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Combined plasma surface modification of austenitic stainless steel for bipolar plates

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ABSTRACT

A fundamental study of a new concept for surface modification of metal surfaces based on two consecutive processes – metal coating and plasma nitriding – is conducted in order to obtain thin plasma-nitrided diffusion layers on austenitic stainless steels enriched with the metal from the coating, with superior surface characteristics with respect to the bipolar plate application of proton-exchange membrane fuel cells. The special feature of the concept is that the metal coating is permeable to the nitrogen diffusion into the base material.

Austenitic stainless steel sheets EN 1.4301 with a thickness of 0.1 mm are coated with chromium films in the range of 5–200 nm by means of magnetron sputtering deposition. Subsequently, short-time plasma-nitriding by means of the strip hollow-cathode method is applied. The diffusion layers are analysed taking into account the nitrogen diffusion into the base material, diffusion processes at the interface between the chromium coating and the base material, the distribution of the elements, and the phase formation, in particular the formation of chromium nitrides. Further investigations are performed to determine the influence of applied plasma treatment on the electrical conductivity and corrosion resistance of the stainless steel surfaces.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are of particular interest in the development of alternative energy sources for various mobile applications, especially for electric car drives. They have a high power density at low volume and weight requirements. One of the main components of the PEMFCs is the bipolar plate. Bipolar plates connect several membrane electrode assemblies in a stack, conduct hydrogen and oxygen-containing gas to the cells and lead the arising heat and water away. They must possess a good corrosion resistance and thermal compatibility with the other components, and they must provide minimal electrical loses. Furthermore, the bipolar plates shall facilitate a very compact design in order to keep the space demand and weight as low as possible [1,2]. Technically, the requirements mentioned above can be met by using bipolar plates made of graphite-based materials or gold-coated stainless steel sheets. However, the former are expensive and require a lot of space due to their appreciable thickness, the latter are too expensive for a mass production [3].

Austenitic stainless steel sheets in the thickness range of 0.1 to 0.2 mm are considered to be very good candidate materials thanks to their excellent mechanical properties and corrosion stability, low gas permeability and applicability to mass production [4]. Their main drawback consists in an increased surface electrical resistance due to the passivation layer, resulting in unacceptable losses under PEMFC operating conditions. Therefore, a cost-effective modification of the steel surface is intended.

High corrosion stability with current density of less than 1.0 $\mu A \cdot cm^{-2}$ at -0.1 and 0.6 V(Ag/AgCl, corr. to approx. 0.6 V(SCE)), and an interfacial contact resistance (ICR) less than 10 $m\Omega \cdot cm^2$ at a compaction force of 138 $N \cdot cm^{-2}$ are the most important recommendations for bipolar plates for mobile application according to the 2020 target developed by the U.S. Department of Energy (DOE) [5]. Concerning the corrosion resistance it should be noted that the potential mentioned above refers to a normal fuel cell operation. Under start operation conditions, local potentials of more than 1.4–1.8 V(SHE, corr. to approx. 1.2–1.6 V(SCE)) can occur on the cathode [6].

Recently, various methods such electrochemical surface treatment, physical or chemical vapour deposition, thermochemical treatments, etc. have been used in order to achieve the surface properties as described above [7]. There already exist appropriate concepts which enable a separate achievement of the recommended ICR or corrosion resistance; however, it still represents a great challenge for simultaneous meeting of both properties. For this purpose, appropriate methods for surface modification especially in the light of the mass production applicability have not been extensively investigated.

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It is well known that the increased content of chromium, titanium, niobium, etc. in austenitic stainless steel contributes to improvement of its corrosion resistance [8]. Higher chromium concentration contributes to higher stability of the surface properties [9]. However, the availability of stainless steel with chromium content larger than 28 wt% is limited due to the low impact strength and manufacturing metallurgical difficulties. That's why approaches are being pursued to increase the chromium content in the near-surface region of stainless steels by means of surface engineering processes.

A significant improvement of the corrosion resistance or ICR, or even of the both properties was detected applying diffusion chromising of austenitic stainless steels without or with formation of nitride layers or nitride phases [10,11], high temperature nitriding of Ni-50Cr alloy [12] and nitriding of chromium-electroplated stainless steel [13,14]. Instead of chromium Wang et al. have developed technologies for surface modification using niobium [15,16] or molybdenum [17]. The produced pure diffusion layers [16] or diffusion layers composed of niobium nitride surface layer and an underlying nitrogen-based diffusion layer [15] led to significant improvement of the corrosion resistance of AISI 304 stainless steel. Although the passive current density at 0.6 V is larger than 1.0 $\mu A \cdot cm^{-2}$, it is remarkable that the passive region is very stable and is extended in the direction to more positive potentials. Hence, the passivation breakdown potential is characterised by a very low current density at potentials significant larger than 0.6 V. The main disadvantage of the reviewed processes is its long duration.

Besides for production of nitride layers, the nitriding and particularly plasma nitriding as a separate process is also of great interest for the surface modification of austenitic stainless steels due to the significant reduction of the ICR [4,18]. However, the stability of the ICR after electrochemical polarisation testing in simulated PEMFC operating conditions is questionable [15]. Thus, in the search for new surface engineering technologies for achievement of stable surface properties, a new hybrid plasma surface technology has been developed, combining low-temperature active-screen plasma co-alloying with both nitrogen and niobium with deposition of a thin niobium layer on the top surface [19]. However, with a process duration of 10 h it seems to be unacceptable for bipolar plate manufacturing.

In view of the requirement of cost-effective continuous processes, the strip hollow-cathode for plasma thermochemical treatment (SHC-PTT) method was developed recently and a high-rate short-time plasma nitriding in a stationary treatment mode was investigated in order to improve the surface electrical properties [20]. Besides, no damage was observed after forming of the plasma carbonitrided steel sheets and thus, the processing route of bipolar plates surface modification followed by forming was successfully validated [21]. Although the method has a large potential for production of austenitic stainless steel strips with very good electrical conductivity in continuous treatment mode under favourable operating conditions, concerning the severe requirements dictated by the fuel cell application, a sufficient corrosion resistance and a stable minimal ICR have not been ensured yet.

Aiming at the achievement of stable minimal ICR and improved corrosion resistance, a new concept for high-rate surface modification of austenitic stainless steel strips with respect to the production of bipolar plates for PEMFC was created. The concept is based on two consecutive processes: deposition of metallic layer of one or more transition metals (such as chromium, titanium, niobium, etc.) and plasma nitriding. The special feature here is that the metallic layer is permeable to the nitrogen diffusion into the base material at the nitriding temperature.

The present work is devoted to the study of the influence of chromium as a main alloying element and the nitrogen on the surface properties of the austenitic stainless steel EN 1.4301. With regard to a cost-effective steel strip treatment in a continuous process, magnetron sputtering for the chromium coating and SHC-PTT for the plasma nitriding were employed. The treated sheet samples are studied in terms of the nitrogen diffusion into the base material, diffusion processes between chromium from the coating and the base material, the distribution of elements and the phase formation, and the chemical state of the elements on the surface.

2. Materials and methods

2.1. Substrate material and plasma treatment

Industrially produced 0.1-mm thick and 150-mm wide bright-annealed (finish 2R) stainless steel strip EN 1.4301 (AISI 304) with chemical composition (in wt%) of 0.0570 C, 0.351 Si, 1.033 Mn, 0.029 P, 0.008 S, 18.120 Cr, 8.050 Ni, 0.032 N and Fe balance was used as substrate material. Before being placed into the low-pressure chamber for chromium coating deposition, the strip was cleaned in aqueous alkaline solution. A chromium target (300 mm × 110 mm) with purity of 99.95 wt% was used as metal source.

One-sided chromium coating deposition was carried out by means of d. c. magnetron sputtering in a continuous strip process on the research and pilot equipment for in-line deposition of plates and metallic strips by Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP (Dresden, Germany) described elsewhere [22]. Primarily, the coating thicknesses on single steel sheets were determined in order to derivate the dynamic deposition rate. The experiments were performed at a distance between the magnetron target and strip of 75 mm, argon flow rate of 834 sccm, working pressure of 0.18–0.22 Pa and magnetron discharge power of 3750 W (power density of 11.4 $W \cdot cm^{-2}$). Under these conditions a dynamic deposition rate of 1.33 $nm \cdot m \cdot s^{-1}$ was found; this figure was used for the determination of appropriate strip rates for the deposition of chromium coatings with different thicknesses in continuous strip process. Just before the coating deposition, the stainless steel strip was sputter-etched using an inverted magnetron arrangement. Independent of the different strip rates, a sufficient etching removal and thus a very good adhesion was achieved for every coating deposition conditions. Varying the strip rate, chromium coatings with different thicknesses with nominal values in the range of 5–200 nm were prepared (Table 1). Finally, the coil was cut into 350-mm long sheets for plasma nitriding.

Short-time plasma nitriding was carried out by means of SHC-PTT in stationary treatment mode. The principle of the method and the device used were described elsewhere [23]. The chromium-coated substrates without any additional treatment were loaded and the vacuum chamber was evacuated 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. The purity of both gases (Linde) was 99.999%. Pulsed glow discharge with a frequency of 145 kHz and reverse time of 3.1 μs was ignited at the working pressure of 6–7 Pa, the substrates were heated for a time of 120 s by gradually increasing the discharge voltage and isothermal plasma nitriding with a holding time of 360 s was conducted. Finally, the sheets were cooled down in low-pressure. The experimental matrix is presented in Table 1.

2.2. Characterisation methods

Glow discharge optical emission spectroscopy (GDOES) was used to investigate the elemental depth profiles after plasma nitriding. The analyses were done with a Spectruma GDA 750 system using an anode tube with a diameter of 2.5 mm. The thin sample sheets were each glued on a thick steel backing for cooling purposes.

Table 1
Applied nominal coating thicknesses, process parameter of plasma nitriding by means of SHC-PTT and sample designation.

Experiment	EN 1.4301PT	A	B	C	D	E	F
Plasma treatment in H_2 atmosphere (s)	360	–					
Nominal chromium coating thickness (nm)[a]	–	–	5	10	20	80	200
Plasma nitriding	–	723 K, 360 s					

[a] Maximum deviation less than 20%.