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Equivalent circuit modelling of Ni–SiC electrodeposition under ramp-up and ramp-down waveforms

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Abstract

An equivalent circuit model (EC) for pulsed electrodeposition of Ni–SiC composite coatings was formulated and fit to electrochemical impedance spectra data for the system. Two different shaped waveforms, ramp-up and ramp-down waveforms both with relaxation time were applied to investigate the electrodeposition behaviour of Ni–SiC and to validate the equivalent circuit model. It was found that under the same average and peak current density, the shape of current waveform has significant effect on the electrodeposition behaviour. A higher instantaneous peak current for charge transfer was obtained by the ramp-up waveform, which results in finer grain size and enhanced hardness of the composites. The morphological characteristics of the Ni–SiC composites were also examined and the experimental results were in accordance with the predictions of the EC model.

Keywords: Equivalent circuit model; Ni–SiC composites; Waveforms; Electrodeposition

1. Introduction

Pulse current electrodeposition is able to produce deposits with more uniform particle distribution and better surface morphology than those obtained under direct current [1,2]. It is believed that a higher instantaneous peak current in pulse current electrodeposition will lead to a more homogeneous surface morphology, a higher nucleation rate, and finer grains [3,4]. Some researchers investigated the influence of pulse current on the double layer between the electrolyte and the solution. It is discovered that in charging and discharging of a pulse, especially for short pulses, the double layer distorts the pulse current [5], and affects the overpotential response acting on the electrolyte [6]. In the past decades, pulse current electrodeposition of Ni–SiC composite has attracted much research attention due to their potential applications for the aerospace and automotive industries, manufacturing and medical devices [7]. It has been proved that the pulse current will result in Ni–SiC composites with better morphology and wear resistance, a more uniform distribution of the particles in the metal matrix, and improved hardness than those attained by direct current techniques [1,4]. Recently, the nature of current waveform has been shown to significantly affect the quality of nickel deposit [8–11]. However, less research work has been done to examine the effect of current waveform on the deposition behaviour and mechanism of composite formation.

Electrochemical impedance spectroscopy (EIS) and description in terms of an equivalent circuit are common techniques to analyze complicated processes involving surface and solution reactions. The EIS technique has been widely used to investigate the mechanism of nickel electrodeposition. Watson and Walters [12,13] have observed two inductive loops in the impedance Nyquist plots. Yeh and Wan [14] reported two semicircles in the Nyquist plots, which showed two consecutive electron transfer reactions to occur during the reduction. Nowak et al. [15] have revealed that a capacitive loop exists in the high frequency range, and in low frequency, there exists a sharp change from a capacitive to an inductive behaviour in a relatively narrow potential range. Benea et al. [16] have found that the two inductance loops in the impedance diagram are converted to a single inductance loop upon the addition of nanosized SiC particles. Recently, some preliminary work has been done by the authors to examine the deposition behaviour of Ni–SiC composites under a triangular waveform [17]. They have simulated the charge transfer current of the deposition system under different

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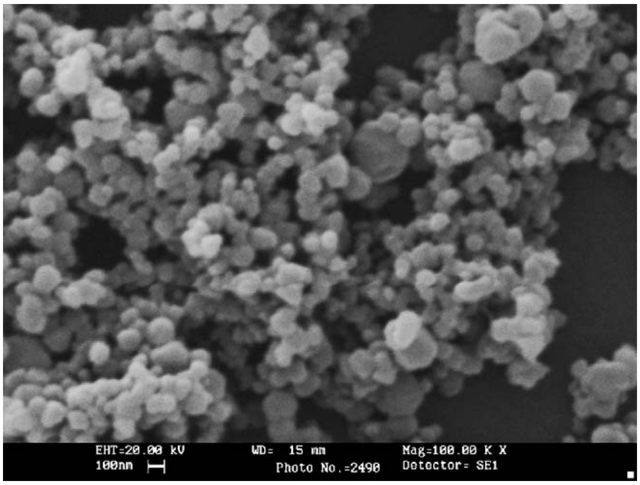

Fig. 1. SEM image showing morphology of as-received SiC particles with diameter of about 100 nm.

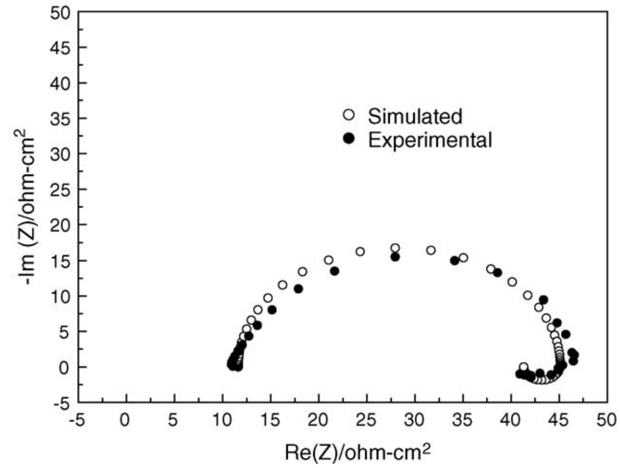

Fig. 3. Comparison between experimental and simulated Nyquist plots in the Ni–SiC electrodeposition system at −750 mV vs. reference electrode (SCE) under a rotation rate of 400 rpm.

cathodic potentials using an equivalent circuit model. In this paper, the deposition behaviour of Ni–SiC composites under different shaped waveforms will be further examined, and the mass transfer effect and the capacitive current of the system will also be simulated by the equivalent circuit model.

2. Experimental

A three-electrode glass cell was used. The working cathode mandrel was made of stainless steel with dimensions of 30 mm × 30 mm × 1 mm, and ground finished on grade 240 emery papers. A saturated calomel reference electrode (SCE) and a counter electrode of pure nickel were used. Electrochemical impedance spectra were acquired in the frequency range of 30 kHz to 5 mHz with a 10 mV amplitude sine wave generated by a frequency response analyzer. Current–voltage curves were recorded at a sweep rate of 20 mV s^{-1}.

The composition of the bath was 330 g l^{-1} nickel sulphamate, 15 g l^{-1} nickel chloride, 30 g l^{-1} boric acid and 1 g l^{-1} sodium dodecylsulfate (SDS). An amount of 20 g l^{-1} SiC (βSiC) of the diameter about 100 nm was added. Fig. 1 shows the morphology of the as-received silicon carbide powders, illustrating that they are of relatively spherical shape. In the experiments, the electrolyte was agitated by a mechanical stirrer with 400 rpm. Temperature was kept at 50 °C, and the initial pH of the electrolyte was 4.2, which is a typical value used in electroforming.

After electroforming, scanning electron microscopy (SEM, Leica Steroscan 440) was used to study the surface morphology of the composite and the X-ray energy dispersion spectroscopy (EDX) system was utilized to determine its composition. Ramp-up and ramp-down current waveforms were introduced to drive electrodeposition. The pulse parameters used were: f = 100 Hz and $t_{on} = t_{off}$, where t_{on} is the deposition time and t_{off} is the relaxation time, and $T = t_{on} + t_{off}$. Fig. 2 is the schematic diagram of the waveforms. Vickers microhardness test was conducted under a load of 25 g on a cross section of the composites. The load and testing surfaces were selected to avoid any subtract effect on the measurements.

3. Theoretical considerations

The Ni–SiC impedance behaviour in nickel sulphamate was studied. As a weak amplitude sine-shaped potential perturbation is superimposed to the steady-state potential value, sine-shaped modulations of θ and I are produced. The Nyquist plots of EIS measurements were shown in Fig. 3. The diagram was composed of a high-frequency capacitive loop followed by a low frequency inductive loop.

The high-frequency capacitive loop represents the reduction mechanism in the nickel sulphamate bath, and it includes the double layer capacitance and the charge transfer resistance.

The reduction of pure nickel in a Watts bath has been described in detail by mechanisms. Epelboin and co-workers [18,19] proposed a model using a chemical impedance procedure. The authors consider that the reaction mechanism involving an intermediate species $(NiOH)^{+}_{ads}$ plays an important role in the rate-determining step. The addition of silicon carbide particles influenced the reactions in three main ways:

(1) offering more nucleation sites that are detrimental to crystal growth;
(2) nanoparticles will enhance the ionic transport, and also activate the nickel reduction [16];

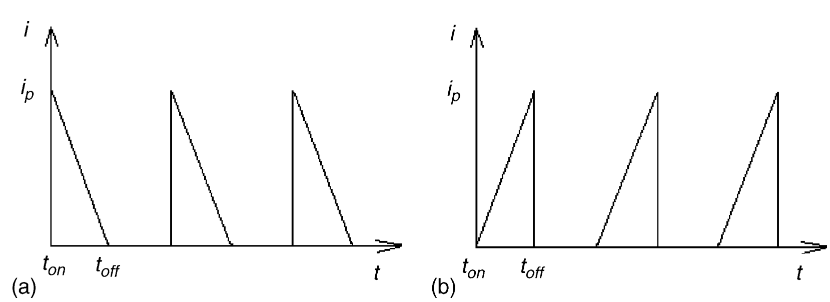

Fig. 2. The schematic diagram of: (a) ramp-down waveform with relaxation time; (b) ramp-up waveform with relaxation time.