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Pd(II)   Pd(I)   Pd(O)

The way that an olefin bind to a Pd-diphosphine complex has substantial differences in coordination number and orientation.[8] Pd(I) has some advantage to accelerate the olefin oxidation in comparision with Pd(II) analogue; i) there are two active metal centers ii) Pd(I) has three coordination number, and thus the four coordinate activated species are easily formed through vacant orbital. However, Pd(I) also has the steric hinderence between two metal centers and bridging ligands. The results of run 11 in Table 1 seems to be compensated for these two aspects. Pd(I) accelerated the oxidation while Pd(O) was less active under the same experimetal conditions (run 12 in Table 1). It has been reported that electron-withdrawing substituent on the metal promote nucleophilic addition to the olefin.[12] Activity decline in Pd(O)-phoshine complex occurs due to the loss of chloride ligand. In binuclear complexes, the role of diphosphine ligand is to prevent dissociation of dimer to monomer and to promote binuclear reactions involving the formation and cleavage of metal-metal bonds. Unfortunately these properties of [Pd$_2$(μ-dppm)$_3$] complex suppressed the styrene activation for the nucleophilic attack. It appears that there is a substantial back donation (M$\rightarrow$olefin) when the activated species, [Pd(P̂P)(olefin)], is formed.

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Passive Films on Chromium Studied by Three-parameter Ellipsometry

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Passive films formed on chromium surface in citrate buffer solution were investigated by means of three-parameter ellipsometry. The citrate buffer was found to be a suitable medium in which oxide film on chromium could be removed by cathodic treatment, providing a reference surface for the optical study. The passive film effectively protecting the chromium surface from corrosion was found to have thicknesses in the range 0.65 to 1.25 nm depending on the potential in the range of -0.20 to 0.60 V (0.1 M KCl calomel electrode). The complex refractive index of the passive film did not show significant potential-dependent changes, indicating that the composition of the film material does not depend on potential.

Introduction

Chromium is a extremely corrosion resistant metal due

to its passivating property. The corrosion resistance of many chromium containing alloys including the stainless steel is due to the chromium content in the surface region. However, studies on the passivating film on the chromium surface have not been very extensive. Ellipsometry,[1~3] Auger spectroscopy,[2]

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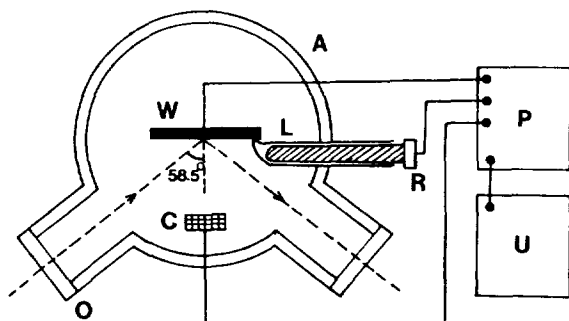
Figure 1. Schematic diagram of the electrochemical-optical cell. A: Pyrex glass cell; W: working (chromium) electrode; C: Pt counter electrode; L: Luggin capillary; O: fused quartz window; P: potentiostat; R: Reference electrode (0.1 M KCl calomel electrode); U: potential programmer.

XPS,[4] and electrochemical methods[1~4] have been employed to study passive films on chromium. The thickness of the passivation films resulted from these studies are reported to be potential dependent,[1,4] and ranged from 0.3 to 2.0 nanometers.[2] The complex refractive index $n = n_f - ik_f$ ranges from (1.80-i0.02) at the wavelength of 550 nm in one report[2] to (2.54-i0.04) at 540 nm in another.[1] The chemical identity of the film has been deduced to be Cr_2O_3,[1] Cr_2O_3 hydrated on the surface,[2] or oxides containing Cr(II), Cr(III), Cr(IV), or Cr(VI), depending on the potential.[3]

One major reason for this lack of agreement among the studies on the passive film on Cr is that the film is extremely thin, and once a passivating film is formed it is very difficult to remove to obtain the film-free surface which is necessary as the reference surface in optical studies. Another reason for the discrepancy is in the inadequate experimental techniques such as the conventional (two-parameter) ellipsometry in studying films with complex refractive index.

In the present study, we used electrochemical and the three-parameter ellipsometry technique,[5,6] that is suitable for studying very thin films with complex refractive index, to investigate the nature and the thickness of the passive film on chromium.

Experimental

Figure 1 depicts the electrochemical-optical cell in which the working electrode is a specimen of chromium. The chromium was electrodeposited from a sulfate bath on copper plate and mechanically polished, the final polishing being made with 0.05 μm alumina polishing powder The ellipsometer used was a manual ellipsometer using a incandescent lamp as the light source. An interference filter of 632.8 nm wavelength and 1.0 nm bandwidth was used as the monochromator. A judicial choice of the angle of incidence is important for a successful ellipsometry, and an angle near 70°, which is the preferred angle of incidence in many conventional (two-parameter) ellipsometry, is a poor choice for the three-parameter ellipsometry.[5] Since our experience with other metals[6~8] such as Fe, Co, and Ni as well as a preliminary calculation for error propagation from experimental error to the final results[9] showed that angles near 55-60° are

suitable, 58.5° was used as the angle of incidence in the present study. After measuring Ψ and Δ by the manual null point method,[†] the relative intensity of the reflected light was measured by rotating the analyzer 90° from the null position. These measurements of the usual ellipsometry parameters Ψ and Δ and the intensity measurements were repeated before and after passivation of the chromium induced by applying an anodic potential so that the changes in Ψ, Δ and the reflectance R ($\delta\Psi$, $\delta\Delta$, $\delta R/R$) due to passive film could be determined.

Because the surface of chromium undergoes spontaneous oxidation in the air immediately after polishing, it is essential that the surface has to be reduced in order to have a reference state for the measurements. We have tried various electrolyte solutions for reducing the passivated surface of chromium and found that the surface can be most efficiently reduced by applying -2.0 V (vs. 0.1 M KCl calomel electrode) to the electrode in an aqueous citrate buffer of pH 4.6 (4.90 g citric acid +7.72 g sodium citrate in 1 L) for about 5 min. Because at this potential vigorous hydrogen evolution and oxygen evolution occur at the working and the counter electrodes, respectively, this electrolytic treatment was performed in a separate vessel. The electrode was then transferred to the experimental cell, also containing the citrate buffer solution. The cathodic treatment at -2.0 V was repeated momentarily in this cell for 2-3 sec. The potential was then raised to -0.85 V, which is still cathodic to the corrosion potential ($\sim$0.8 V). The optical measurements for the reference surface were made at this stage. Subsequently the potential was stepped up to a passivating potential in the range $-0.2 \sim +0.6$ V. the optical measurements were made after about 15 min when a steady state was reached in the film formation. The differences in the optical Ψ, Δ, R measurements, $\delta\Psi$, $\delta\Delta$, $\delta R/R$ were recorded.

Results and Discussions

The reduction of the oxidized chromium surface was evidenced by the Δ measured before and after potentiostatic oxidation and reduction treatments; Δ decreased about one degree on oxidation at a passivating potential and returns close to the original value within 0.1 degree on reduction at -2.0 V. The reference surface gave $\Psi° = 33.64(\pm 0.23)°$ and $\Delta° = 154.9(\pm 0.39)°$. From these values the complex refractive index of the bare Cr metal is calculated to be $n = 4.42$-i4.34 which is close to the literature values at similar wavelengths.[1,2]

The values of $\delta\Psi$, $\delta\Delta$, $\delta R/R$ were used in the three-parameter ellipsometry calculations to obtain the thickness and the optical constants of the passive film. The optical constants are the real and the imaginary parts of the complex refractive index $n = n_f - ik_f$. The results are shown in Figures 2-4 as the functions of the passivating potential.

The thickness of the passive films increased with the potential approximately linearly from 0.65 nm at -0.20 V to 1.25 nm at 0.60 V in general agreement with the results

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[†] The relative amplitude diminution on reflection is $tan\Psi = r_p/r_s$, where r_p and r_s are the reflection coefficients of the light components of the p-and s- polarizations, respectively. Δ is the relative phase difference between the reflected p- and s- polarizations.

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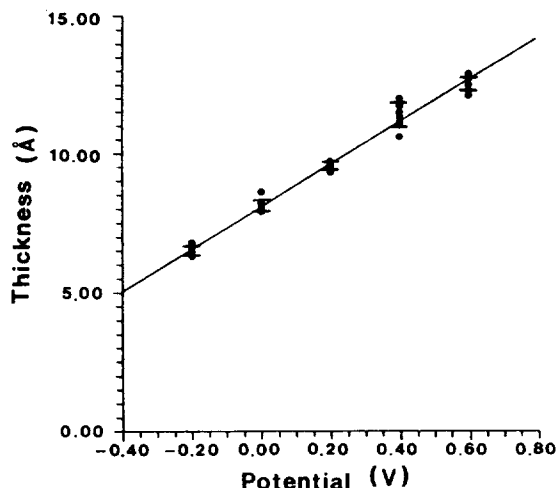
Figure 2. Thickness of passive films on chromium formed at various potentials. The potential is with respect to 0.1 M KCl calomel electrode.
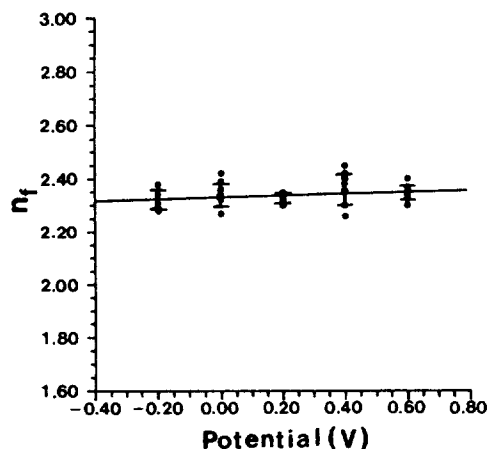
Figure 3. The real part of the refractive index of passive films on chromium formed at various potentials.

reported in the literature,[1,2,4] while the real part of the refractive index n_f did not show significant changes with the potential within the range of experimental error. The values of the imaginary part of the refractive index k_f were close to zero with somewhat large relative error range. The thickness smaller than 0.65 nm could have been observed if we had studied at potentials lower than -0.2 V because chromium is also passivated at potentials near -0.8 V. We did not include the more negative potential range because as the film becomes thinner, accurate ellipsometric measurement is more difficult.

The average value of $n = n_f - ik_f$ is $2.34(\pm 0.04)-i0.051(\pm 0.02)$, which is close to the Genshaw's result[1] both in the real and the imaginary parts, but larger than the result of Sato et al.[2] The comparison is not rigorous because of the difference in the wavelengths used in the studies. The magnitude of the refractive index is a measure of the compactness or density of the material. The imaginary part is proportional to the absorption coefficient and is related to the
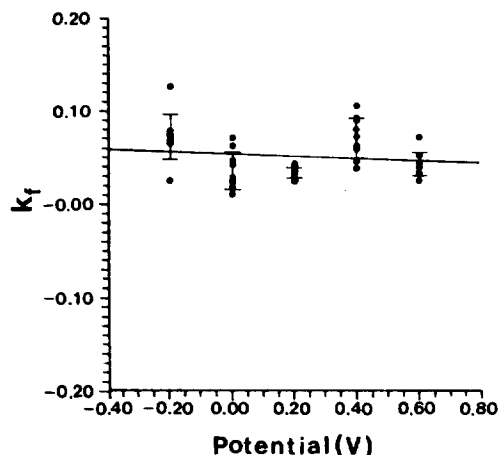
Figure 4. The imaginary part of the refractive index of passive films formed on chromium at various potentials.

electronic conductivity. The only known refractive index data of chromium oxide is the one[10] for Cr_2O_3 $n = 2.55$ at the wavelength of 590 nm. In view of the fact that only Cr_2O_3 or its hydrated form is thermodynamically stable in this potential and pH range (from, *e.g.* Pourbaix diagrams[11]) and from the proximity of the n_f value of the film to that of Cr_2O_3 it can be concluded that the passive film has a composition that is close to Cr_2O_3, possibly hydrated partially, and is unaffected by the potential within the potential range we investigated. The hydration of the oxide and defects in the solid may have caused the value of n_f to be smaller than the literature n value and also caused the k_f value to be nonzero. The transient behavior of the passive film during the short period before reaching the steady state passivity is currently under study in our laboratory.

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