANODIC PASSIVITY OF SPUTTER-DEPOSITED NANOCRYSTALLINE W-Cr ALLOYS IN 12 M HCl

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INTRODUCTION

The formation of anodic passive films on alloys has gained great scientific interest for a long time. It is important from a practical point of view that the anodic film causes the passivity. Passivating elements such as chromium and tungsten can improve corrosion resistance of alloy. The properties of anodic films formed on tungsten in a number of solutions have been studied by Heumann and Stolica (1971); El-Basiouney et.al. (1981). Di Qarto et al. (1983) in reporting photoelectrochemical studies have stated that anodic film formed on tungsten shows a duplex structure consisting of an inner amorphous barrier-type anodic WO_3 film and an outer porous crystalline layer.

On the other hand, chromium is one of the most effective alloying elements to provide high passivating ability for conventional steels and nickel-base alloys. Naka et al., (1979) reported the remarkably high corrosion resistance of amorphous Fe-Cr- metalloid metallic alloys. Only a small amount of chromium (8at%) addition was enough to cause passivity in 1 M HCl and these alloys showed significantly higher pitting corrosion resistance than stainless steels. It was reported that a thin oxide containing a high concentration of chromium enhances the stability of ferritic stainless in aggressive chloride solutions (Elfstrom, 1980).

Recently, a new approach to the roles of alloying elements in the passivation of alloys has been reported by Marcus (1994) which are based on two fundamental properties of metals, namely, the heat of adsorption of oxygen of OH and the heat of sublimation of the metal. Therefore, a subtle balance between these properties of the metal is crucial in the selection of allying constituents for the binary alloys enhancing passivation. Chromium corresponds to a passivity promoter, and shows such unique properties as a relatively high heat of adsorption of oxygen (737 kJ mol^{-1}) (Tanaka and Tumura, 1963) and a relatively low chromium-chromium bond strength (99 kJ mol^{-1}) (Marcus, 1994). On the other hand, tungsten is known as the dissolution moderator or blocker with a high heat of adsorption of oxygen (819 kJ mol^{-1}) (Tanaka and Tamura, 1963) and high tungsten-tungsten bond strength (212 kJ mol^{-1}) (Marcus, 1994). It is, therefore, very interesting to study the role of tungsten in the anodic passivity of W-Cr alloys in aggressive environments.

Furthermore, some of the present authors have been reported that the high corrosion resistance of sputter-deposited nanocrystalline W-Cr alloys in 12 M HCl is based on the formation of new passive double oxhydroxide films of tetravalent tungsten and Cr^{3+} (Bhattarai et.al., 1997; Bhattari et.al. 1998.a and Bhattari, 1998)

According to Habazaki et.al. (1992), the passive film on tungsten is tetravalent tungsten oxyhydroxide, and hexavalent tungsten oxyhydroxide is not the true passive film. However, the transpassivation of tungsten is clearly different from that of chromium and molybdenum. Tranpassivation of chromium and molybdenum results in a sharp increases in the anodic current density. By contrast, Bhattarai (1998) has been sown in polarization curves of tungsten metal and tungsten alloys that the oxidation from the tetravalent state to the hexavalent state of tungsten alloys that the oxidation from the tetravalent state to the hexavalent state of tungsten did not lead to the transpassivation, although the anodic current density was significantly high. Therefore, it is interesting to study the potential dependence of the surface composition of the passive films formed on the W-Cr alloys to clarify mechanisms of the passivity of W-Cr alloys in hydrochloric acids.

The main objectives of the present study are to characterize the composition and structure of anodic passive films formed on the sputter-deposited binary W-xCr (x=25,57 and 91 at%) alloys after potentiostatic polarzation in 12 M HCl at 30°C by electrochemical measurements and X-ray photoelectron spectroscopy (XPS) analysis.

EXPERIMENTAL METHODS

The W- xCr (x=25, 57 and 91 at %) alloys were prepared by direct current (D.C.) magnetron sputtering on glass plants as described elsewhere (Bhattari, 1998). An electron probe microanalysis (EPMA) was used to determine the composition of the sputter deposits. The structure of sputter--deposited W- Cr alloys was confirmed as nanocrystalline by X-ray diffraction (Bhattarai et. al., 1998.a).

Prior to immersion tests and XPS analyses the surface of specimens was polished mechanically with silicon carbide paper up to grit 1500 in cyclohexane, rinsed with acetone and dried in air. Open circuit immersion and potentiostatic polarzation at several potentials for 1 h in 12 M CHl at 30°C. Open to air were carried out. A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrons, respectively. All the potentials given in this paper are relative to SCE.

Before and after immersion or potentiostaic polarzation, compositions of the surface film and the underlying alloy surface were analyzed by XPS using a Shimadzu ESCA-850 photoelectron spectrometer. A vacuum of the XPS spectra over a wide binding energy region (0-100 eV) exhibited peaks of carbon. chlorine, oxygen, tungsten, and chromium. The most intense peaks of the C ls Cl 2p, O is W 4f and Cr 2p electrons were measured in the binding energy range of 20 eV for all the spectra. The binding energies of electrons were calibrated using the method described elsewhere (Asami, 1976; Asami and Hashimoto, 1977). The binding energies of the Au-$4f_{7/2}$ and $4f_{5/2}$ electrons of gold metal and Cu $2p_{1/2}$ and $2p_{1/2}$ electrons of copper metal were taken as 84.07, 87. 74 and 923.53 and 952. 35 eV, receptively, and the kinetic energy of the Cu L3M4,5 M4,5 Augur electrons of copper was taken as 918.65 eV (Asami, 1976). The peak binding energies of each peak were further corrected using the value of energy of C is level (285 eV) for contaminant hydrocarbons. The composition and thickness of the surface films and the composition of the underlying alloy surface were quantitatively determined by a previously proposed method (Asami et.al., 1977) using integrated intensities of photoelectrons under the assumption of a three layer model of the outermost contaminant hydrocarbon layer of uniform thickness, the surface film of uniform thickness and the underlying alloy surface of X-ray photoelectron spectroscopically infinite thickness. The photoionization cross-section of the W 4f and Cr 2p3/2 electrons relative to the O ls electrons used were 2.97 (Kawashima et al., 1984) and 1.71 (Asami and Hashimoto, 1977) respectively.

RESULTS

ELECTROCHEMICAL MEASUREMENTS

Potentiostatic polarization measurements were carried out for nanocrystalline W -Cr alloys to gain a better understanding of the anodic passivity of the alloys after potentiostatic polarzation for 1 h in 12 M HCl at 30°. Figure 1 shows the change in anodic current density of the W-57 Cr alloys as a function of polarzation time. The current density of the alloy decreases with polarisation time till about 5 minutes and becomes almost steady. The same trend of the continuous decrease in the anodic current densities with the polarization time is observed for W -25Cr and W-91 Cr alloys. Accordingly, the protective quality of the anodic passive films formed on the W-Cr alloy increases with polarzation time in 12 M HCl.

Figure 2 shows potentiostatic ploarzation curves for the W-Cr alloys after potentiostatic polarzation for 1 in 12 M HCl at 30° C. Increasing chromium content of the alloys gives rise to the ennoblement of the open circuit potential indicating that open circuit corrosion occurs in the potential regions where tungsten is oxidzed to w^{6+} and the passive region of chromium. The anodic current density decreases with increasing chromium content in the W-Cr alloys. The lowest anodic passive current density is observed for the W-91 Cr alloy. The potentials of the transpassive dissolution of the W-Cr alloys decrease with increasing chromium content. The W-57Cr alloys show high current densities at 1.2. V (SCE) and 1.0 V (SCE) or high potentials, respectively, due to the transpassivation of chromium.

SURFACE COMPOSITION OF ANODIC PASSIVE FILM

The surface analyses of the films formed on the alloys give an important information for a better understanding of the synergistic effect of tungsten and chromium in the anodic passivity of the W-Cr alloys. For this purpose, the surface of the W -Cr alloys before and after immersion or potentiostatic polarzation for 1 h in 12 M HCl at 30° C was analyzed by XPS technique. XPS spectra for W- Cr alloys over a wide binding energy region exhibited peaks of tungsten, chromium, oxygen, chlorine and carbon. The C is spectrum arose from a contaminant hydrocarbon layer covering the specimen surface. For the specimen polarized or immersed in 12 M HCI the Cl 2p spectrum was detected at about 1999.0 eV, which comes from chloride ions. However, the intensity of the Cl 2p peak was very low. Therefore the concentration of chloride ions is not considered in the calculation.

The O ls is spectrum is composed of two peaks; the lower binding energy peak at 530.2-531.1 eV is assigned to OM oxygen, and the higher binding energy peak at 532.1-533.1 eV arises from OH oxygen (Asami and Hahimoto, 1977; Asami et al., 1977). The OM oxygen corresponds to O^{2-} ions in oxyhydroxide and/or oxide. The OH oxygen is oxygen linked to hydrogen and is composed of OH ions and bound water in the surface film. An example of an deconvolution of the O ls spectrum measured for W-57 Cr alloy is shown in Fig 3, The O^{2-} peak is substantially more intense than the OH peak in the O ls spectrum measured for the W-57 Cr alloy after immersion for l h in 12 m HCl. Accordingly, the passive films formed spontaneously on the alloy consist of oxyhydroxide in which O^{2-} ion is the major oxygen species.

The spectra from W-Cr alloys constituents indicated the presence of the oxidzed and metallic species; the former from the surface film and the latter from the underlying alloy surface. The measured spectra of W 4f electrons and Cr $2p_{3/2}$ electrons were separated into W^{ox} and W^0 4f, and Cr^{3+} and C^0 $2p_{3/2}$ state spectra, respectively. The superscripts, "ox", "3+" and "0" denote oxidized, trivalent and metallic states, respectively. Figure 4 shows an example of the deconvolution of the W 4f spectrum measured for the W-57 Cr alloy after immersion for l h in 12 M HCl at 30°C. Four doublets of the overlapped peaks can be identified in the W 4f spectrum, that is, three doublets of $W^{6+}W^{5+}$ and W^{4+} states and a pair of metallic states W0, peaks at about 35.2 and 37.3., 33.2 35.3, 32.2 and 34.3, 30.7 and 32.8 eV, respectively. The integrated intensities of these spectra were separately obtained by the same method as that described elsewhere (Asami et.al., 1986; Bhattarai et.al., 1995; Bhattarai et.al., 1998.b). Figure 5 shows an example of the deconvolution of the Cr 2p spectrum measured for the W-57 Cr allot after immersion for l h in 12 M HCl at 30°C. All the measured Cr 2p3/2 spectra are composed of a peak and a shoulder. The higher binding energy peak corresponding tot he CR^{3+} $2p_{3/2}$ state appears at 576/7 eV and the lower binding energy shoulder corresponding to the Cr^0 $2p_{3/2}$ state appears at 573/7 eV/. After integrated intensified of the spectra for individual specious were obtained, the thickness and composition of the surface film and the composition of the underlying alloy surface were determined quantitatively by using previously proposed method (Asami et.al., 1977).

The change in the surface composition of the anodic films formed on W-Cr alloys before and after immersion or potenyiostatic polarzation for l h in 12 M HCl at 30°C, open air were analyzed by XPS. Figures 6 (a) and (b) show the cationic fractions in the surface films and atomic fractions in the underlying alloy surface films and atomic fractions in the underlying alloy surface, respectively, as a function of polarzation potential. The cationic fractions in the air-formed film and atomic fractions in the underlying alloy surface after mechanical polishing are also shown for comparison. Although the enrichment of tungsten is observed in the passive films formed on W-25 Cr and W-57 Cr alloys at open circuit potential and cathodic potentials, anodic polarzation leads to an increase in the chromium content in the passive films and the cationic fractions of chromium ions exceed the alloy composition. The chromium content in the passive film is remarkably concentrated when the alloys are polarized in the passive potential region of chromium. At further higher potentials, the cationic fraction of chromium decreases near the transpassive region of chromium as a result of oxidation of Cr^{3+} to Cr^{6+}, because

Cr^{6+} ions dissolve easily into concentrated hydrochloric acids. By contrast, this complicated phenomenon is not clearly observed for the W-91Cr alloy. The cationic fraction of chromium is slightly decreased with potential near the transpassive region of chromium, while the cationic fraction of chromium is slightly concentrated in both spontaneously passivated and anodic passive films formed on the W-91Cr alloy. The chromium content of the underlying alloy surface slightly increases with polazrization potential for all alloys.

As mentioned above in Fig. 3, the passive films formed spontaneously on the W-57Cr alloy consist of oxyhydroxides of cations in which 0^{2-} ion is a major oxygen species. Fig. 7 shows the quantitative results of the ratios of [OH^-]/[cations] and [$O2^-$}/[cations] in the anodic passive films formed on the W-57Cr alloy, as a function of potential. The ratio of [OH^-]/[cations] and [O^{2-}]/[cations] in for comparison. The anodic passive films formed on the alloy consist of oxyhydroxide in which O^{2-} ion is significantly higher than OH^- ion in all potential. The ratio of [OH^-]/[cations] slightly decreases with potentials, while the ratio of [O^{2-}]/[cations] slightly increases with increasing the anodic polarzation. This is the general trend observed for W-25Cr and W-91 Cr alloys in 12 M HCl at 30°C. Accordingly, the anodic passive films formed on the W-Cr alloys are composed of oxhydroxides of both tungsten and chromium ions in which O^{2-} ion is remarkably higher than OH^- ion.

ANODIC FILM THICKING AND DISTRIBUTION OF TUNGSTEN IONS

The anodic polarization leads to thickening of the anodic passive films for all tungsten alloys in hydrochloric acids. According to Bhattari (1998), remarkable anodic film thickening of the sputter-deposited binary tungsten-valve metal alloys was observed at +0.4 V (SEC) or higher potentials. The distribution of both cations of the binary tungsten alloys in the anodic passive films play an important role in the film thickening of the alloys. Similarly, the change in different oxidation states of tungsten ions in the anodic film greatly affects the film thickening. Therefore, effects of cations of ally-constituting elements, i.e., tungsten ions and Cr^{3+} ions, in the anodic thickening of W-Cr alloys are discussed in detail.

Figure 8 shows the change in the thickness of the films formed on the W-25Cr, W-57Cr and W-91Cr alloys before and after immersion or polarzation for 1 h in 12 M HCl at 30°C. The air-formed films on the W-25Cr and W-57Cr alloys are slightly thicker than the passive films formed after plarzation at potentials lower than 0.4V (SCE), although the air-formed film formed on the W-91Cr alloy is almost the same as the passive films formed after polarzation at low potentials in 12 M HCl. The andoic polarization leads to thickening of the anodic passive film. In particular, the anodic film thickening is clearly observed in the anodic potential range between +o.4 and 1.2 V (SCE).

Figures 9(a) and (b) show the change in the weight of cations in films formed on W-25Cr and W-91Cr alloys, respectively, as a function of potential. The weight of both cations of tungsten and chromium increases with anodic polarzation. As shown in Fig. 8 film thinking is clearly observed with anodic polarization on the

W-Cr alloys, although the cationic fractions in the surface film are almost constant, particularly on the W-91Cr alloy (Fig.6). Consequently, both tungsten ions and Cr^{3+} ions contribute for anodic film thickening of W-Cr alloys.

Furthermore, distribution of different oxidation sates of tungsten ions in the anodic film may also play an important role on the film thickening of the W-Cr alloys. Figures 10 (a) and 10 (b) show quantitative results of the change in the weights of W^{4+}, W^{5+} and W^{6+} ions in the films formed on W-25 Cr and W-57 Cr alloys, respectively, W^{6+} ions increase with decreasing of W^{4+} and W^{5+} ions with anodic polarzation in 12 M HCl at 30°C. The same trend is observed for the W-91 Cr alloy. Consequently, anodic polarzation results in film thickening due to increases in W^{6+} and Cr^{3+} ions.

CHANGE IN BINDING ENERGY WITH COMPOSITION OF ANODIC FILM

As shown in Figs 10 (a) and 10 (b), the tetravalent tungsten is the main oxidation state of tungsten for W-25Cr and W-57 Cr alloys, respectively, at +0.2 V (SCE) or lower potentials, while the hexavalent tungsten is the main oxidation state of tungsten at +0.4V 9SCE) or higher potentials in 12 M HCl. According to Bhattari et.al. (1998.a), the tetravalent tungsten and trivalent chromium are located very closely in the films formed on the spontaneously passivated W-Cr alloy so as to show the electronic interaction between W^{4+} and Cr^{3+} ions. Furthermore, Fig. 11 shows the change in the binding energies of core electrons, that is W^{6+} 4f $_{7/2}$ and Cr^{3+} $2p_{3/2}$ electrons in the anodic passive film formed on the W-Cr alloys after potentiostatic polarization at 1.0 V (SCE) for 1 h in 12 M HCl, as a function of cationic fractions in the film. The binding energy of W^{6+} $4f_{7/2}$ electrons decreases with the chromium content of the anodic passive film, while that of the Cr^{3+} $2p_{3/2}$ electrons increase with the tungsten content of the film. This implies that charge transfer occurs from Cr^{3+} to W^{6+} ion and hence tungsten and chromium ions are located very closely in the anodic passive film, so as to show the electronic interaction between W^{6+} and Cr^{3+} ions. The same trend of the electronic interaction between W^{6+} and Cr^{3+} ions is observed in the anodic passive film at 0.4 V (SCE). Accordingly, the anodic passive film on W-Cr alloys is not a heterogeneous mixture of tungsten oxhyhydroxide consisting of W^{6+} and Cr^{3+} ions. consequently, the passive films formed on the W-Cr alloys under open circuit condition and at catholic potentials consist of double oxyhydrooxides of W^{4+} and Cr^{3+} ions, and those formed by anodic polarzation consist of W^{6+} and Cr^{3+} ions.

DISCUSSIONS

The anodic current densities of the W-Cr alloys decrease with addition of chromium in 12 M HCl, indicating that the protectiveness of the anodic passive films of W-Cr alloys is better than that of tungsten. The open circuit potentials of W-Cr alloys are shifted to more positive direction than those of alloy-constituting elements after immersion for 1 in 12 M HCl at 30°C.

The passive film composition of W-Cr alloys changes mainly in three regions, that is, the active regions of chromium, the passive and transpassive regions of chromium, and the region where oxidation of W^{4+} to W^{6+} occurs. If the W-Cr alloy is polarized near the active potential regions of chromium, that is between -0.7

V to 0.2 V(SCE) (Bhattarai et al., 1998.a), a significant enrichment of tungsten is observed. Consequently, tungsten is remarkably concentrated in the passive films formed on W-Cr alloys near the active region of chromium in 12 M HCl at 30°C. When tetravalent tungsten is oxidized to hexavalent tungsten by anodic polarztion, the concentration of tungsten ions slightly decreases with increasing the cationic fraction of chromium in the passive films formed of W-25Cr and W-57 Cr alloys. In particular, the chromium content in the passive film is remarkably higher than the alloy composition when W-25Cr and W-57 Cr alloys are polarized in the passive region of chromium. Where tetravalent tungsten is oxidized to hexavalent tungsten. When W-Cr alloys are polarized near the transpassive region of chromium, the concentration of tungsten is slightly increases with decreasing chromium content in the passive film.

The presence of Cr^{3+} ions of corrosion-resistant chromium increases the stability of W4+ ions up to about 0.2 V (SCE), while oxidation of W^{4+} to W^{6+} occurs at about 0.1 V9SCE) on tungsten metal. At the same time, anodic polarzation leads to film thickening of W-Cr alloys in 12 M HCl at 30°C. Both cations of the W-Cr alloys contribute for the anodic film thickening. The main contributor among tungsten ions for the anodic film thickening of the W-Cr alloys is W^{6+} ions, because a relatively stable and sparingly soluble W^{6+} ions increase remarkably in the anodic passive film in the potential region where film thickening is remarkable in 12 M HCl.

CONCLUSIONS

A beneficial effect of tungsten in the passivity of the anodic passive films formed on the sputter-deposited nanocrystalline W-Cr alloys by potentiostatic polarization for 1 h in 12 M HCl at 30°C, has been studied by electrochemical measurements and XPS analysis. The following conclusions are drawn from the results.

(1) The open circuit potential of the W-Cr alloys is ennobled with increasing chromium content of the alloys, and anodic passive current densities of the alloys decrease with addition of chromium.

(2) Alloying with corrosion-resistant chromium extends the stable region of W^{4+} ions in the film. W^{4+} ions are stable up to about 0.2 V (SCE) in the passive films on W-Cr alloys in contrast to the fact that W^{4+} ions are stable at about 0.1 V (SCE) on tungsten metal.

(3) The anodic polarzation at about 0.4 V (SCE) or higher potentials leads to thickening of the anodic passive films for W-Cr alloys, mainly due to an increase in W^{6+} ions in addition to Cr^{3+}.

(4) The quantitative surface analysis by XPS clarifies that the improved passivity of the W-Cr alloys than those of alloy-constituting elements is based on the formation of new anodic passive double oxyhydroxide films composed of W^{6+} and Cr^{3+} ions. These films have higher protectiveness and stability than those of passive oxyhydroside films of alloying elements, that is, oxyhydroxides of hexavalent tungsten and trivalent chromium

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WORKS CITED

Asami, K. (1976), *J. Electron Spectrose*. 9, p. 469.

Asami, K. and K. Hashimoto (1977), *Corros. Sci.* 17, p. 559.

Asami, K., K. Hashimoto and S. Shimodaria (1977), *Corros, Scri,* 17, p. 713.

Asami, K., M.S. De Sa and V. Ashworth, (1986), *Corros. Sci.*, 26 p.15.

Bhattari, J., E. Akiyama, A. Kawashima, K. Asami and K. Hasimoto, (1955), *Corros, Sci.*, 37, p. 2071.

Bhattari, J., E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hasimoto, (1977), In Abstracts of 121st Meeting of Japan Institute of Metals, Sendai, Japan *Abstract No.* 1007, p. 460.

Bhattari, J.(1988), *Tailoring of Corrosion-resistant Tungsten Alloys by Sputtering.*

Bhattari, J., E. Akiyama, H. Habazaki, A. Kawashima, K. Asami, and K. Hasimoto, (1998.a), *Corros, Sci.*, 40, 155.

Bhattarai, J., E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hasimoto, (1998.b), *Corros, Sci.*, 40, p.19.

Di Quarti, F., S. Piazza, and C. Sunseri, (1983), *In Proc. 5th Int. Symp. on Passivity;*

Passivity of Metals and Semiconductors (ed. M. Forment), Bombannes, France.The Societe de Chimie Physique, p. 497.

El-Basiouny, M.S., El-Taibheakel, F. and Hefny, M.M. (1981), *Corrosion,* 37, p. 175.

Elfstrom. B.O. (1980), *Mat. Sci.* Eng., 42, p. 173.

Habazaki, H., A. Kawashima, K. Asami, and K. Hashimoto, (1992), *Corros. Sci.*, 33, p. 225.

Henumann, T.H. and H. Stolica, (1971), *Electrochim*, Acta, 16, p. 643.

Kawashima. A., K. Asami and K. Hashimoto, (1984), *Corros. Sci.*, 24. p. 807.

Marcus, P. (1994), *Corros.* Sci., 36, p. 2155.

Naka. M., K. Hasimoto, A. Inoue and T. Masumoto, (1979), J. *Non-Cryst. Solids*, 31, p. 374.

Tanaka, K. and K. Tamura, (1963), *J. Catalysis*, 31 p. 366.

ANNEX

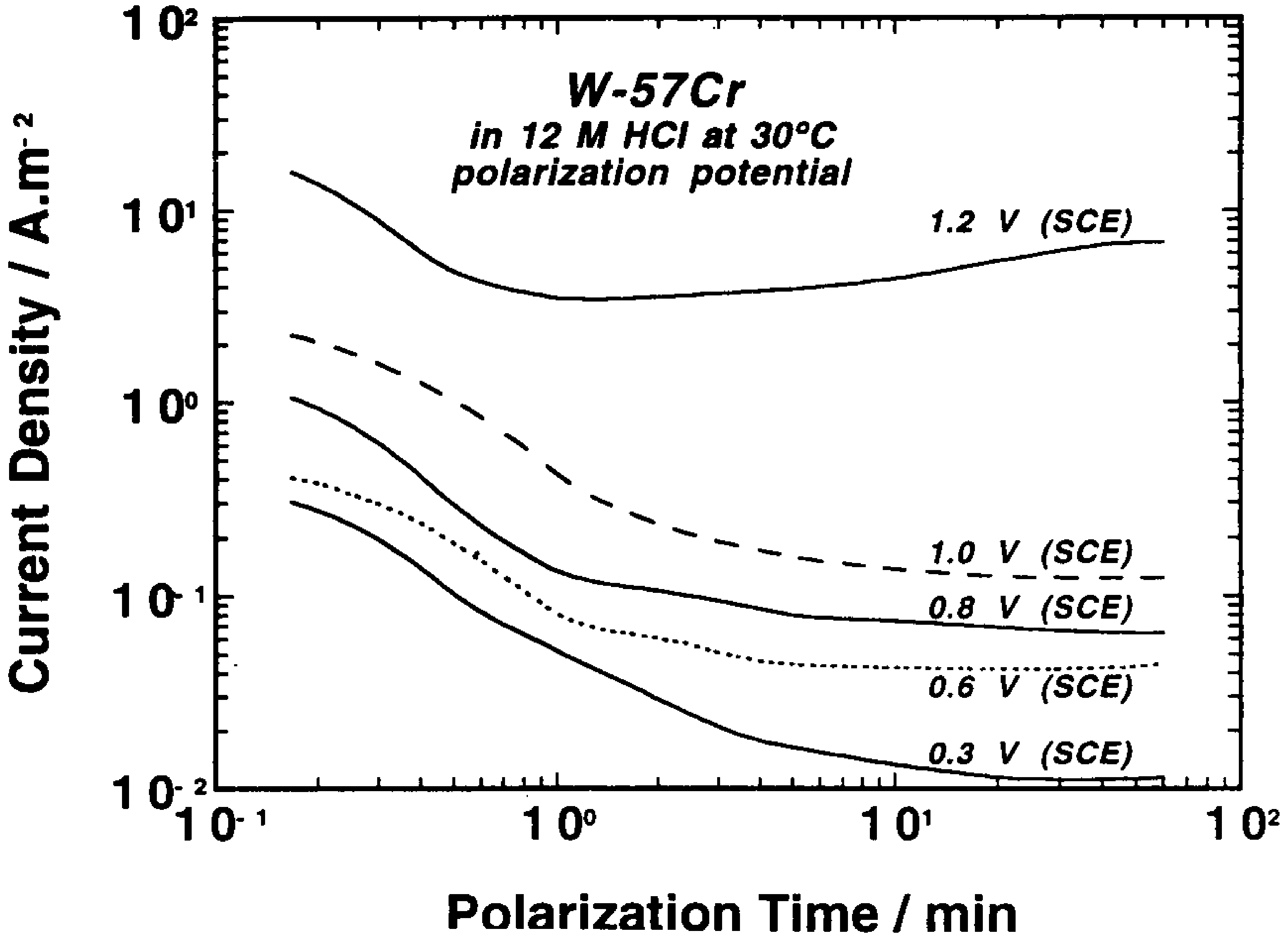

Figure-1: The change in the anodic current density with polarzation time fort he W-57 Cr alloy in 12 M HCl at 30°C.

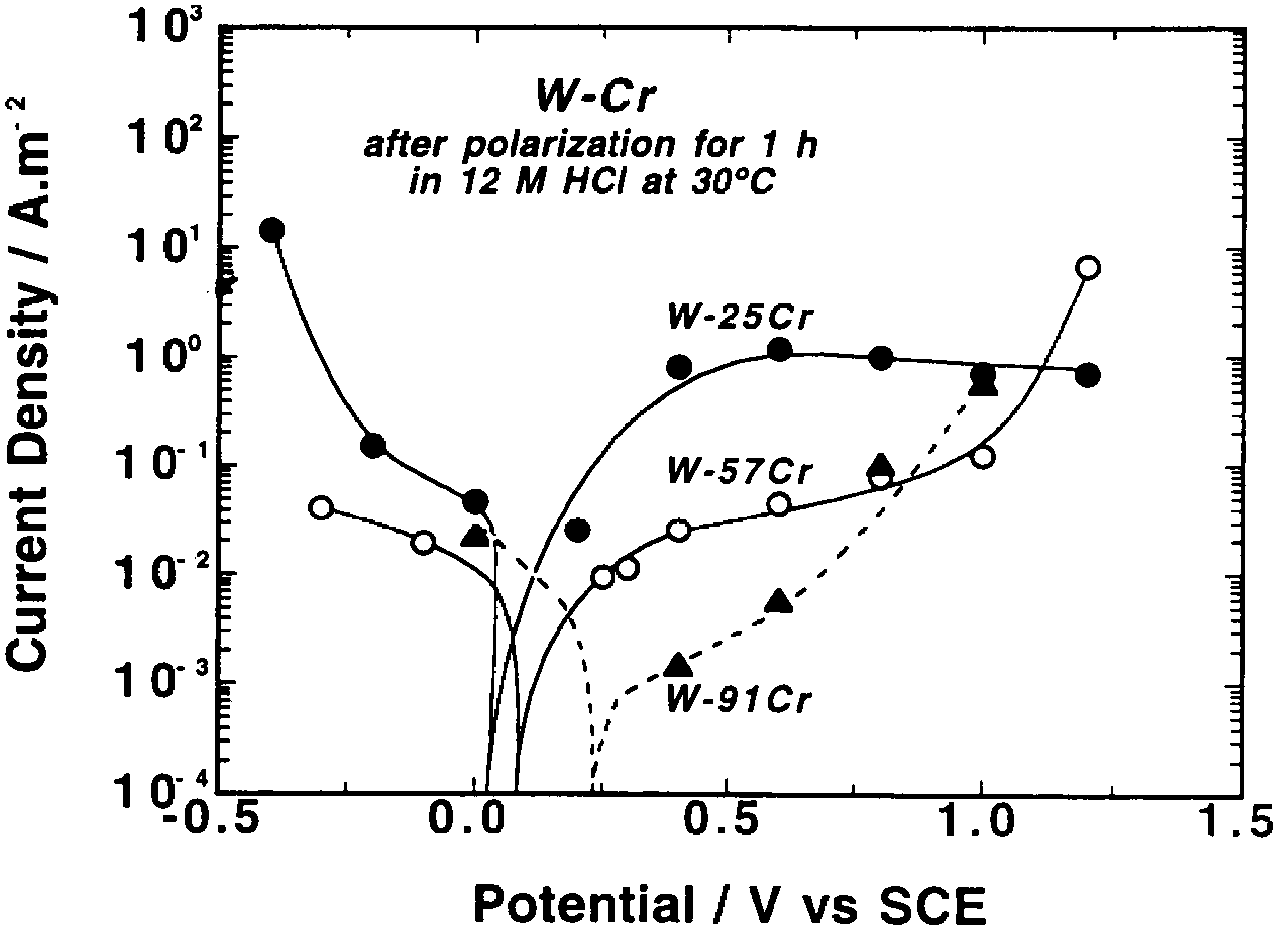

Figure-2. The Potentionstatic polarzation curves of W-25 Cr, W-57 Cr and W-91Cr alloys in 12 M HCl at 30° C.

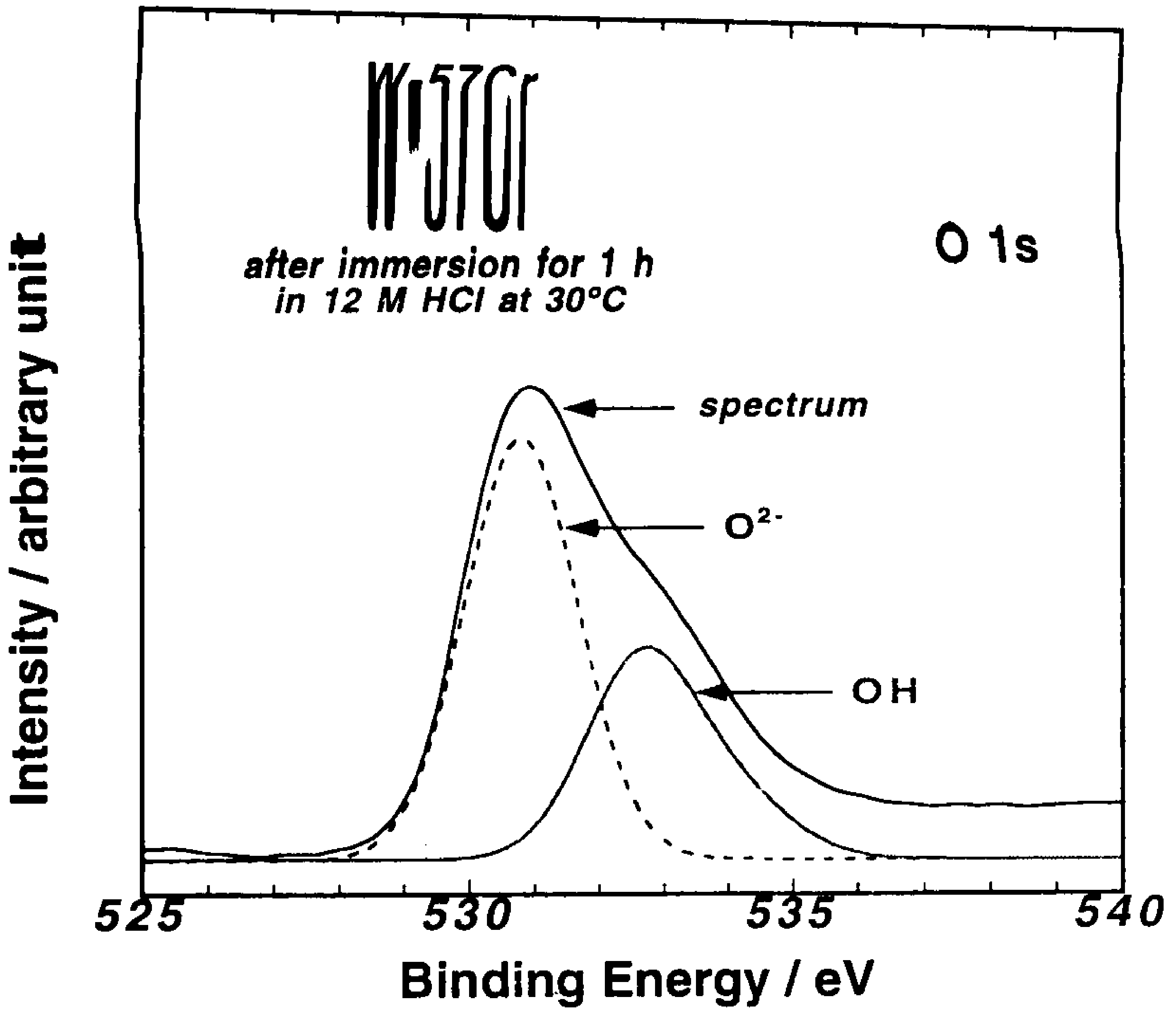

Figure-3. An example of the deconvoolution of the O ls spectrum measured for the W-57 Cr alloy after immersion for 1 h in 12 M HCl at 30° C.

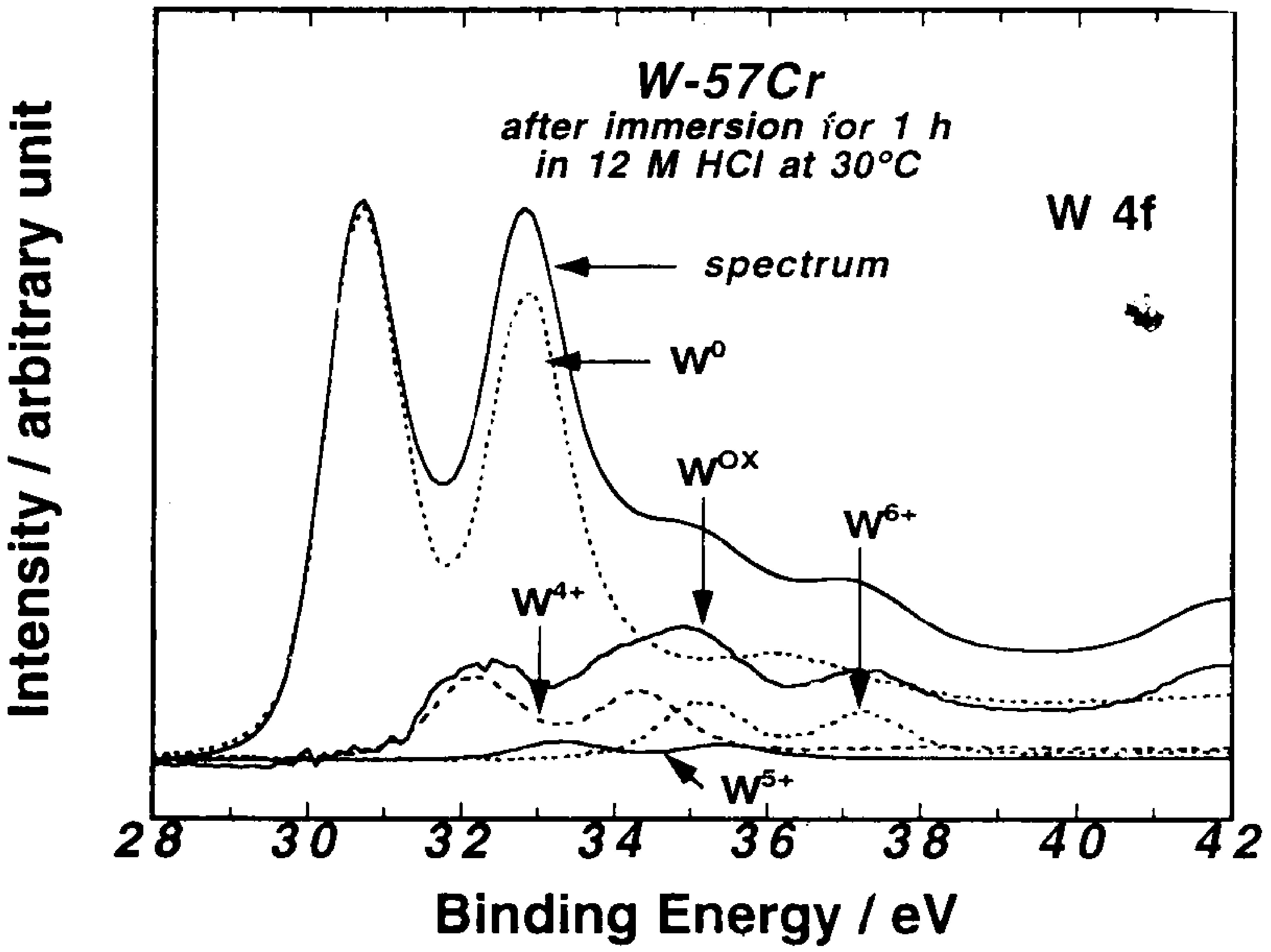

Figure-4. An Example of the deconvolution of the Q 4f spectrum measured for the W- 57 Cr after immersion for 1 h in 12 M HCl at 30° C.

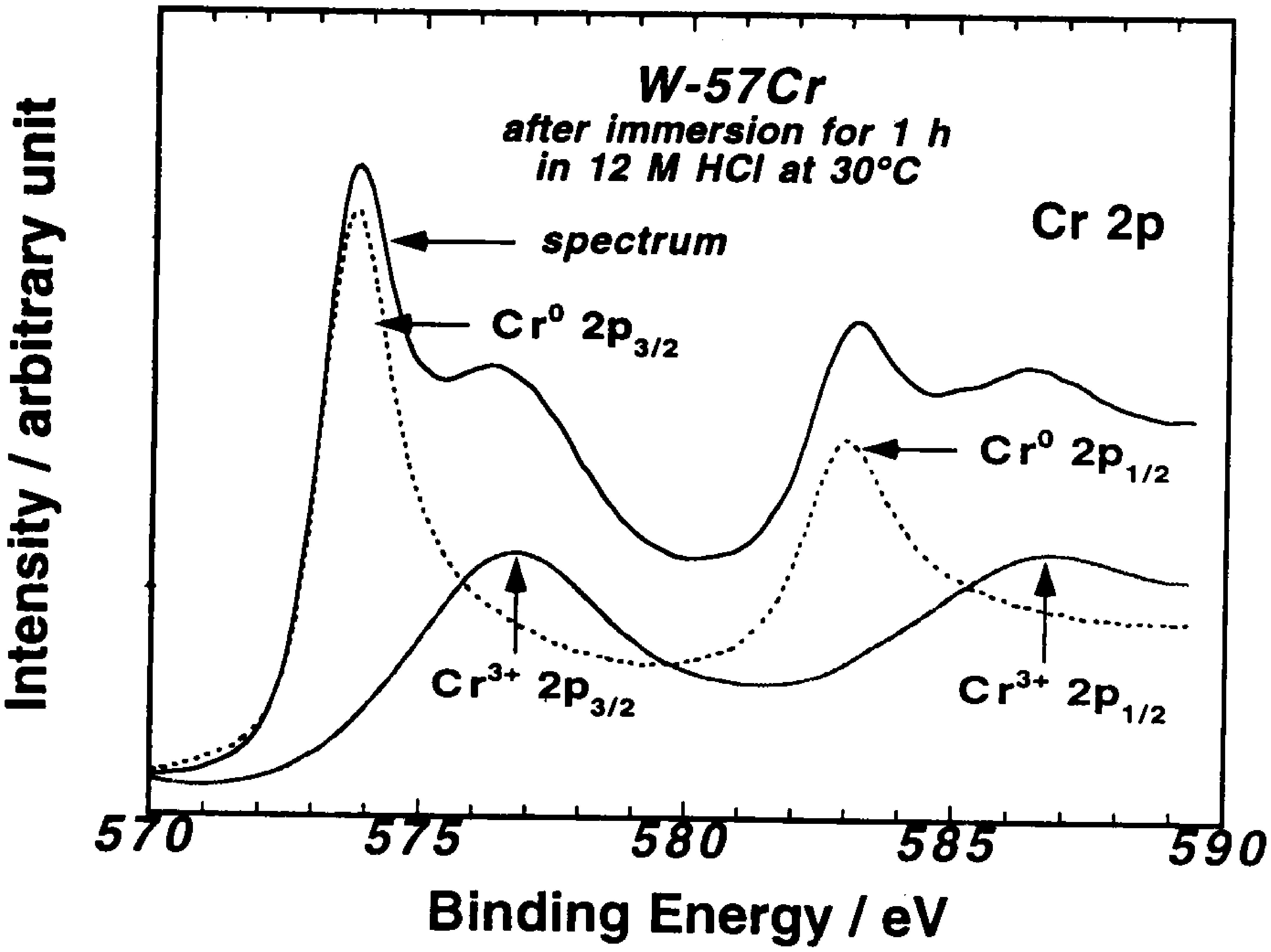

Figure-5. An example of the deconvolution of the Cr 2p spectrum measured for the W-57 Cr after immersion for l h i 12 M Hci at 30° C.

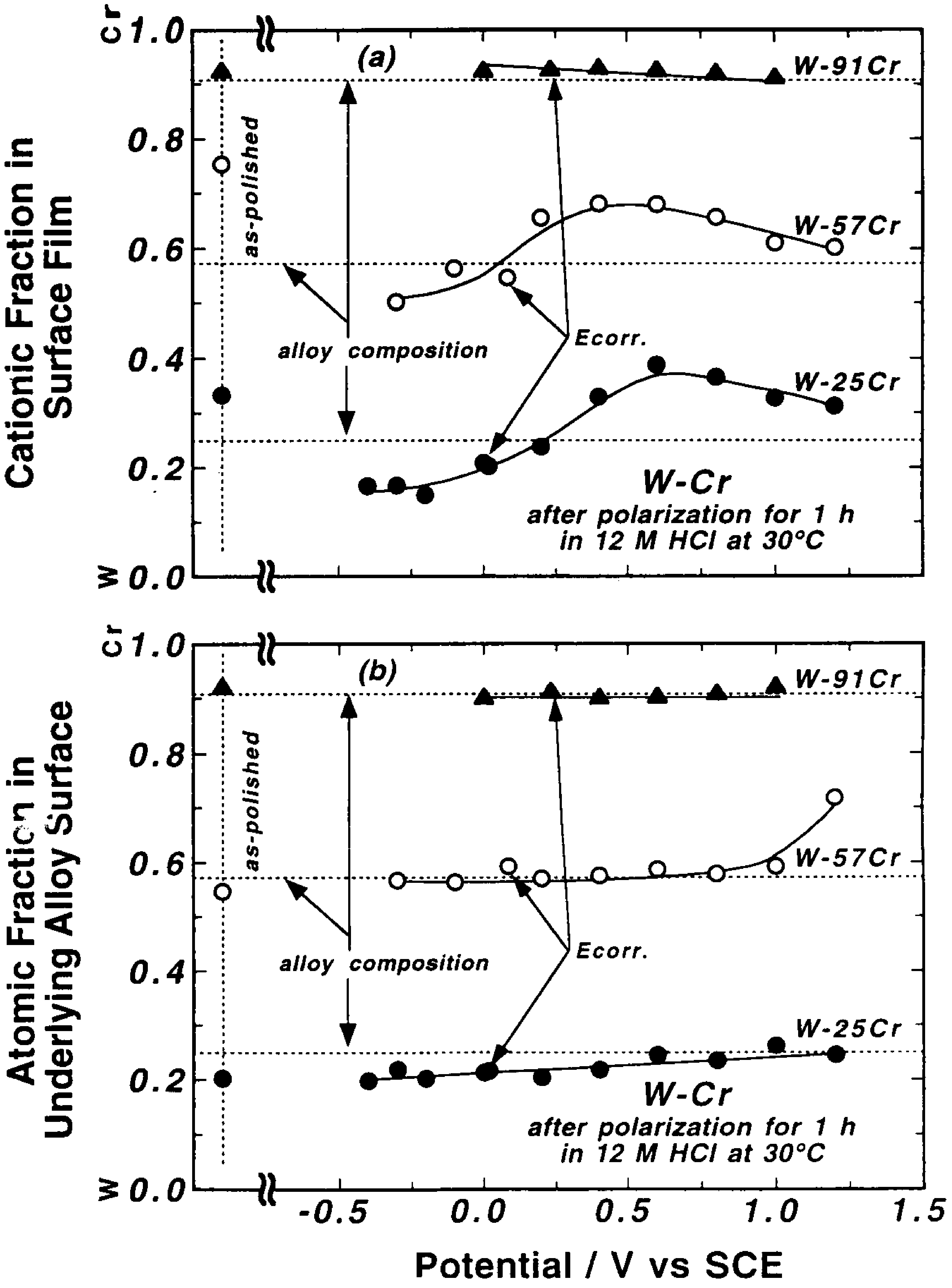

Figure-6. Changes in (a) catuionic fractions in the surface films and (b) atomic fractions in the underlying alloy surface for W- 25Cr, W-57 Cr and W-91 Cr alloys after potentiostatic polarzation for 1 h in 12 M MHl at 30° C, as a function of potential.

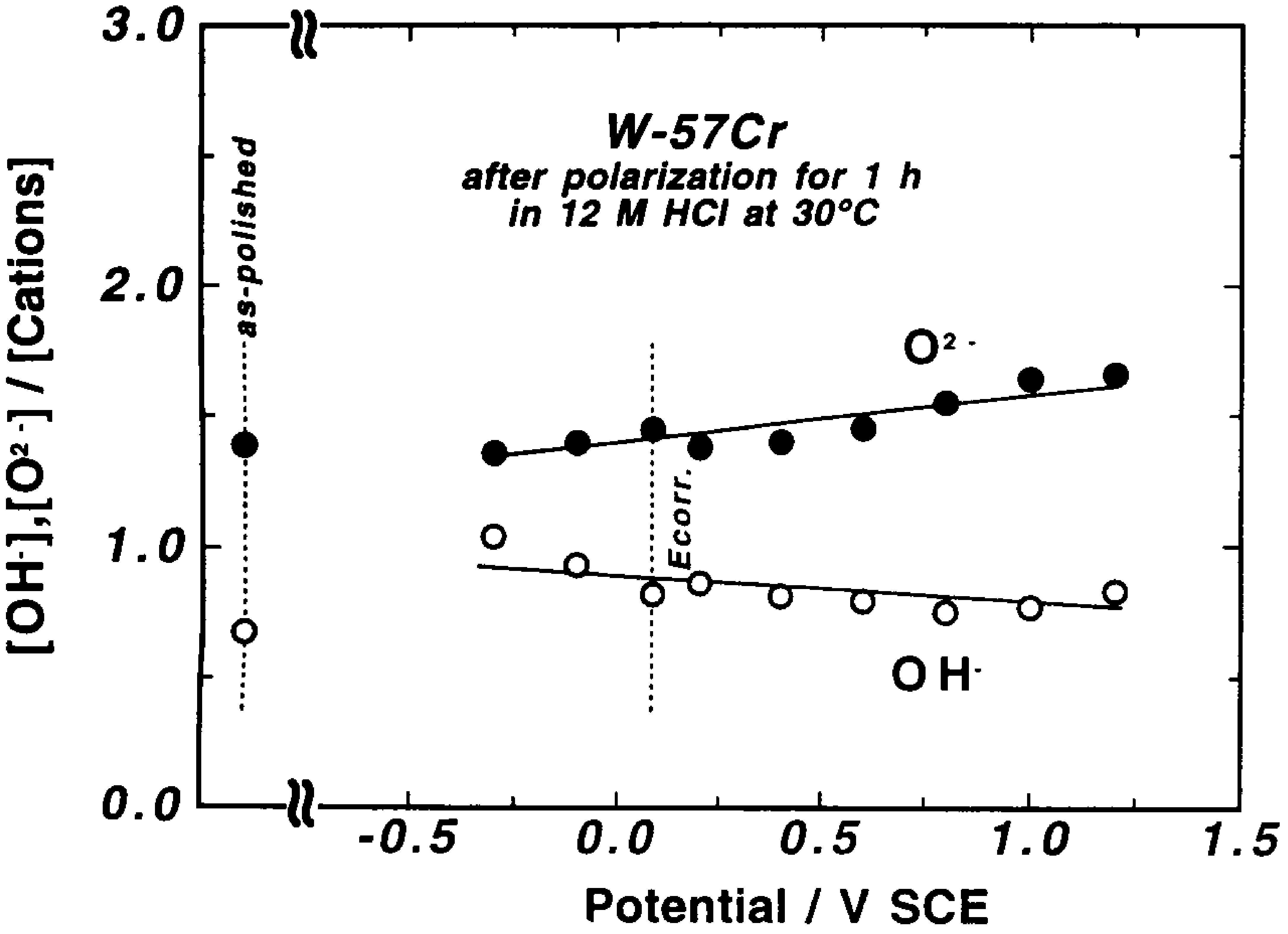

Figure-7. Changes in the ratios of [O^{2-}]/[cation] and [OH^-]/[cation] in the film formed on the W-57 Cr alloy after potentiostatic polarzation for 1 h in 12 M HCl at 30° C as a function of potential.

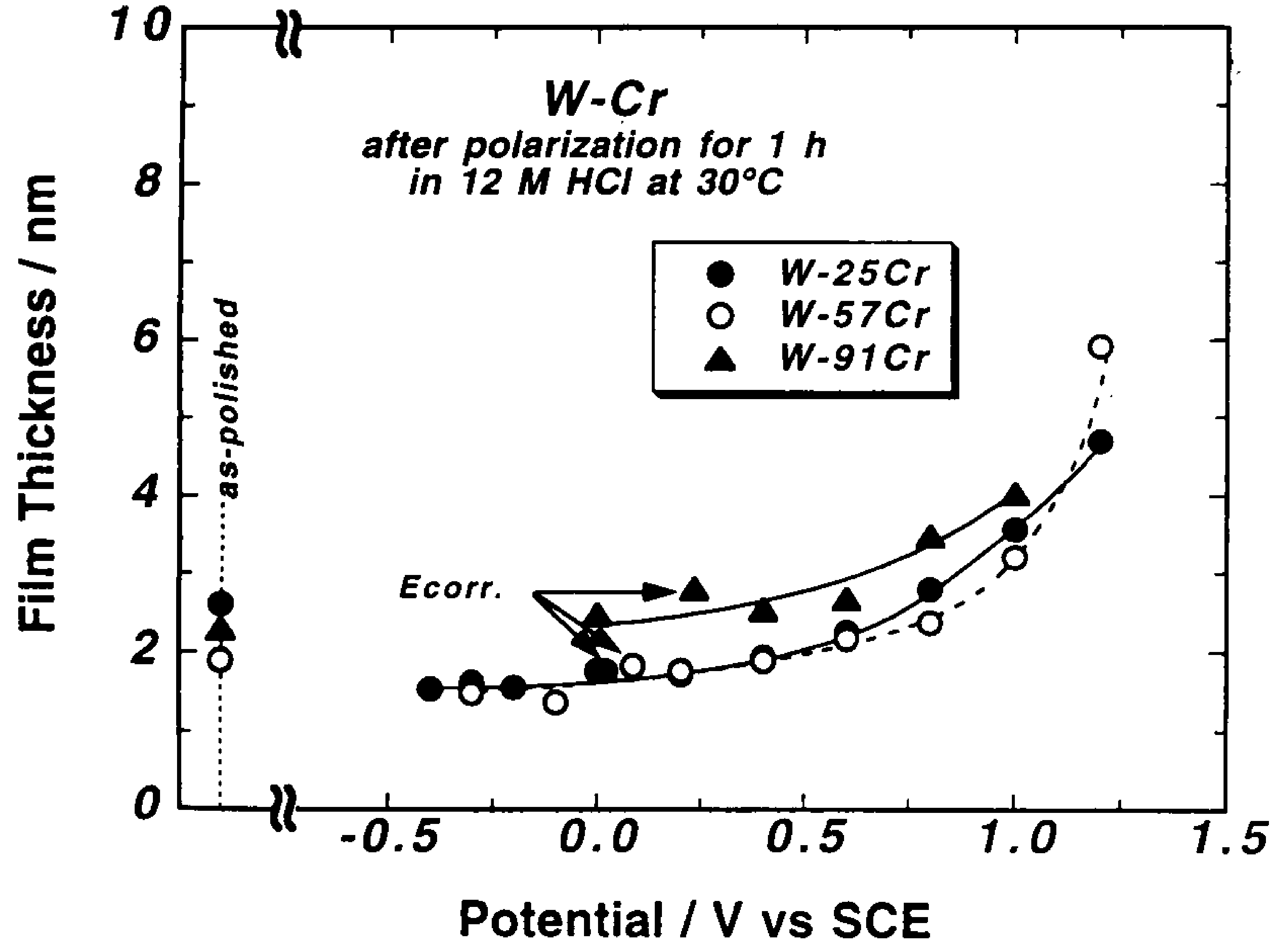

Figure-8. Thickneses of the films formed on W-25 Cr, W-57 Cr and W-91 alloys after potentiostatic polarzation for 1 h in 12 M HCl at 30° C, as a function of potential.

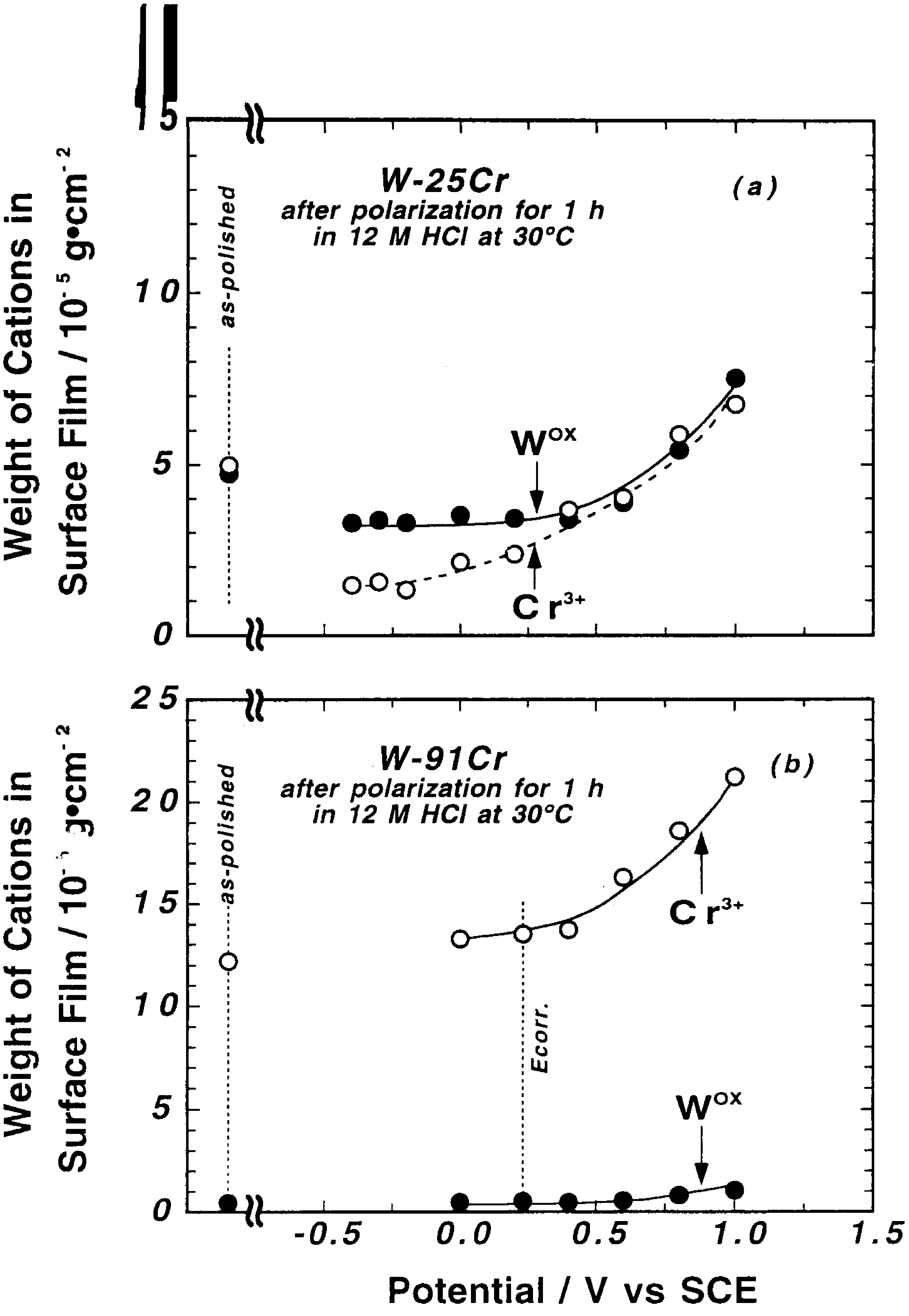

Figure-9. Changes in weights of cations in the surface films formed on (a) W-25 Cr and (b) W-91 Cr alloys after potentiostatic polarzation foe 1 h in 12 M HCl, as a function of potential.

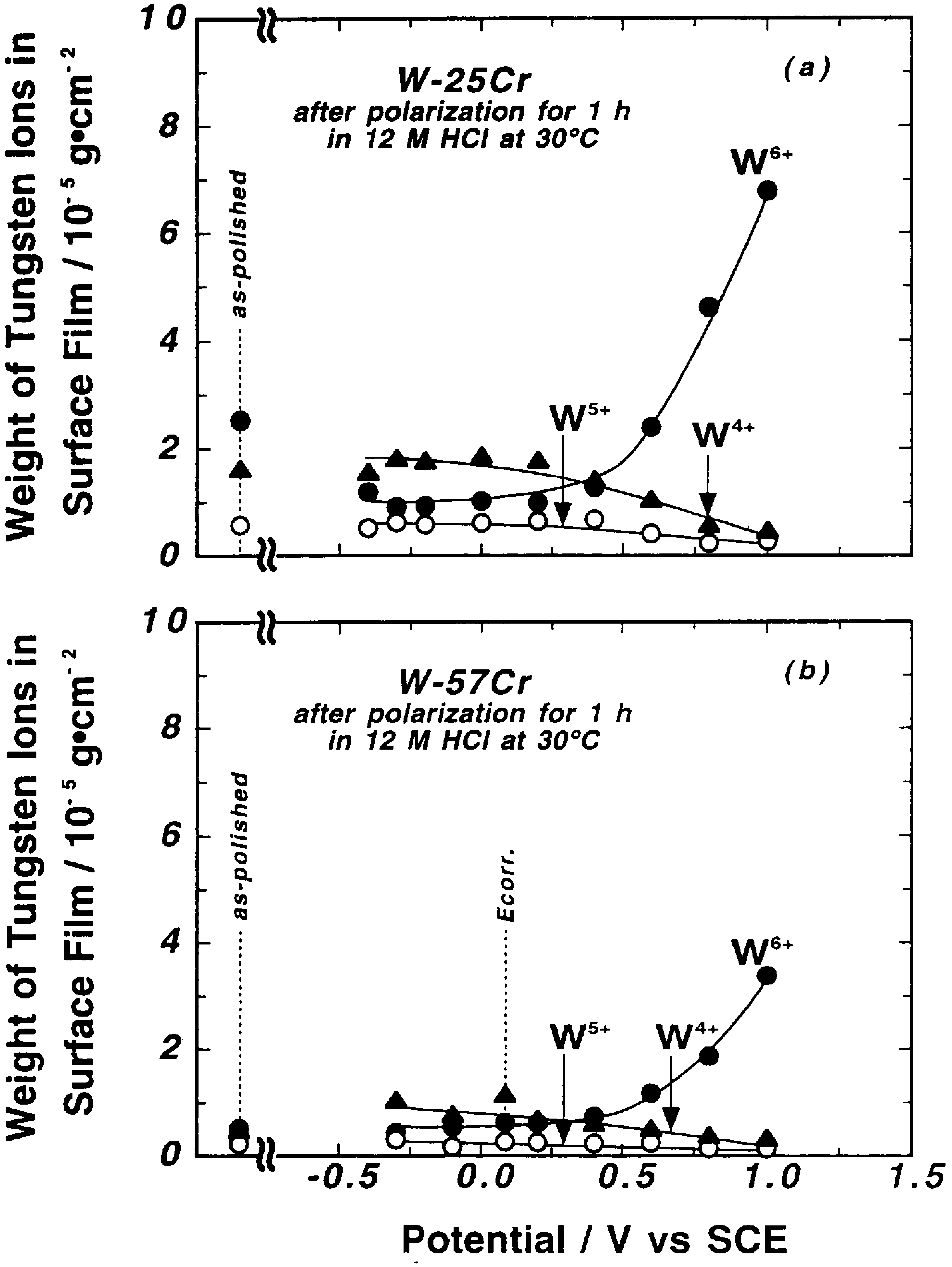

Figure-10. Changes in weights of W^{4+}, W^{5+} and W^{6+} ions in the surface films formed on (a) W-25 Cr and (b) W-57 Cr alloys after potentiostatic polarzation for 1 h in 12 M HCl, as a function of potential.

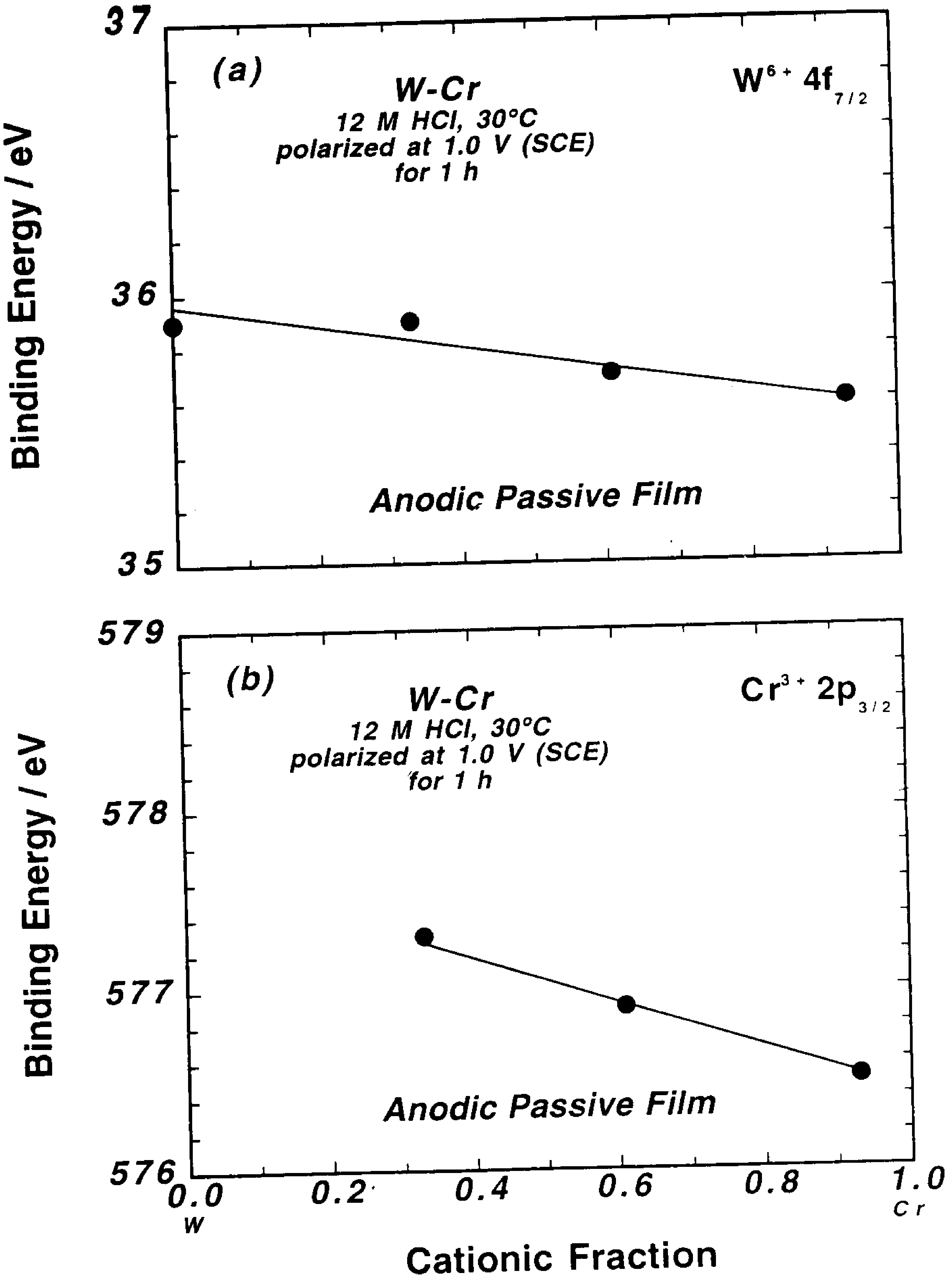

Figure-11. Changes in the binding enegies of (a) W^{6+} $4f_{7/2}$ electron and (b) Cr^{3+} $2p_{3/2}$ electrons in the anodic passive films formed on W- Cr alloys after potentiostatic for 1 for h at 1.0. V (SCE) in 12 M HCi at 30° C, as a function of cationic fractions in the film.