

Structure and Characteristics of Highly Durable Fuel Cell Bipolar Plate Material, NC Titanium

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Abstract

Bipolar plates are vital elements of fuel cell vehicles which are expected to be a key technology for reducing CO₂ emissions. They are required to have many functions and properties, such as acting as flow channels for fuel gas and acting as current collectors, also resisting corrosion, and possessing thinness for downsizing and lightening. Since several hundred bipolar plates are installed in each fuel cell vehicle, their productivity and cost reduction are also essential. Hence, Kobe Steel has developed NC (nano-carbon composite-coated) titanium, the world's first pre-coated bipolar plate material that meets the above requirements. NC titanium is installed in vehicles such as the fuel cell vehicle MIRAI, which Toyota Motor Corporation launched in 2020. This paper explains the development concept, structure, and characteristics of NC titanium.

Introduction

The transportation sector accounts for 20% to 25% of carbon emissions, making it a primary source of global warming,¹⁾ and thus reducing carbon emissions a key issue for the industry. This has led to a shift from internal combustion engine vehicles toward electric vehicles, including fuel cell vehicles. Fuel cell vehicles run on electricity produced by the reaction between hydrogen and oxygen. Because they only emit water, these are clean vehicles free of carbon emissions. There are several types of fuel cells, but the ones used in vehicles are polymer electrolyte membrane fuel cells (PEMFC), which are characterized by low-temperature operation, low size and weight, and quick startup.

One of the core components of a PEMFC is the bipolar plate. Automotive fuel cells contain hundreds of bipolar plates, each about the size of a sheet of A4 paper. They must be thin to minimize size and weight, yet strong enough to withstand shock during vehicle operation, which is why they are most commonly made of metal. The bipolar plate serves not only as a flow channel for hydrogen, oxygen, and the water generated, but also as a current collector, which collects and conducts electrons generated by the reaction through its surface. Metal bipolar plates have a surface treatment that ensures both conductivity

and corrosion resistance. High productivity and low cost are further important issues for bipolar plates. The pre-coating method of production, in which the metal foil coil undergoes continuous surface treatment and is then press-formed into a bipolar plate, supports these factors.^{2), 3)} However, pre-coated bipolar plates have not been incorporated into a vehicle released to market because press-forming damages the surface treatment, degrading performance.

In response, Kobe Steel developed the world's first pre-coated titanium material for bipolar plates: NC (nano-carbon composite-coated) titanium, which exhibits both surface conductivity and corrosion resistance.⁴⁾ This material is used in vehicles such as the Mirai fuel cell vehicle, which Toyota Motor Corporation released in 2020.⁵⁾ This paper covers the development concept, structure, and features of NC titanium.

1. PEMFC structure and key characteristics of metal bipolar plates

To achieve high output in PEMFCs for vehicles, hundreds of layers of cells, the foundational unit of a fuel cell, are stacked. **Fig. 1** shows a schematic illustration of a cell. The center of the cell is a polymer electrolyte membrane (PEM), which is a proton conductor, with a Pt catalyst layer on both sides. On either side of the PEM is a gas diffusion layer (GDL) made of carbon fiber. Outside each GDL is a bipolar plate sandwiching the entire assembly. Since one cell uses two bipolar plates, the fuel cell module of a vehicle in turn uses several hundred bipolar plates. Bipolar plates must therefore be lightweight and thin to fit in the limited space inside the vehicle, yet strong enough to withstand shock during vehicle operation. In addition, as shown in Fig. 1, the bipolar plate serves as a flow channel for fuel gas and the water generated, so this component must be able to be press-formed into the shape of the flow channel. Furthermore, the bipolar plate acts as a current collector, collecting and discharging through its surface the electrons generated by the hydrogen decomposition reaction on the catalyst on the hydrogen gas side. As such, it must have high surface conductivity, or in other words, low surface resistance (called contact

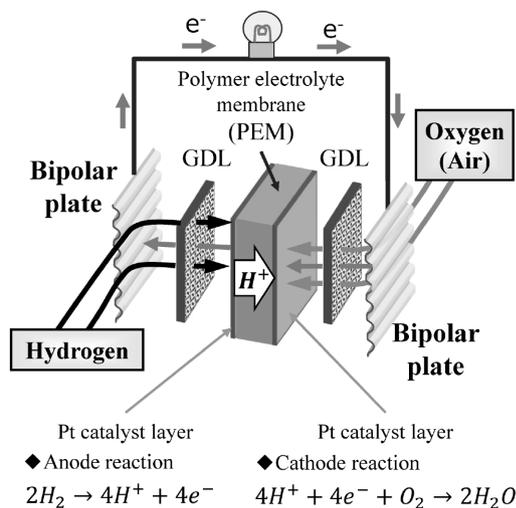


Fig. 1 Schematic structure of a PEMFC⁹⁾

resistance). The bipolar plate must also be corrosion resistant because the inside of the fuel cell is an acidic corrosion environment where the fluorine and sulfonic acid ions of the polymer electrolyte membrane are released. Corrosion of the bipolar plate not only reduces surface conductivity, but also causes the release of metal ions that contaminate the catalyst and inhibit the conduction of hydrogen ions in the polymer electrolyte membrane.⁶⁾ In particular, iron ions act as a catalyst to decompose the by-product hydrogen peroxide and generate hydroxyl radicals. Hydroxyl radicals destroy the polymer electrolyte membrane and reduce fuel cell performance.⁷⁾ This is why corrosion-resistant metals such as stainless steel and titanium are used for metal bipolar plates.^{4), 8)} Corrosion-resistant metals have this property because they form a passive layer, which is a natural oxide film several nm to several dozen nm thickness, on their surfaces. However, the conductivity of the passive layer decreases in an acidic corrosion environment, making surface conductivity and corrosion resistance mutually exclusive. Therefore, a surface treatment with high conductivity and corrosion resistance is required even for corrosion-resistant metals.

Additionally, fostering more widespread acceptance of fuel cells requires greater productivity and reduced cost of bipolar plates, of which hundreds are used in a single vehicle.

As shown in Fig. 2, there are two types of manufacturing methods for metal bipolar plates: the post-coating method, in which surface treatment occurs after flow channel press forming, and the pre-coating method, in which flow channel press forming occurs after continuous surface treatment of the metal foil coil.⁹⁾ The post-coating method is the mainstream method, but it is characterized by

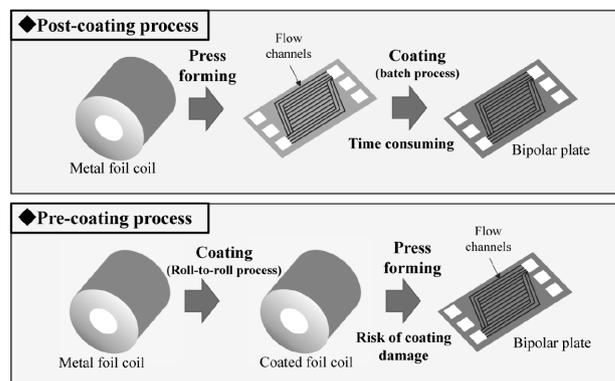


Fig. 2 Two typical production processes for metal bipolar plates⁹⁾

low productivity. Each piece of metal foil formed into a bipolar plate must be set up, processed, and retrieved individually for surface treatment - this one-by-one process is time consuming. Conversely, the pre-coating method has higher productivity and lower cost because there is no need to set up and retrieve individual bipolar plates for surface treatment. The disadvantage of this method, however, is that the surface treatment can be damaged during press forming. This leads to peeling, reducing electrical conductivity and corrosion resistance. As such, this method has not yet been implemented in live products.

2. Concept behind the development of surface-treated titanium for bipolar plates

Titanium is characterized by high corrosion resistance, meaning it is less likely to be released in an environment with high electrical potential; however, it is more expensive than stainless steel. W. Li et al.¹⁰⁾ tested the corrosion resistance of SUS316L and Grade 2 titanium, each coated with a conductive amorphous carbon film using titanium as an intermediate film. Testing conditions were designed to simulate start-up and shutdown conditions, which are the most severe corrosion environments in fuel cell vehicles. Specifically, a potential of 1.4 V (vs. SCE) was applied for 1 hour in a 0.5 kmol/m³ sulfuric acid aqueous solution containing 2 ppm fluoride ions at 70°C. The authors reported pitting in the pinholes of the coating on SUS316L, but not on titanium. This means that defects such as pinholes in the coating are acceptable with titanium. As such, the surface treatment time can be reduced because there is no need to form a thick film to eliminate pinholes, and cracks in the surface treatment from press forming the flow channels are tolerable even if the base material is exposed. Therefore, the pre-coating method could be feasible. To summarize,

although using titanium increases the cost of the base material, curtailing surface treatment time and using the pre-coating method improve bipolar plate productivity, potentially yielding an overall cost reduction for the bipolar plate when considering everything from the base material to production.

However, pre-coating requires that the adhesion properties of the surface treatment support press forming. Hence, the concept behind developing surface-treated titanium for bipolar plates is to make pre-coating feasible by developing a coating with high corrosion resistance, high electrical conductivity, and adhesion properties that support press forming. NC titanium is the surface-treated titanium we developed in line with this concept. The next section covers the structure and features of NC titanium.

3. Structure, formation process, and features of NC titanium

3.1 Structure of NC titanium

Fig. 3 shows a cross-sectional SEM image of NC titanium.¹¹⁾ The NC layer consists of a titanium oxide film 40 to 50 nm in thickness (gray area) and carbon nanoparticles dispersed in the film (black area). The carbon nanoparticles act as a conductive path, and the titanium oxide film ensures adhesion to the titanium substrate. The high corrosion resistance of the carbon and titanium oxide lends high corrosion resistance to the NC layer.

3.2 Formation process of NC titanium

Fig. 4 shows the formation process of the NC layer and cross-sectional SEM images of the titanium substrate after each process.⁹⁾ The formation process of the NC layer consists of a coating process in which the surface of the titanium substrate is coated with carbon nanoparticles; an NC formation process in which high-temperature oxidation is performed under low oxygen pressure; and post-processing, which includes processes such as removing excess carbon nanoparticles. Cross-sectional SEM images after high-temperature oxidation under low oxygen pressure show that the carbon nanoparticles are incorporated into the titanium oxide. Upon high-temperature oxidation of titanium under atmospheric pressure, oxygen generally diffuses from the surface of the titanium inward, causing

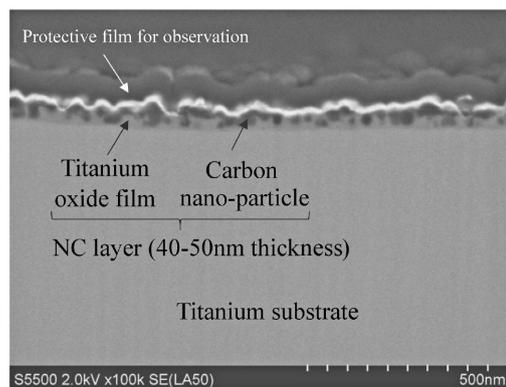


Fig. 3 Cross-sectional SEM image of NC titanium¹¹⁾

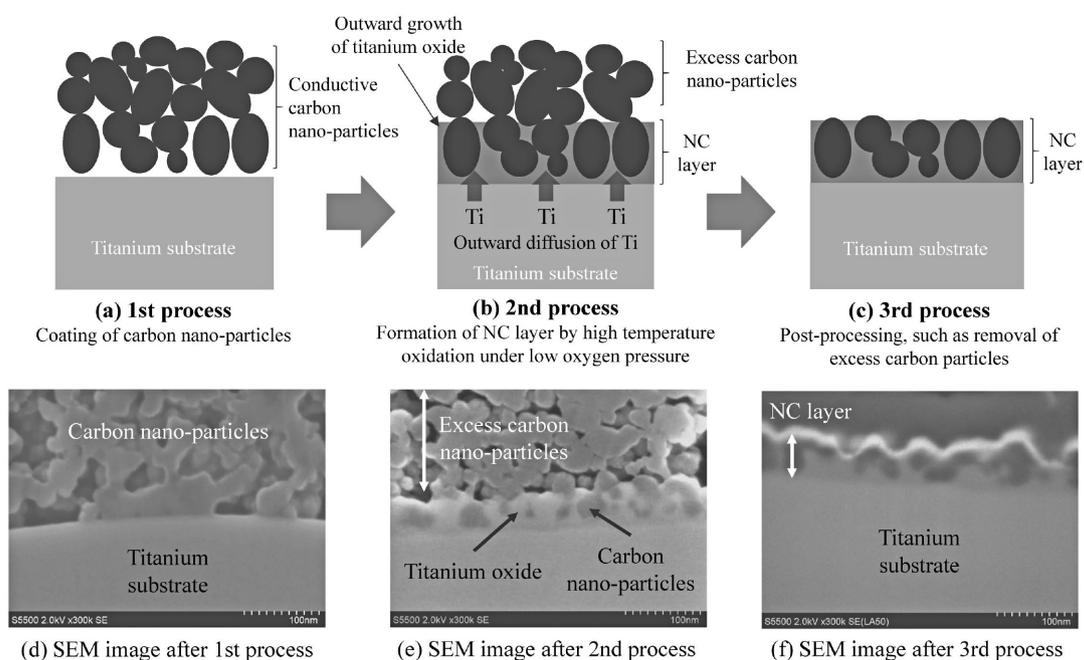


Fig. 4 NC titanium formation process (a), (b), (c) and cross-sectional SEM images after each process (d), (e), (f)⁹⁾

titanium oxide to form in this same direction.¹²⁾

However, the authors had investigated the oxidation of Ti-Pd alloys pickled to precipitate Pd nanoparticles on their surfaces, from a low oxygen pressure to atmospheric pressure.¹³⁾ At atmospheric pressure, a titanium oxide layer formed between the Pd nanoparticles and the Ti-Pd alloy due to inward oxidation, in line with conventional knowledge. However, at a low oxygen pressure, outward oxidation occurred, in which titanium oxide grew from the surface of the Ti-Pd alloy toward the Pd nanoparticles, and the Pd nanoparticles were incorporated into the titanium oxide layer. We developed an NC layer structure by exploiting the outward oxidation of titanium, which had not been reported on previously, and by replacing the Pd nanoparticles with economical carbon nanoparticles.

3.3 Features of NC titanium

3.3.1 NC titanium adhesion

Fig. 5 shows a cross-sectional TEM image of NC titanium after press forming.¹¹⁾ The NC layer remains adhered without peeling, even near the step in the surface created by the plastic deformation of titanium during press forming. This proves that NC titanium has sufficient adhesion to withstand press forming.

3.3.2 Contact resistance and durability of NC titanium

Fig. 6 compares the contact resistance of NC titanium with contact resistances measured for corrosion testing of coated stainless steel and titanium in bipolar plates of fuel cells as published in research over the six-year period from 2017 to 2022.^{14)~20)} The films compared were those evaluated under the corrosion resistance test conditions most common in the research, that is, films subjected to a potentiostatic test involving immersion in an aqueous solution of 0.5 M sulfuric acid containing 2 to 5 ppm fluoride ions for 4 to 5 hours at 70 to 80°C and the application of 0.6 V (vs. SCE). Contact resistance was measured before and after the potentiostatic test in the selected studies, and the

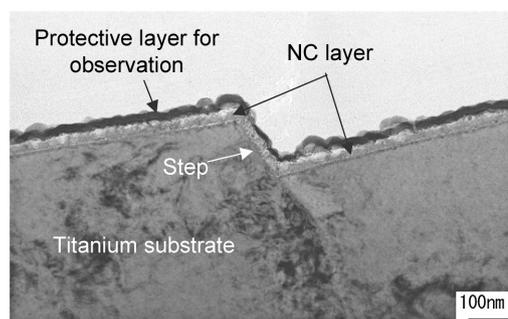
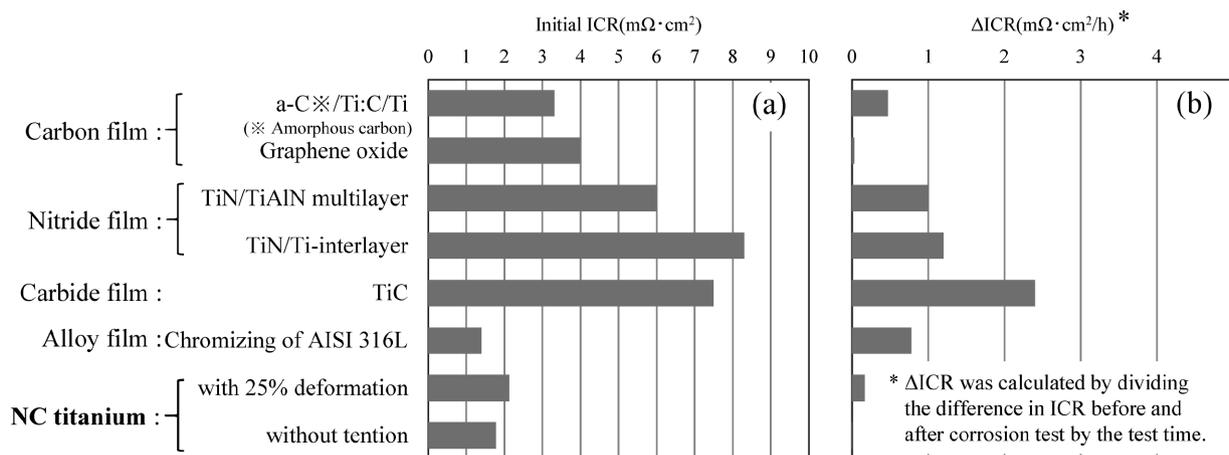


Fig. 5 Cross-sectional TEM image of NC titanium after press forming¹¹⁾



Corrosion test (potentiostatic test) conditions

	Coatings in the literature	NC titanium
Solution	0.5M H ₂ SO ₄ + 2-5ppm F ⁻ with air or oxygen bubbling	0.5M H ₂ SO ₄ +5ppm F ⁻ with air bubbling
Temperature	70-80°C	80°C
Potential	0.6V vs.SCE	0.6V vs.SCE
Immersion time	4-5h	5h

Fig. 6 Comparison of interfacial contact resistance (ICR) before corrosion test (initial ICR) (a) and average increase rate of ICR (ΔICR) (b) of coatings studied in the literature and NC titanium^{14)~20)}

comparison was limited to films whose contact resistance before the test was $10 \text{ m}\Omega \cdot \text{cm}^2$ or less, which is the target set by the U.S. Department of Energy (DOE). Corrosion resistance and conductivity testing results have been published for many different films. However, the results suitable for comparison are limited because of great variation in corrosion resistance test conditions and because most studies measure contact resistance only before corrosion resistance testing. Regardless, the types of films considered can be broadly classified into carbon, nitride, carbide, and alloy films, covering a fairly comprehensive breadth. To compare the films in the selected papers with NC titanium, the contact resistance of NC titanium was also measured in the same manner as in the papers: after immersion for 5 hours in a 0.5 M sulfuric acid aqueous solution containing 5 ppm fluoride ions at 80°C with the application of a potential of 0.6 V (vs. SCE). To evaluate the durability of NC titanium after press forming, the same test was also performed on NC titanium subjected to 25% uniaxial tensile deformation. To compare durability, the average increase rate of contact resistance was calculated by dividing the difference in contact resistance before versus after the potentiostatic test by the duration of the potentiostatic test. The lower this value, the higher the durability. Fig. 6 shows that the initial contact resistance of NC titanium without tensile deformation and NC titanium with 25% tensile deformation is among the lowest of all the types of film, at about 1/5 or less of the contact resistance limit specified by the DOE.

Further, the average increase rate of contact resistance is lowest with NC titanium, at a value similar to carbon film. As such, NC titanium exhibits lower contact resistance and higher durability than other films, even after uniaxial tensile deformation in a way that simulates press forming.

3.3.3 NC titanium for improved bipolar plate productivity

Fig. 7 shows an NC titanium coil.⁴⁾ The productivity of NC titanium is exceptionally high because the NC layer forms quickly and because all NC titanium production processes are an integral part of the continuous manufacturing process of the titanium foil coil. In addition, the surface treatment process, which reduces fuel cell throughput, can be omitted by fuel cell manufacturers. As a result, bipolar plates can be manufactured simply by press forming NC titanium coils, improving fuel cell manufacturers' productivity and thus reducing expenditure.

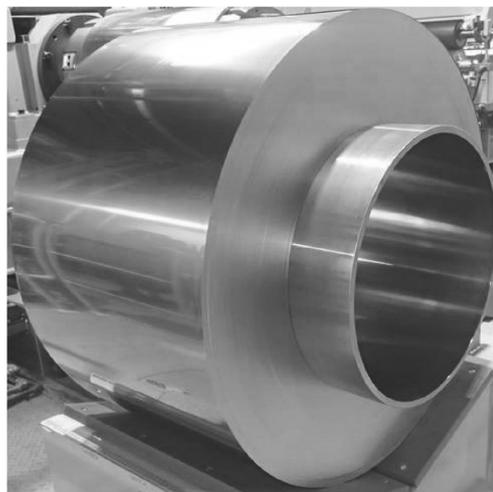


Fig. 7 Appearance of NC titanium foil coil⁴⁾

Conclusions

The outward oxidation of titanium was discovered and exploited to develop a film used to create coated NC titanium, which has high corrosion resistance, high surface conductivity, and high adhesion, and has been implemented in the world's first pre-coated bipolar plate material. NC titanium is used in fuel cell electric vehicles such as Toyota Motor Corporation's Mirai, released in 2020, and Crown FCEV.

Since NC titanium is highly durable and lighter than stainless steel, it is expected to see application not only in passenger cars but also in equipment that must be made lighter, such as aircraft and drones, and in equipment that must be highly durable, including semi-trucks, buses, rail transport applications, and vessels.

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