On the Evaluation of Corrosion Resistances of Amorphous Chromium-Carbon Thin-Films

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ABSTRACT

The possibility of evaluating the corrosion resistance of amorphous chromium carbide (Cr-C) films containing nanometre-sized carbide grains embedded in an amorphous carbon matrix on the basis of polarization curves, voltammograms and the oxidation charge have been studied for Cr-C films with different carbon concentrations. The films, which were manufactured by non-reactive direct-current magnetron sputtering, were studied in 1.0 mM H_2SO_4 at both 22 °C and 80 °C, and with scanning electron microscopy and X-ray photoelectron spectroscopy prior to and after the electrochemical experiments. It is demonstrated that the oxidation of these Cr-C films gives rise to a surface composed of Cr_2O_3 and partially oxidized carbon and that the non-corroding oxidation current due to carbon oxidation increases with increasing carbon concentration in the films as well as with the electrolyte temperature. Since the oxidation current is composed of contributions from both Cr–C and carbon oxidation it is not straightforward to evaluate the corrosion resistances of these films based on the current in the passive region, the mixed potential (i.e., the corrosion potential) or the open circuit potential. The present results in fact indicate that Cr-C films with high carbon concentrations may have better corrosion resistances than the corresponding films with lower carbon concentrations although larger currents in the passive region can be seen in polarization curves.

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1. Introduction

Chromium carbide (Cr-C) is a promising material system for various applications due to properties such as low friction and high hardness, wear resistance and corrosion resistance [1–13]. For corrosion prevention, thin Cr-C films are particularly versatile as it has been shown that a passive film of chromium oxide is formed at elevated temperatures in air [11,14,15] as well as during oxidation in supercritical water [12], aqueous solutions [16–19] and chloride-containing non-aqueous media [13]. Despite this, relatively little is known about the influence of the composition and morphology on the corrosion resistance for Cr-C thin films. This is somewhat surprising since it is well-known that different deposition conditions, when using deposition techniques such as magnetron sputtering, can give rise to Cr-C films that are amorphous, polycrystalline or composites of nanocrystalline carbide grains distributed in an amorphous carbon matrix [18–20] and that the carbon contents of the films can be varied over a wide range [18,19].

Good wear properties in combination with high corrosion resistances have been reported for nanocrystalline/amorphous films [3–8] and the effects of different deposition parameters on the corrosion resistance and other properties have also been studied for magnetron-sputtered films [21] based on salt fog tests. Although the corrosion resistance was found to depend on the deposition conditions, the authors did, however, not discuss the reasons for this dependence. While it has been proposed [22,23] that the corrosion rate should decrease with reduced grain size for materials such as Cr-C that exhibit passive behaviour, less attention has been paid to the influence of the composition of Cr-C films on their corrosion resistance. The latter point was addressed recently in two studies [18,19] involving magnetron sputtered Cr-C amorphous films and nanocomposites with different carbon contents. In these reports it was shown that the corrosion resistance of Cr-C films depends on the microstructure and composition, but also that the oxidation currents obtained during the recording of polarization curves and in chronoamperometric experiments contained contributions from both chromium oxide formation and carbon oxidation. The latter finding is interesting since polarization curves and chronoamperometric experiments are commonly used to measure the corrosion resistance of thin Cr-C films, and suggests that the evaluation of the corrosion resistances of different Cr-C films may not be as straightforward as previously assumed,

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as the magnitude of the oxidation current may not directly reflect the corrosion rate. This raises the question as to how the corrosion properties of different Cr-C films should be evaluated and compared for Cr-C films with different composition and morphology.

Polarization curves and chronoamperometric experiments are generally used for the evaluation of the corrosion resistances of materials such as chromium and stainless steel [24,25] but have also been used to study chromium carbides [4,6,10,26–30] and other glassy metal alloys [31]. The fact that the oxidation of Cr-C films generally includes both oxidation of carbon and formation of a passive film of Cr_2O_3[18,19] may, however, render these methods less straightforward to use as the currents and potentials evaluated in these approaches cannot be ascribed solely to the formation of the Cr_2O_3 passive layer. Since these problems are expected to depend on the carbon concentration in the Cr-C film, different results may also be obtained for Cr-C films with different compositions. A Cr-C film with a high carbon concentration may hence yield a larger current in the passive region than a Cr-C film with a lower carbon concentration due to the oxidative formation of oxygen-containing groups on the carbon surface, although the corrosion resistance of the two films may in fact be similar. It is therefore important to revisit the appropriateness of these electrochemical approaches for the determination of the corrosion resistances of Cr-C films with different carbon concentrations.

Another related question is whether the oxidation of the carbon present in the Cr-C films, which should follow the electrochemical behaviour of carbonaceous materials in general [32], merely involves the formation of oxygen-containing surface groups, or if carbon is actually lost from the surface, *e.g.*, via the formation of CO_2, HCO_3^- or CO_3^{2-}. Such a carbon corrosion process could assist in the formation of a complete surface layer of chromium oxide, at least for Cr-C films with sufficiently low carbon concentrations. This phenomenon would hence be analogous to the selective dissolution of iron during the formation of the passive layer on stainless steel [33]. A similar dissolution behaviour has also been proposed for metal borides containing combinations of chromium and iron as well as several other metals [34]. Binary chromium alloys containing boron or phosphorous have also been reported [35–38] to decrease the corrosion rate of chromium due to the formation of passive films containing oxidized boron.

In the present work, comparisons of the corrosion resistances of magnetron-sputtered amorphous Cr-C films with different carbon concentrations are discussed based on polarization curves, chronoamperograms, open circuit potentials (OCPs), electrochemical quarts crystal microbalance (EQCM) results, as well as scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) data and inductively coupled plasma -optical emission spectroscopy (ICP-OES) analyses of the electrolytes. The results of the experiments, which were carried out at both 22 °C and 80 °C, indicate that the oxidation current mainly is due to the oxidation of Cr–C but that a contribution from the oxidation of carbon also is present. It is also shown that the magnitude of the oxidation currents depends on the morphology of the Cr-C films.

2. Experimental

The amorphous chromium carbide (Cr-C) films studied in this paper were manufactured by non-reactive direct-current magnetron sputtering, as previously described [18], using elemental targets and a substrate temperature of 300 °C. The compositions of the films, which contained nanometre-sized carbide grains embedded in an amorphous carbon matrix [18,19,39], were altered by varying the target currents, and the substrates used were square-shaped, 0.3 mm thick 316L steel pieces, with 2-cm sides. The films studied had the following atomic fraction compositions: $Cr_{0.74}C_{0.26}$, $Cr_{0.61}C_{0.39}$, $Cr_{0.53}C_{0.47}$ and $Cr_{0.37}C_{0.63}$. As has been demonstrated previously, all films contain a mixture of Cr–C and amorphous carbon [18,19,39]. Electrochemical experiments were also carried out on a different set of Cr-C films manufactured using the same deposition technique. In the latter case the atomic fraction compositions of the films obtained were slightly different, *i.e.*, $Cr_{0.82}C_{0.18}$, $Cr_{0.65}C_{0.35}$, $Cr_{0.45}C_{0.55}$ and $Cr_{0.22}C_{0.78}$. Whereas the $Cr_{0.74}C_{0.26}$ and $Cr_{0.82}C_{0.18}$ samples mainly contained carbidic carbon, the other samples contained a mixture of Cr–C and amorphous carbon [18]. The films used in the EQCM experiments, which had a surface area of 0.75 cm^2, were fabricated on a gold-coated quartz crystal microbalance and had a composition of $Cr_{0.75}C_{0.25}$.

The polarization curves and the chronoamperometric experiments were recorded with a Solartron 1285 potentiostat in 1.0 mM H_2SO_4 (in contact with air), using an Ag/AgCl (KCl sat.) reference electrode, equipped with a bridge also containing 1.0 mM H_2SO_4. The bridge served both as a barrier for ions leaking from the reference electrode, and to some extent also as thermal insulation for the reference electrode with respect to elevated electrolyte temperatures. Polarization curves were recorded both at 22 °C and at 80 °C, while the chronoamperometric experiments were performed at 80 °C. In each electrochemical experiment, a circular 0.25-cm^2 area was used which meant that each coated substrate could be tested four times, once in each quadrant. The electrolyte volume was 65 ml both in the polarization curve and the chronoamperometric experiments, and a new sample area and fresh electrolyte were used in each experiment. The potential was scanned from −0.5 to +1.5 V *vs.* Ag/AgCl (KCl sat.) at a rate of 5 mV/s during the recording of the polarization curves, whereas it was kept constant at +0.643 V *vs.* Ag/AgCl (KCl sat.) during the chronoamperometric tests. At least two polarization curves were recorded for each type of Cr-C film, at each temperature, whereas five sets of chronoamperometric curves were recorded for each type of Cr-C film. The experiments at 80 °C were started when the temperature of the electrolyte had reached 78 °C. The OCP measurements were carried out prior to each experiment, approximately 3 minutes after the sample was immersed in the electrolyte.

The EQCM experiments were performed in an electrolyte containing 5.0 mM H_2SO_4, 0.10 M Na_2SO_4 and 5.0 μM NaF. This electrolyte was used to minimize the iR drop in the flow cell used and to facilitate the detection of any corrosion of the films. The potential was either scanned (at 5 mV/s) from −0.5 to +0.795 V *vs.* Ag/AgCl (KCl sat.) and back again, or from −0.5 to +1.5 V *vs.* Ag/AgCl (KCl sat.) followed by an open circuit period.

ICP-OES experiments were used to determine the concentrations of chromium, iron and nickel in the electrolytes after the chronoamperometric experiments. The latter concentrations were compared to those obtained in blank experiments, performed on electrolyte that had been in contact with the experimental equipment, but not the sample, at the same temperature as that used during the actual electrochemical tests. All experimental equipment made of glass, including the glass jars used to store the used electrolytes employed in ICP-OES experiments, were washed for several hours in 1 M HNO_3 at 80 °C and subsequently thoroughly rinsed with deionized water prior to use.

SEM micrographs were obtained with the in-lens detector of a Zeiss LEO 1550 employing a working distance of 3 mm and an acceleration voltage of 3 kV. XPS spectra were recorded using a Phi Quantum 2000, employing a step size of 0.05 eV and a pass energy of 11.75 eV. The C1s peak was fitted as previously described [18], while the Cr2p and O1s peaks were fitted according to the procedure described by Salvi *et al.*[40].