



Influence of deposition temperature and amorphous carbon on microstructure and oxidation resistance of magnetron sputtered nanocomposite Cr–C films



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ABSTRACT

It is known that mechanical and tribological properties of transition metal carbide films can be tailored by adding an amorphous carbon (a-C) phase, thus making them nanocomposites. This paper addresses deposition, microstructure, and for the first time oxidation resistance of magnetron sputtered nanocomposite Cr–C/a-C films with emphasis on studies of both phases. By varying the deposition temperature between 20 and 700 °C and alternating the film composition, it was possible to deposit amorphous, nanocomposite, and crystalline Cr–C films containing about 70% C and 30% Cr, or 40% C and 60% Cr. The films deposited at temperatures below 300 °C were X-ray amorphous and 500 °C was required to grow crystalline phases. Chronoamperometric polarization at +0.6 V vs. Ag/AgCl (sat. KCl) in hot 1 mM H₂SO₄ resulted in oxidation of Cr–C, yielding Cr₂O₃ and C, as well as oxidation of C. The oxidation resistance is shown to depend on the deposition temperature and the presence of the a-C phase. Physical characterization of film surfaces show that very thin C/Cr₂O₃/Cr–C layers develop on the present material, which can be used to improve the oxidation resistance of, e.g. stainless steel electrodes.

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Introduction

The possibilities of combining high hardness, high wear resistance, low friction, and high corrosion resistance make transition metal carbides (TM–C) potential candidates for many thin film applications [1]. Chromium carbide (Cr–C) is a TM–C known [2,3] to provide excellent corrosion resistance due to the formation of a thin, but strongly adherent, surface layer of chromium oxide which effectively prevents further oxidation of the bulk material at elevated temperatures in air [4–6] as well as in supercritical water [7]. Cr–C has, in fact, been claimed to have the highest oxidation resistance of group VI transition metal carbides [6]. While Cr–C has been shown to develop passive films in acidic solutions [8] and chloride containing non-aqueous media [9], the corrosion resistance has been found to be poor at elevated temperatures in alkaline solutions [10]. Carbon-rich Cr–C films have also been suggested as candidates for corrosion protection of metallic bipolar plates in proton exchange membrane fuel cells (PEMFC), which present hot acidic conditions [11,12]. In addition, combined multilayered Cr–C

and amorphous carbon films were recently reported to meet year 2020 technical targets for bipolar plates [13]. Increasing the corrosion resistance while maintaining a high electrical conductivity (i.e. preventing thick passive layers) and keeping cost down is an on-going challenge for the fuel cell industry [14,15].

Cr–C films can be made by physical vapor deposition (PVD) techniques like magnetron sputtering and the concept has received continuous interest [3,16–22] ever since the first publications in the late 1970s. A group of studies [23–28] show that the deposition temperature is a very decisive parameter when synthesizing Cr₂₃C₆, Cr₇C₃, and Cr₃C₂, as the crystallization of these phases requires a temperature of at least 500 °C. Magnetron sputtering can also be used to deposit nanocomposite and amorphous Cr–C films, using both reactive [21,29] and non-reactive processes [24,30]. The nanocomposite has nanometer-sized carbide grains embedded in an amorphous carbon matrix (a-C) and is commonly denoted Cr–C/a-C. Magnuson et al. recently studied the phase composition of Cr–C films formed by non-reactive sputtering from elemental targets and observed formation of amorphous films at most compositions [22]. The TEM and XPS results, nevertheless, indicated the existence of two non-crystalline phases: one amorphous carbon phase with mainly C–C bonds and one amorphous carbide phase with mainly Cr–C bonds. Intricate phase combinations can also be

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obtained by reactive evaporation [31], and local growth of the three crystalline Cr–C phases has been shown to occur simultaneously due to variations in composition on the microscopic scale [32]. The phase composition and phase distribution can thus be complex as completely amorphous or crystalline films, or a mixture of amorphous and crystalline phases, can be obtained. This complexity very likely influences the corrosion resistance.

For metals which exhibit passivity the corrosion rate has been found to decrease when the grain size decreases due to more rapid passivation, and a change in microstructure can in fact alter the corrosion rate by up to one order of magnitude [33,34]. One following indication is that eliminating grain boundaries by designing amorphous materials may yield excellent corrosion resistance. The electrochemical properties of amorphous and nanocomposite Cr–C films have received only limited attention. Lin et al. showed that amorphous Cr–C gave rise to higher corrosion currents when compared to crystalline Cr_3C_2 as a consequence of defects in the amorphous coating which exposed the substrate [35]. Merl et al. have also reported that similar microstructural growth defects can be linked to the corrosion properties for related Cr–(C,N) hard coatings on steel [36]. However, recent electrochemical experiments on amorphous Cr–C/a-C films made by Andersson et al. indicate that oxidation of a-C contributes to the current in the passive region [30]. The latter current is normally attributed to initial losses of Cr ions into the electrolyte followed by the formation of a passive Cr(III) oxide film. From a corrosion point-of-view, the passive current observed for a nanocomposite film can therefore be expected to contain contributions from both the Cr–C phase and the a-C phase. This aspect distinctly differs from that of pure Cr–C and has not been reported in literature previously. In addition, the electroactive surface area should play an important role and it is likely affected by crystallographic order, film density, and presence of a-C phase. Deposition temperature and film composition are fundamental yet crucial parameters in this context.

The objective of this study is to investigate how changes in deposition temperature and film composition affect the microstructure and the oxidation resistance of nanocomposite Cr–C/a-C films grown using non-reactive direct current magnetron sputtering (DCMS). It is shown that films can be tailored into amorphous, nanocomposite, and nanocrystalline microstructures. An increase in deposition temperature and the addition of a-C phase by control of composition affect the electrochemical properties, which can be linked to the surface chemistry as confirmed by analysis using X-ray photoelectron spectroscopy and scanning electron microscopy.

Experimental details

Deposition

Cr–C films were deposited by non-reactive, unbalanced DCMS from two circular 2-in. elemental targets of Cr and C (purity >99.995%, and >99.999%, respectively, Kurt J. Lesker Company) in a UHV chamber (base pressure 10^{-7} Pa). The stationary substrate holder, placed approximately 14 cm below the magnetrons, was either unheated or heated up to temperatures of 700 °C employing an integrated resistive wire. The targets were tilted toward the center of the substrate holder, and no geometric differences in film composition could be detected. A thermocouple was used to monitor the temperature and calibration of the surface temperature was made by infrared pyrometry. Argon was introduced into the chamber and a regulatory valve system maintained an Ar-plasma at a constant pressure of 3.0 mTorr (0.4 Pa). Prior to each deposition, the targets were presputtered and the substrate holder was heated for 45 min to achieve a steady state. Films were grown on ultrasonically cleaned Si(001), Al_2O_3 (0001), and 316 L grade stainless steel

substrates. To improve the adhesion, a plasma etch was run for five min (–400 V bias, Cr-magnetron current 15 mA). Additionally, an adhesion layer of 100 nm Cr was deposited. The composition of the subsequent Cr–C layer was controlled by setting the current for the Cr-magnetron to either 30 or 100 mA, while the C-magnetron current was kept constant at 300 mA. The deposition voltages were steady (<5% drift) and growth rates of 1.5–3.0 nm/min, depending on the magnetron current, were obtained as determined by ex situ X-ray reflectivity. The deposition time was adjusted to yield films 500 nm in thickness. During the deposition of the Cr and Cr–C layers the substrate holder was biased to –50 V. All samples remained in UHV and were allowed to reach room temperature before exposure to the atmosphere.

Characterization

Film composition and chemical binding energies were determined by X-ray photoelectron spectroscopy (XPS), using a PHI Quantum 2000 spectrometer with monochromatic Al $K\alpha$ radiation and a pass energy of 11.75 eV. Intensity calibrations for Cr and C were made by elastic recoil detection analysis of reference samples. To quantitatively determine oxygen content, a sensitivity factor given by the manufacturer of the instrument was used [37] whereas energy calibration was performed using a gold reference sample. Information regarding the bulk composition was obtained by through-film depth profiling using 4 keV Ar^+ ions, rastered over a $1\text{ mm} \times 1\text{ mm}$ area, at a rate of $\sim 40\text{ nm/min}$. High-resolution spectra were acquired after pre-sputtering using 0.2 keV Ar^+ ions, rastered over a $1\text{ mm} \times 1\text{ mm}$ area, at a rate of $\sim 0.1\text{ nm/min}$. However, data suggests that 4 keV Ar^+ ions preferentially sputter carbon, and pre-sputtering at 4 keV, compared to 0.2 keV, resulted in 14% less observed carbon on average. To minimize sputter-induced errors, the reported compositions in this study are based on spectra obtained after pre-sputtering using 0.2 keV to a depth of 9 nm. Four Gaussian–Lorentzian contributions (20% GL), centered at 282.9 eV (C–Cr(1)), 283.4 eV (C–Cr(2)), 284.4 eV (a-C sp^2) [38] and 285.3 eV (a-C sp^3) [38], were used to fit the C1s spectra on top of a Shirley-type background, and care was taken to keep the fitting parameters constant for all fits. Crystallographic information was obtained by grazing incidence X-ray diffraction (GIXRD), using a Philips MRD X'pert diffractometer with Cu $K\alpha$ radiation and parallel beam geometry. A Leo 1550 scanning electron microscope (SEM) was used to image cross-sections of fractured Si samples and surfaces of coated 316 L samples. The electrochemical experiments were performed in 1.0 mM H_2SO_4 , using a Solartron 1285 potentiostat and a jacketed cell that was heated by recirculating water. An electrolyte temperature of 80 °C was used to increase the rates of the electrochemical reactions, and in combination with the acidity the electrolyte also loosely resembled an environment inside a PEMFC. In these measurements, Cr–C films deposited on 316 L grade stainless steel substrates were used as working electrode while Ag/AgCl (sat. KCl) and Pt were used as reference and counter electrodes, respectively. Films deposited at 700 °C were excluded because of too poor adhesion to the substrate for meaningful electrochemical characterizations. In each measurement, a circular film area of 0.25 cm^2 film was exposed to the electrolyte. The reference electrode was equipped with a bridge containing the electrolyte and all potentials are given with respect to this reference electrode (which has a potential of approximately +0.14 V vs. the standard hydrogen electrode (SHE) at 80 °C). To study the corrosion resistance, polarization curves were recorded by increasing the potential from –0.5 to 1.5 V at 5 mV/s, and chronoamperometric experiments were performed at potentials of +0.450 V and +0.643 V for 60 min. Wilcoxon signed-rank tests were used to pair-wise compare total chronoamperometric charges. The Wilcoxon signed-rank test is a statistical

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