Application of Nuclear Convergence Technology and Materials : 3D Laser Cladding Method and CrAl Alloy Coating for Highly Corrosion-Resistant for Fuel Cells

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1. Introduction

The 3D laser coating technology using CrAl alloy powder is considered and have been developed to enhance the oxidation resistance as accident tolerant fuel (ATF) under loss of coolant accident (LOCA) conditions [1],[2],[3]. 3D laser cladding coating is a technology of coating a dissimilar metal on a base metal melted with a laser while supplying metal powder. This technology has the characteristics of forming a local molten area to minimize the heat-affected zone and to minimize deformation and damage of the base material. It is also evaluated as an efficient and economical protective coating technology compared to the vacuum coating process [2],[3],[4]. In addition, it has been reported that CrAl alloy coating was very effective in enhancing the oxidation resistance of metals at high temperatures [5]. Since Cr_2O_3 and Al_2O_3 can form on the surface of CrAl, so the possibility of further increasing oxidation resistance has been confirmed. [1],[3].

On the other hand, the proton exchange membrane fuel cells (PEMFCs) directly convert chemical energy into electrical energy, so the conversion efficiency is high, and the by-products after the reaction are clean and reliable power is produced [6]. The bipolar plate is one of the key components because it supplies and cuts off fuel and air to each pole, exhausts the reaction products from the cell, and exchanges heat generated in the electrochemical reaction. However, metallic bipolar plates, the surface is corroded in the fuel cell environment in an acidic environment, and metal ions are eluted, which contaminates the catalyst and membrane, thereby reducing PEMFC performance [7],[8].

Since coating technology can achieve improved resistance and surface properties without changing the base material, numerous studies have been conducted in the field of metallic bipolar plates [9],[10]. The cost of the vacuum coating process and corrosion resistance and electrical conductivity of the coating materials are still under discussion. In order to improve the corrosion resistance of metallic bipolar plates, we select materials and technologies that are in the spotlight at ATF and conduct convergence research. The 3D laser cladding method was applied to the base material as metallic bipolar plate and the CrAl binary alloy was coated to evaluate its performance.

2. Methods and Results

2.1 Coating Method

The selection of the coating materials was based on the physical properties such as thermal conductivity and expansion, melting points and phase transformation behavior. For plate-shaped substrates, laser cladding parameters such as laser power, specimen velocity, powder injection and gas flow have been systematically discussed in previous studies [1],[2],[3]. The continuous wave (CW) diode laser (wavelength of 1062 nm) with a maximum power of 300 W (PF-1500F) and a power supply (Pwp14Y04K). The continuous wave (CW) laser (wavelength of 1062 nm) was applied with power ranged 80 to 250 W (PF-1500F), and the scanning speed ranged was adjusted 12 to 15 mm/s for the surface coating on stainless steels 316L (SS316L). A photograph of the laser equipment for coating is shown in Fig 1. To prevent any oxidation during the process, an inert gas (Ar) was continuously blowing into the melted surface of specimen. SS316L Bare plates were cut to a size of 60 mm × 60 mm × 0.1 mm. The substrates were molded using etching techniques. The CrAl coatings were deposited on the SS316L Bipolar plate using 3D Laser cladding coating method with CrAl powder (0.85Cr-0.15Al) and cleaned sonically in ethanol and acetone solution.

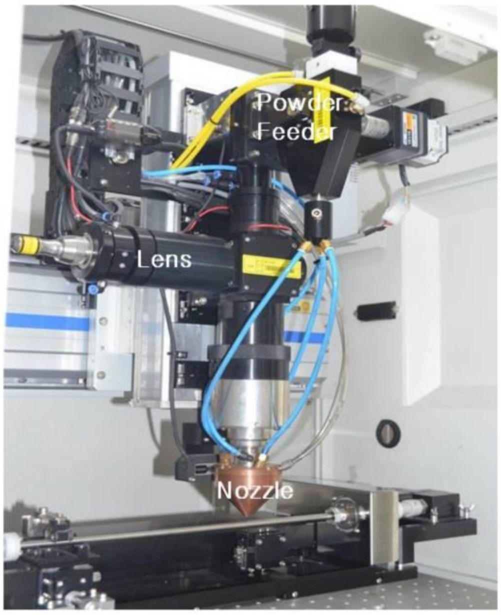

Fig 1. Appearance of the laser equipment for coating (adapted with permission from ref. [1].

2.2 Surface Analysis

The morphology of the coating surface was determined by the following analysis. The microstructure of the specimens were examined under a scanning electron microscope (SEM, S-4700, Hitachi) and operated at secondary electron mode. Chemical compositions of different selected micro-areas were analyzed by SEM energy dispersive spectrometry (EDS). Cross-sectional samples were prepared using a focused ion beam (FIB, Nova Nano SEM 200, FEI) system and investigated by transmission electron microscopy (TEM, Tecnai, FEI). The cross-sectional morphology, thickness, and microstructure of the CrAl films were determined by TEM analysis at an acceleration voltage of 200 kV. Electron diffraction and energy-dispersive spectroscopy (EDS) line-scan analyses were also conducted in the TEM to investigate the cross-section.

Fig 2. and Fig 3. are shown the cross-sectional SEM and TEM image of the CrAl coated SS316L by 3D Laser cladding method. The coating layer appears 2.5 ㎛ thickness and no crack and void are observed. For a more detailed study of the coating layer, Fig 2.(b), Fig 3.(b) show the EDS profiles from the base substrate to the coating layer. These results indicate that the coating layer consists of two composition of Cr and Al.

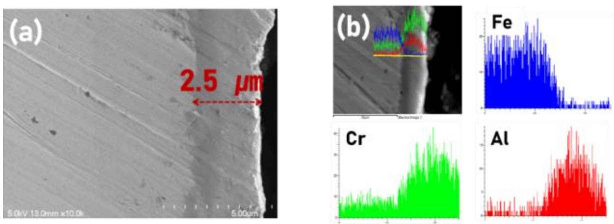

Fig 2. (a), (b) show the cross-sectional SEM-EDS analysis of the CrAl coating layer.

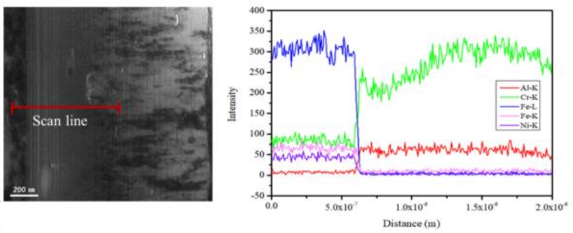

Fig 3. Cross-sectional TEM image and line scan mappings of CrAl coated specimen

2.3 Corrosion Studies

In the case of PEMFC system, it operates in the operating temperature range of 80–120 °C and the hydrogen ion concentration in the range of 2–4. In addition, a wet fuel injection environment promotes corrosion of the metal bipolar plates [6],[8]. Damage to the passivation film occurs due to various causes such as temperature, humidity, and pH, and eventually, ionic dissolution of the base material is derived. In response, potentiodynamic polarization test was conducted to confirm the corrosion behavior of bare SS316L and CrAl coated substrates in a sulfuric acid environment in the PEMFC environment was simulated ex-situ conditions (0.5 M H_2SO_4, 80°C) [7],[8].

Potentiodynamic polarization is a method to test the corrosion reaction of fuel cell bipolar plates using the LSV technique. Measuring the current value in operating voltage range of the fuel cell, it is possible to know the active and the passivation region. The electrochemical process of corrosion potential and passivation behavior is determined by the Butler-Volmer equation and the Tafel plot. The Butler-Volmer equation is expressed for a current that varies with an applied voltage when the overall reaction rate is governed by the charge transfer process [6],[9],[10].

$$I = I_0 \left[exp\left(\frac{-\alpha F\eta}{RT}\right) - \exp\left(\frac{(1-\alpha)F\eta}{RT}\right)\right] \quad (1)$$

Where,
I : Electrode current density
α : Charge transfer coefficient
F : Faraday constant
H : Activation over potential (defined as E–Eeq)
R : universal gas constant
T : absolute temperature

Potentiodynamic polarization curves of Bare SS316L (uncoated SS316L), CrAl on SS316L in the simulated acidic environment are shown in Fig 4. The corrosion behaviors of specimens are confirmed through the current value generated on the metal surface, and the potential at which the anode and cathode current become equal is expressed as the corrosion potential (E_{corr}). The corrosion potential means a potential value at which corrosion starts after the surface passivation film is formed. That is, the smaller the corrosion potential value, the greater the oxidation tendency. the current density (I_{corr}) is larger, which means that the electron transfer due to the elution of ions is activated, which means that more corrosion occurs. In the LSV results, the corrosion potential value of the CrAl coated specimen was higher than that of stainless steel and the corrosion current was lower. These results showed that the CrAl coating had a positive effect on the corrosion inhibition properties compared to SS316L.

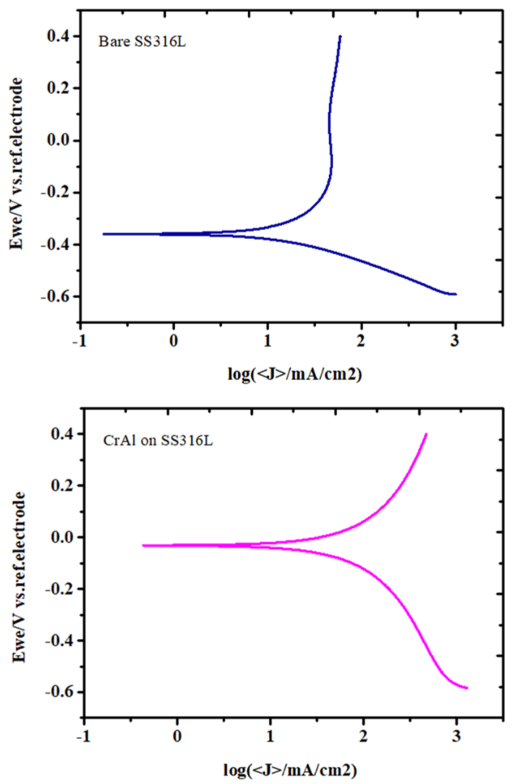

Fig . Polarization curves of bare SS316L and CrAl coated SS316L in 0.5 M H_2SO_4 solution at 80℃

3. Conclusions

3D Laser cladding coating technique is applied to CrAl on the surface of metal bipolar plates. The CrAl film as a protecting layer was successfully deposited on the SS316L bare substrate and uniform microstructure by Laser cladding system. Moreover, In PEMFC acidic environment, CrAl coated SS316L was excellent high corrosion durability compared SS316L, which will form the basis for electrochemical thin film process of the next generation of the bipolar plates for Fuel Cells. In this study, we demonstrated that ATF coating materials and coating Convergence techniques can also be applied in the fuel cell future industry.

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