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High-efficient surface modification of thin austenitic stainless steel sheets applying short-time plasma nitriding by means of strip hollow cathode method for plasma thermochemical treatment

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The present work is devoted to the short-time plasma nitriding of EN 1.4301 (AISI 304) austenitic stainless steel sheets in a pulsed glow discharge by means of a novel strip hollow cathode process for plasma thermochemical treatment (SHC-PTT) aiming at their use as bipolar plates of proton exchange membrane fuel cells (PEMFC). The fundamental trends in the change of the interfacial contact resistance (ICR) and corrosion resistance in dependence on the duration of plasma nitriding were studied. The investigations were focused on the capability of the method to reduce the ICR without deterioration of the corrosion resistance in a high-rate process. Within the range of experiments it could be shown that at a certain temperature, defined by improved or at least non-deteriorated corrosion resistance, the plasma nitriding rate is determined by the requested value of ICR. The simultaneously reduced ICR and improved corrosion resistance are explained by the formation of chromium nitrides on the substrate surfaces during the plasma nitriding. Acceptable ICR and corrosion resistance could be achieved in a continuous non-isothermal plasma nitriding process at a simulated strip rate up to 23 m h^{-1} with further potential to speed up the process.

1. Introduction

Recently we published a paper on the new strip hollow cathode method for plasma thermochemical treatment (SHC-PTT) of large-area metallic substrates such as sheets or strips [1]. Using this method, plasma nitriding of EN 1.4301 (AISI 304) austenitic stainless steel sheets was investigated in a stationary treatment mode at 673 K for 1200 s, aiming at the fulfilment of requirements for bipolar plates of proton exchange membrane fuel cells (PEMFC) with respect to interface contact resistance (ICR) and corrosion resistance. It was found that a 1.3 μm thick nitrogen-expanded austenite diffusion layer (for brevity will be called nitrided layer) could be generated, indicating a plasma nitriding rate about two times higher as compared to the literature [2]. The recommendation of the U.S. Department of Energy (DOE) [3,4] – ICR less than 20 mΩ cm^2 at a contact force of 140 N cm^{-2} and corrosion resistance, characterized by the current density at 0.6 V(Ag/AgCl), less than 1 μA cm^{-2} – is applied here as a benchmark. Accordingly, aiming at the requirements of cost-effective mass production the following investigations were focused on the capability of the method for even faster short-time plasma nitriding and finally, to give an idea of the implementation of a continuous process of surface modification of steel strip. Another purpose of this work is to identify fundamental trends in the change of the ICR and corrosion resistance in dependence on the duration of plasma nitriding and the nitrided layer thickness, respectively, and to interpret the simultaneously reduced ICR and improved corrosion resistance.

A simple and effective way for accelerating the plasma nitriding as a diffusion process is to increase the diffusion rate of nitrogen by increasing substrate temperature. As the heating of the substrates to the required temperature by means of SHC-PTT occurs only by the glow discharge, nitriding at higher temperatures involves processing at higher electrical power and therefore at higher current density, which will further increase the plasma nitriding rate due to higher degree of ionization near the treated surface [5,6]. Here, despite the short process duration, particular care must be taken to avoid the exceeding of the critical temperature, specific for each type of austenitic stainless steel, above which chromium nitride is formed within the nitrided layer and the corrosion

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resistance may be deteriorate [7]. The heating rate of the substrates and the substrate temperature, which can be reached, are significantly higher when the glow discharge is intensified by a hollow-cathode effect mode [6]. Taking into account the small thickness of the substrates used in this work (0.1 mm), the only way to implement a high-power glow discharge without exceeding a certain substrate temperature is to use pulse-mode operation – resulting in repeated successive heating and cooling of the substrate – at which the diffusion is significantly facilitated as compared to a constant temperature due to the occurrence of large internal stresses and formation of structural defects [8].

ICR and corrosion resistance of plasma-nitrided austenitic stainless steels in chloride free acidic solutions are usually considered separately and related to the properties of the nitrogen-expanded austenite (S phase [9]) [2,10,11]. The reduction of the ICR is explained by the removal of the native passive layer and the formation of the S phase [11]. Also an improved corrosion resistance is being suggested to be due to a dense S phase without an explanation whether it acts as a barrier or in a different way [2,11]. The decreased corrosion resistance is generally associated with the formation of chromium nitride and the resulting chromium depletion of the passive layer [12] or by defects such as slip lines and dislocations [10].

Transition metal nitrides and particularly those of chromium – CrN and Cr_2N – are characterized by a combination of high electrical conductivity and chemical stability. More specifically, Cr_2N possesses significantly better electrical conductivity compared to CrN. Owing to the considerably reduced charge carrier concentration for CrN, it has been suggested that its conductivity may have semiconducting character [13]. The formation of chromium nitrides by the nitriding of austenitic stainless steels starts from the surface with the highest nitrogen concentration [10]. It is also well known that the alloying of 12.5–13.0 at% chromium to iron leads to surface passivation of the resulting iron–chromium alloys [14,15]. Hence, we assumed that the reduction of the ICR by means of plasma nitriding of austenitic stainless steels is due to the formation of chromium nitrides on the substrate surfaces. The simultaneously changed corrosion resistance, compared to the untreated material, may be determined by the rate of the chromium depletion of the matrix – improved or unchanged at chromium content more than 13 at% and deteriorated at less than 13 at% chromium.

2. Experimental

2.1. Plasma nitriding by means of SHC-PTT

Plasma nitriding was carried out by means of SHC-PTT in stationary treatment mode which was described in detail in Ref. [1]. The device is designed for simultaneous, one-sided processing of two grounded metal sheets within one experiment. The substrates sized 350 mm × 150 mm are positioned parallel to each other at a distance of 30 mm. The glow discharge volume is delimited by sections of the internal substrate surface with height of 150 mm and width of 140 mm each. Only these sections are undergoing the nitriding treatment. Special screens are used in order to avoid the flow of the glow discharge into undesired areas. A Pinnacle™ Plus generator (Advanced Energy) with 5 kW maximum power and frequency of 0–350 kHz was used to power the pulsed direct current glow discharge. The substrate temperature was measured by NiCr–Ni thermocouple spot welded on the outside of one of both substrates and positioned in the center of the treated area.

2.2. Materials and experimental conditions

Sheet samples of EN 1.4301 (AISI 304) austenitic stainless steel with chemical composition (in wt%) of 0.049 C, 0.64 Si, 1.11 Mn, 0.032 P, 0.002 S, 18.04 Cr, 8.0 Ni, 0.27 Mo, 0.052 N were cut from industrially produced 0.1 mm thick strip with finish 2R (bright annealed). Before being placed into the vacuum chamber the samples were manually cleaned with ethanol (99.9% absolute, VWR). Hydrogen and nitrogen of 99.999% purity (Linde) were used as process gases.

Experiments were carried out aiming at high-rate short-time plasma nitriding. After loading the substrates and evacuation of the vacuum chamber to the final pressure of $8 \cdot 10^{-3}$ Pa, a gas mixture of 50 vol% H_2 and 50 vol% N_2 was fed in and the pulsed glow discharge with a frequency of 145 kHz and reverse time of 3.1 μs was ignited. Two types of plasma nitriding were conducted – at continuously increasing substrate temperature without an isothermal stage (A, C and E) and at a fixed substrate temperature (B and D in Table 1), respectively. The time–temperature graphs of the main experiments A – D are presented in Fig. 1. The time–temperature graph of the additional experiment E, which was carried out to simulate a dynamic strip process, is shown separately in Fig. 2. The plasma nitriding at a fixed substrate temperature actually also included a non-isothermal stage of nitriding, i.e. the substrate heating up to the temperature of the isothermal nitriding; this was achieved by gradually increasing the discharge voltage, and was carried out in the same nitrogen-containing atmosphere as the subsequent isothermal nitriding. Due to the presence of nitrogen in the gas atmosphere, this first stage of processing includes a plasma pretreatment and as well a stage of non-isothermal nitriding at increasing substrate temperature up to the temperature of isothermal nitriding. Further, for more simplicity, the terms *non-isothermal plasma nitriding* for the plasma nitriding at continuously increasing substrate temperature without isothermal stage and *isothermal plasma nitriding* for the plasma nitriding at a fixed substrate temperature (including a non-isothermal nitriding pre-stage, as mentioned) are used in this article. The working pressure in both cases of plasma nitriding was 6–7 Pa. After the treatment the sheets were cooled down to room temperature in vacuum.

2.3. Analysis

Glow discharge optical emission spectroscopy (GDOES) using a GDA 750 (Spectruma) spectrometer was employed to analyze the distribution of nitrogen within the nitrided layers and to determine their thickness. The interface between the nitrided layers and the base material was arbitrarily defined as the plane at which the nitrogen concentration had decreased to 1.5 at%. Detailed description of the applied measurement procedure was reported elsewhere [1].

X-ray diffraction (XRD) in Bragg–Brentano geometry using CuK_α radiation was performed to investigate the phase composition of the plasma-nitrided layer. The measurements were operated in the 2θ angle range of 30°–80° with a scanning speed of $0.24^\circ\ min^{-1}$.

Surfaces chemical analysis using X-ray photoelectron spectroscopy (XPS) was carried out with a PHI 5500 ESCA system (Physical Electronics) using a MgK_α source ($E = 1253.6$ eV) without monochromator. High-resolution spectra were collected using an analysis area of approximately 2000 μm × 800 μm and 11.75 eV pass energy. The binding energy scale was normalized relative to the C–C/C–H-component in the C 1s peak from the surface contamination at 284.8 eV. The analysis angle was 47° with respect to the surface plane. Spectra were analyzed using PHI MultiPak instrument software.

The ICR measurements were carried out with double-sided plasma-nitrided substrates. Both sides of the sheets were nitrided by means of two separate experiments with break of the vacuum. A modified David's method [16], described in Ref. [17] was used. Sandwiched between two carbon papers (Sigracet® GDL 24 BC by