Vacuum 102 (2014) 31–37

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Strip hollow cathode method for plasma thermochemical treatment for surface modification of thin metal strips: Plasma nitriding of austenitic stainless steel sheets for bipolar plates

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ARTICLE INFO

Article history:
Received 18 May 2013
Received in revised form
23 September 2013
Accepted 4 November 2013

Keywords:
Strip hollow cathode for plasma thermochemical treatment
Austenitic stainless steel sheet
Plasma nitriding
Interfacial contact resistance
Corrosion resistance

ABSTRACT

Beside its conventional applications such as improving the wear resistance of machine parts and tools, plasma thermochemical treatment (PTT) can be successfully used as a method for surface modification to achieve specific surface properties. Surface electrical conductivity of austenitic stainless steel sheets, for example, can be significantly enhanced by means of plasma nitriding. Such materials are of interest for the use as bipolar plates of proton exchange membrane fuel cells (PEMFC). In this regard a new PTT method based on a strip hollow cathode (SHC-PTT) has been developed as a cost-effective process for surface modification of thin metal strips in continuous operation. A laboratory-scale SHC-PTT device operating in stationary treatment mode has been realized and short-time plasma nitriding of EN 1.4301 (AISI 304) austenitic stainless steel sheets has been studied. The obtained nitrided layers were investigated using GDOES and XRD. Further, the interfacial contact resistance of the sheets was measured and the corrosion behaviour was investigated by means of electrochemical methods. The obtained results clearly demonstrate the high potential of the new SHC-PTT method for further development in terms of treating thin steel strips in continuous operation.

1. Introduction

Different plasma thermochemical treatments (PTT) such as plasma nitriding, plasma carburizing or plasma boriding are widely used to improve the mechanical properties of the surface of engineering parts and tools. Recently, nitriding in a glow discharge has been of great interest for the development of metallic bipolar plates for proton exchange membrane fuel cells (PEMFC). The bipolar plates which are among the most expensive components of the fuel cells stacks must have a good corrosion resistance and thermal compatibility with the other components, and must provide minimal electrical losses [1]. Graphite-based materials being used today meet these requirements. However, the production of such graphite bipolar plates is expensive, moreover, the possibility of reducing their thickness and accordingly the volume and weight of the fuel cell stacks is strongly limited. For that reason many investigations have been focused on the possibility of replacing graphite with metallic materials which are able to fulfil the mechanical requirements demanded by this application at a thickness of about 0.1 up to 1 mm [2]. Austenitic stainless steel sheets in the thickness range of 0.1–0.2 mm are considered to be very good candidate materials for PEMFC due to their excellent mechanical properties and corrosion stability, low gas permeability and applicability to mass production [3]. The main drawback consists in an increased surface electrical resistance due to the passivation layer, resulting in unacceptable losses under PEMFC operating conditions. An interfacial contact resistance (ICR) less than 20 mΩ cm^2 at a compaction force of 140 N cm^{-2} and high corrosion stability with a passive current density of less than 1 μA cm^{-2} at 0.6 V (Ag/AgCl) are the most important requirements for bipolar plates for mobile application according to U.S. Department of Energy (DOE) [4,5]. An improvement of the electrical properties of the surface with unchanged or even improved corrosion resistance has been reported using physical vapour deposition (PVD) [6], plasma-enhanced chemical vapour deposition (PECVD) [7], low-temperature (<500 °C) [8] plasma nitriding [2,9,10] and other processes. The particular interest in plasma nitriding is due to the potential improvements of the properties of the outermost surface. In contrast to conventional surface-hardening, presumably only relatively thin nitrided layers need to be applied in order to minimize the surface electrical resistance.

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0042-207X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2013.11.001

Accordingly, any negative mechanical influence on the forming process due to surface hardening effect, which is required to create the final profile of the bipolar plates from the sheet material, should be minimized.

The attainment of the aforesaid properties of the austenitic stainless steels by means of plasma nitriding has to be achieved under such process conditions (substrate temperature, duration) in which only expanded austenite, well known as a single phase S [11], is formed on the substrate surface besides the base austenite phase, i.e., the formation of any chromium nitrides, deteriorating the corrosion resistance, must be avoided. Despite the relatively low thickness of the nitrided layers (2–5 μm), the duration of the conventional plasma nitriding process is typically in the range of 2–4 h [2]. In addition, other new methods of nitriding have been developed, such as low-pressure plasma arc source ion nitriding [12], nitriding in inductively coupled plasma (ICP) [10], etc. Compared to these methods, the conventional glow discharge nitriding is characterized by a simple principle and robustness for practical applications in industrial production [13]. A major disadvantage is the duration of the process which does not meet the requirements of cost-effective mass production and is certainly one important drawback that there is virtually no application of PTT on large area substrates such as metals sheets or strips.

Conventional plasma nitriding may be intensified by increasing the diffusion rate of nitrogen through elevated substrate temperatures. Taking into account the very short process duration it can be significantly increased without forming chromium nitrides [14]. Another effective way to increase the plasma nitriding rate is the increase of nitrogen ionization degree in plasma which results in the increase of nitrogen concentration transferred into the specimen surface and accordingly, a higher growth rate of nitride layer [15]. High ionization degrees may be provided by magnetron discharge [16], low-pressure plasma arc source [12] and hollow cathode glow discharge [17,18]. The latter is of particular interest for the processing of thin metal sheets in static and dynamic mode as well because of the easy formation of the discharge zone geometry. Hollow cathode conditions enable an increase of nitriding speed of austenitic stainless steels by a factor of two, compared with conventional plasma nitriding processes [17].

In the present work a new strip hollow cathode method for plasma thermochemical treatment (SHC-PTT) is presented, which is based on the strip hollow cathode method (SHC) [19,20] and has been particularly designed for one-sided surface modification of grounded thin metal strips in continuous process. In order to assess the potential of the method, short-time plasma nitriding of thin austenitic stainless steel sheets in stationary treatment mode has been studied. The goal was to improve the surface electrical properties without deterioration of the corrosion resistance.

2. Experimental

2.1. Setup of SHC-PTT

The experimental setup used in this work is shown in Fig. 1.The substrates (350 mm × 150 mm, thickness 0.1–0.2 mm) are attached face to face in parallel in a distance of 30 mm and hence the hollow cathode configuration with a length of 140 mm, a width of 30 mm and a height of 150 mm is formed. In this way, only the portion of their internal surfaces with a length of 140 mm and a height of 150 mm is processed. One-sided processing offers the advantage of separate treatment of each substrate surface if different surface properties are required. If both-side surface treatment is needed, at least two SHC-PTT modules for subsequent treatment of upper and lower substrate surface are required or a module for simultaneous treatment of both surfaces has to be designed, respectively.

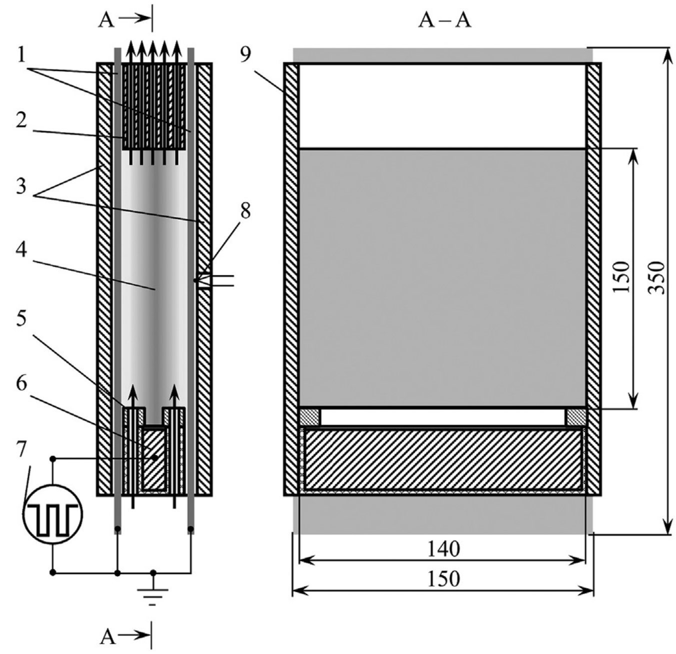

Fig. 1. Schematic drawing of SHC-PTT in stationary treatment mode: (1) metal sheet, (2) exhaust block, (3) backside screen, (4) glow discharge, (5) anode block, (6) anode, (7) dc pulsed generator, (8) thermocouple, (9) sidewise screens.

In order to limit the extent of the glow discharge 4 to the volume between both substrates, special sidewise screens 9 have been used (Fig. 1). At the bottom of the device the glow discharge is limited by the anode block 5 and at the top by the exhaust block 2. The external substrate surfaces are shielded by specific backside screens 3, to prevent the discharge glow on them. The copper anode (6) is water-cooled and located in a special box at the bottom of the device. The box is made of ceramic and metal components and designed to shield all surfaces of the anode with the exception of its work surface – a part of its upper surface, orientated to the hollow cathode space. Thus the box prevents the broadening of the glow discharge outwards. Just in front of its working surface the process gases are fed in. The flow rates *q* of working gases are controlled automatically by means of mass flow controllers. The exhaust block 2 must prevent the spread of the glow discharge outside the hollow cathode space and at the same time not to hinder the pumping-out of the working gases. Meeting these requirements is achieved by a system of rectangular ceramic plates, suitably spaced from each other so as to form a number of interspaces.

The substrates are heated to the process temperature through the glow discharge. The substrate temperature is measured by a NiCr–Ni thermocouple 8, spot-welded on the outside of one of the substrates and positioned in the centre of the treated area. Thanks to the ground potential of the substrates and the shielding of their external surfaces, simple and reliable temperature measurement was realized. Moreover, the significantly reduced inertness of the measuring system due to the low substrate thickness also allows accurate temperature measurements at high heating rates.

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 negative potential was grounded purposely, aiming at the future usage of the method in continuous operation.