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Full Length Article

Characterization of stainless steel surface processed using electrolytic oxidation and titanium complex ion solution

Yubin Kang, Jaeyoung Choi, Jinju Park, Woo-Byoung Kim, Kun-Jae Lee*

Department of Energy Engineering, Dankook University, Cheonan, 31116, Republic of Korea

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ABSTRACT

This study attempts to improve the physical and chemical adhesion between metals and ceramics by using electrolytic oxidation and a titanium organic/inorganic complex ion solution on the SS-304 plate. Surface analysis confirmed the existence of the Ti—O—M_x bonds formed by the bonding between the metal ions and the Ti oxide at the surface of the pre-processed SS plate, and improved chemical adhesion during ceramic coating was expected by confirming the presence of the carboxylic group. The adhesion was evaluated by using the ceramic coating solution in order to assess the improved adhesion of the SS plate under conditions. The results showed that both the adhesion and durability were largely improved in the sample processed with all the pre-processing steps, thus confirming that the physical and chemical adhesion between metals and ceramics can be improved by enhancing the physical roughness via electrolytic oxidation and pre-processing using a Ti complex ion solution.

1. Introduction

Surface processing of metals is the most widely used technique for improving their properties. Therefore, various deposition and coating processes such as chemical vapor deposition [1–3], electrochemical process [4–7], sol-gel process [8–11] and spray pyrolysis technique, etc. have been proposed for coating the surface of metals with non-homogeneous materials like ceramics. However, metallic materials including stainless steel inherently show poor physical and chemical adhesion to ceramics because of their metaphysical and material differences. Many efforts are being made by researchers to resolve this problem [12,13]. The approaches such as the addition of a binder to a coating solution containing an organic solvent or the use of a coating of a buffer layer with relatively high adhesion are currently being implemented to improve the adhesion between metals and ceramics [14–16]. However, these approaches include smaller surface area of the activated layer. The other disadvantages include decrease in adhesion because of the decomposition of the organic solvent at high temperatures and high processing cost. Therefore, an alternative surface processing technology is highly imperative.

This study proposes a surface processing method for improving the adhesion of a TiO_2-based catalyst coating liquid to a metal support by focusing on the tendency of the honeycomb-shaped catalyst support being replaced by metallic materials with high thermal conductivity [17]. Electrolytic oxidation was used to improve the physical adhesion to the coating layer by generating pores on the metal surface, and the chemical structure of the surface before and after the electrolytic oxidation was examined via surface analysis. In order to compensate for the defects of the binder or buffer layer which cannot form chemical bonds, a titanium complex ion solution (called citratoperoxotitanate) [18], which has the potential for chemical bonding, was coated on the surface of an stainless steel (SS) plate to improve its chemical adhesion with the ceramic coating solution. Surface analysis was used to confirm the presence of chemical bonds such as Ti—O—M_x and to determine whether the bonding type affected the adhesion. Furthermore, the adhesion of the ceramic coating solution to the metal plate for each condition was evaluated based on the surface analysis results. The method proposed here is more economical than the existing methods and has a potential for chemical bonding as well. Thus, along with improving the adhesion between the materials, this method can also improve the material performance.

* Corresponding author.
E-mail address: kjlee@dankook.ac.kr (K.-J. Lee).

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2. Experimental

2.1. Electrolytic oxidation of the stainless steel plate

In order to perform surface analysis before and after the electrolytic oxidation of the SS-304 plate, an SS plate with porous microstructure was fabricated. Dilute nitrohydrochloric acid obtained by mixing hydrochloric (Daejung, 35%) and nitric acids (JT Baker, 68%) diluted to 3.6 and 1.8%, respectively, was used as the electrolyte. The SS-304 plate (20 mm × 20 mm) was used for both the cathode and the anode. The distance between the electrodes was fixed to 5 cm. The area ratio of the anode and cathode exposed to the electrolyte was 4:1. The edges of the electrodes were masked with an insulating tape in order to prevent the edge-rounding phenomenon due to the concentrated charges on the edges of the anode. For the proper application of voltage, a direct-voltage-type rectifier was used for the electrolytic oxidation on both the electrodes for 3 min at an applied voltage of 15 V. For the proper control of the electrolyte temperature, the temperature-controlled water in the jacket beaker was cycled flow-type using a thermostatic bath at 25 °C. The fabricated etched-SS plate was immediately washed using distilled water to remove any remaining impurities followed by sonication for 10 min and drying in an oven for 24 h at 60 °C.

2.2. Formation of coating layer using titanium complex ion

The complex ion solution for the coating layer formation was produced by the ligand exchange reaction between titanium and citric acid, as described in the protocol by Tada et al. [19]. The titanium complex ion solution so obtained was coated on the SS plate using the dip coating method and was vacuum-processed for 10 min at 80 kPa in order to prevent the formation of air bubbles. The coated SS plate underwent a heat treatment in air at 200 °C for 4 h.

2.3. Specimen preparation and evaluation of adhesion

The selective catalytic reduction (SCR) catalyst powder (TiO_2, 20 wt% Mn, 4 wt% Ce, 5 wt% W) was used as the coating powder. The weight ratio of the coating powder and distilled water in the coating solution was 3:7. Ludox®-AS 40 was used as the binder and it was added with 10 wt% of the coating powder. The SS304 plate was dip-coated under each condition (Whether or not to conduct the etching process or titanium coating process), and after the coating process, the air bubbles were removed by vacuum processing at 80 kPa for 10 min. Then the coated-SS plate was sonicated at 40 kHz for 30, 60, and 120 s and completely dried in an oven for an hour at 110 °C. The adhesion rate of the dried specimen was calculated by comparing the initial coating weight and the weight after the removal of the coating.

Table 1
Elements composition of titanium coated SS plate surface.

Element	C	O	Cr	Fe	Ni	Mn	Si	Ti
Atom%	19.84	18.53	11.71	43.43	3.15	0.91	0.64	1.79

2.4. Characterization

Field emission scanning electron microscopy, (FE-SEM, XEISS, Gemini 500) was used to perform the surface microanalysis of the SS plate before and after etching, and Fourier transform infrared spectroscopy (FT-IR, Agilent, Cary-630) as well as X-ray photoelectron spectroscopy (XPS, ThermoVG, SIGMA PROBE) were used for the surface and structural analyses of the chemical bonds. Deconvolution process was conducted with XPSPEAK41 software (ver. 4.0).

3. Results and discussion

In an electrochemical system, when a voltage is applied to the anode and cathode, oxidation-reduction of the metals generates metallic ions from both the electrodes because of the voltage drop and ion exchange via the electrolyte, and any excess electron is transferred to the cathode where it combines with the cations to form a precipitate. The electrolytic oxidation technique used in this study utilizes the formation of pores on the metal surface by the pitting phenomenon when the metal is eluted. The microstructure created at the surface of both the electrodes could be controlled

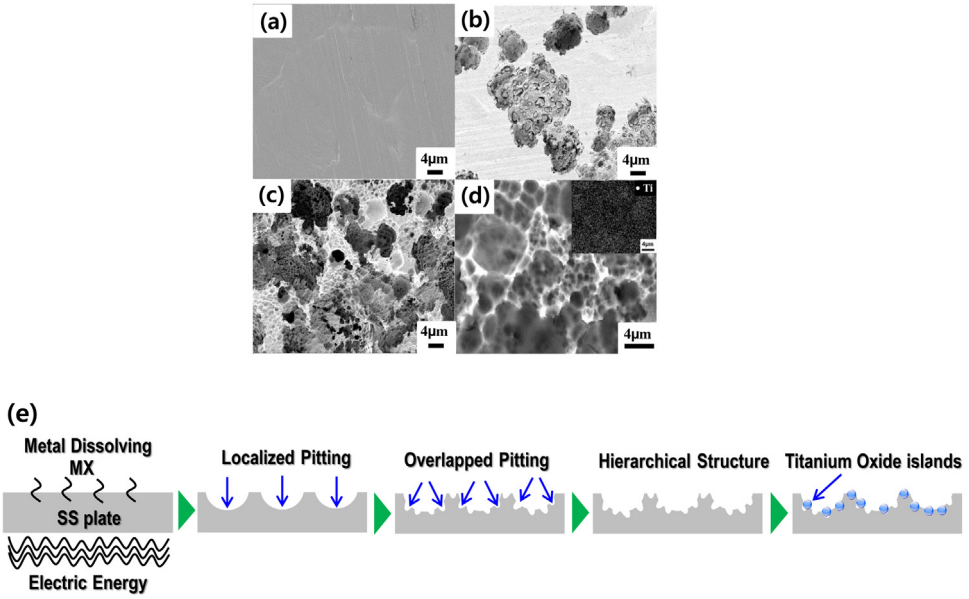

Fig. 1. SEM images of the bare SS plate (a), etched SS plate with 1 min (b) and 3 min reaction time (c) and titanium coated SS plate (d); and the schematic of porous structure formation (e).

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