Development of High Corrosion Resistance Celmet

Kazuki OKUNO*, Masatoshi MAJIMA, Tomoyuki AWAZU, Kengo TSUKAMOTO, Hitoshi TSUCHIDA and Hidetoshi SAITO

The authors have developed a novel porous metal with high corrosion resistance. Porous materials are used in fuel cells as the current collector and gas diffusion layer of the electrode. Typical porous materials include carbon sheet, molded carbon and porous metals such as stainless used steel (SUS) and nickel chrome (Ni-Cr) alloys. Among these materials, porous metals are preferable because of their high gas diffusion performance. Because of the highly oxidizing atmosphere in fuel cells, porous metals are required to have a high corrosion resistance, and for this purpose, chromium is generally added. However, the use of chromium has recently been regulated according to environmental protection regulations. Therefore, the authors have focused on Tin (Sn), which shows a high corrosion resistance in a fuel cell atmosphere, and developed Ni-Sn alloy Celmet. This new Celmet has achieved a current density comparable to that of Ni-Cr alloy. Overall, the Ni-Sn alloy Celmet is highly resistant to corrosion in a fuel cell atmosphere and environmentally friendly.

Keywords: Celmet, fuel cell, high corrosion resistance

1. Introduction

In recent years, the demand for batteries has grown rapidly in various sectors as a result of the increasing awareness of global environmental issues. In electric and hybrid electric vehicles, nickel-metal hydride or lithium-ion batteries are used as a power source. Regarding today's hybrid electric vehicles, models particularly growing in demand typically have nickel-metal hydride batteries installed. As for current collectors in these batteries, the negative electrode is made of two-dimensionally structured (perforated) base metal, while the positive electrode is made of three-dimensionally structured nickel foam due to the poor electrical conductivity of the positive-electrode active material. The nickel foam base metal increases the capacity of nickel-metal hydride batteries[(1)-(3)].

Meanwhile, regarding fuel cells, manufacturers in the automotive sector have made concept fuel-cell car announcements. In addition, home-use stationary models have been placed on the market. Fuel cells differ from rechargeable batteries in that they generate power using fuel such as hydrogen. Ideally, they should emit only water and carbon dioxide. Infrastructure development for fuel cells is a major challenge. However, expectations are high for fuel cells as a future automotive power source since fossil fuels and fuel for fuel cell vehicles are presently similar in the way they are used, hydrogen, the fuel for fuel cells, is abundant, and emissions from fuel cells are clean.

A fuel cell requires a gas diffusion layer in it to achieve uniform reaction of the fuel gas. For that purpose, grooved, molded carbon, porous metal and the like are used. In this regard, porous metal serves the purpose due to its high gas diffusion capability[(4)]. Materials for fuel cells need to be highly corrosion-resistant since oxidizing reactions occur in the cell at high temperature. Conventional candidate materials have been stainless steel and nickel-chromium (Ni-Cr) alloys, both with chromium used as an ingredient. From the perspective of environmental contamination prevention, a chromium-free corrosion-resistant alloy is desired.

Taking these into consideration, we aimed to develop a highly corrosion-resistant nickel-based porous alloy that can be produced through simple processes as a substitute for Ni-Cr alloys. Noticing that nickel-tin (Ni-Sn) alloy production processes are relatively simple, we have developed Ni-Sn alloy Celmet.

We have used our Celmet technology to produce Ni-Sn alloy Celmet specifically as a nickel-based material for current collectors and gas diffusion layers in fuel cells. This paper is a report on corrosion and heat resistance analysis results of the newly developed material.

2. Test Methods

2-1 Test specimen preparation

2-1-1 Preparation of nickel Celmet

Plastic foam with interconnected cells was treated to become conductive, followed by the application of a predetermined amount of nickel via electrodeposition. The base material, or plastic foam, was removed at 800°C. Remaining nickel was reduced in a reducing gas at approximately 1000°C to become nickel Celmet.

2-1-2 Preparation of Ni-Cr alloy Celmet

Metallic chromium was diffused into nickel Celmet described in 2-1-1 (chromizing process). More specifically, the Celmet was filled with a powder, with chromium being the main ingredient, heated to 1000°C in an inert gas and had a predetermined amount of chromium diffused into itself, becoming Ni-Cr alloy Celmet.

2-1-3 Preparation of Ni-Sn alloy Celmet

Nickel Celmet prepared in 2-1-1 was coated with a predetermined amount of tin via electrodeposition. Heat treatment followed, processing the Celmet in a reducing gas at approximately 1000°C to diffuse tin into nickel to

Table 1. Typical physical properties of Ni-Sn alloy Celmet

Item	Characteristic value
Weight per unit area of metal (g/m^2)	630
Solute concentration (wt%)	approx. 20
Thickness (mm)	1.0
Average pore size (μm)	500

produce Ni-Sn alloy Celmet. **Table 1** shows the specifications for Ni-Sn alloy Celmet.

2-2 Mechanical property evaluation

The produced Ni-Sn alloy Celmet changes in strength and electrical resistivity depending on its weight per unit area. Since, in fuel cells, it is stacked and used as a gas diffusion layer and also as a current collector under pressure, we measured the Celmet's compression characteristics and electrical resistance under pressure, as well as tensile strength as a common strength characteristic. Tensile test specimens were cut to a size of 20 mm in width and 100 mm in length. For compression testing, Ni-Sn alloy Celmet punched into a 10 mm diameter disc was sandwiched between electrode-equipped stainless-used steel (SUS) plates and compressed to a predetermined pressure. Thickness changes and changes in electrical resistance of the test specimens were measured during compression.

2-3 Corrosion resistance evaluation

Different types of corrosion resistance are required in fuel cells. In polymer electrolyte fuel cells (PEFCs), resistance to electrolyte, which is an acidic aqueous solution, is required, while in solid oxide fuel cells (SOFCs), oxidation resistance to high-temperature oxidizing atmosphere is required.

A material's resistance to electrolyte is evaluated by anode current values determined through anodic polarization measurement of the material within the actual range of potentials of the fuel cell. Standards such as JIS G 0579[(5)] and ASTM G5-94[(6)] specify anodic polarization measurement for metals. Specifically, ASTM G5-94 provides for evaluation intended for fuel cells and is employed for material corrosion resistance testing in the field of fuel cells. Accordingly, we conducted evaluations using the methods described in the standard as a reference[(7)-(9)]. A sodium sulfate aqueous solution of concentration 1 mol/L was prepared and its pH was adjusted with sulfuric acid as an acidic solution for anodic polarization measurement. The test temperature was 60°C. The solution was saturated with hydrogen by bubbling during the test. The voltammetry potential range was from 0 V to 1.0 V as compared with the standard hydrogen electrode. Potentials were deemed to be applied in this range in fuel cells. The sweep rate was 5 mV/s.

Meanwhile, regarding high-temperature oxidation resistance, a heating test was conducted in the air at 600°C and at 900°C, representing actual operating temperatures of SOFC. The rate of weight gain resulting from oxidation and post-heating-test changes in strength were measured.

3. Results and Discussion

3-1 Fundamental properties of Ni-Sn alloy Celmet

The fundamental properties of the newly developed Ni-Sn alloy Celmet were evaluated. A wide elastic region is desirable since the material is placed under pressure in the fuel cell. For the material to serve as a current collector, its contact resistance should be as low as possible. Compared with nickel Celmet, Ni-Cr alloy Celmet exhibits smaller changes in thickness under compression and its mechanical strength is higher. However, the contact resistance of Ni-Cr alloy Celmet tends to be higher than that of nickel Celmet, since the surfaces of Ni-Cr alloy Celmet are covered with strong oxide films.

Figure 1 shows the relationships between tin concentration and tensile strength of Ni-Sn alloy Celmet. It clearly reveals that tin concentration is strongly correlated with tensile strength, indicating a tendency that tensile strength increases with increasing tin concentration.

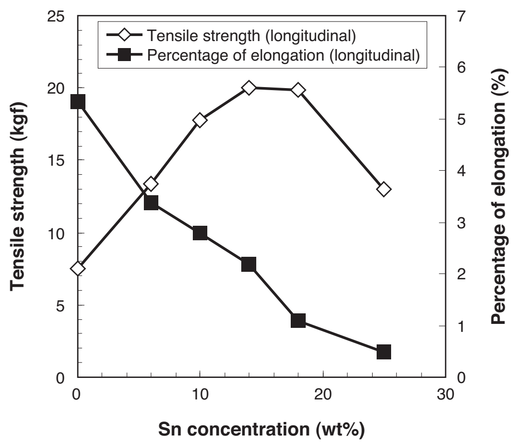

Fig. 1. Effects of concentration of added tin on longitudinal tensile strength (20 mm in width) and percentage of elongation of test specimens

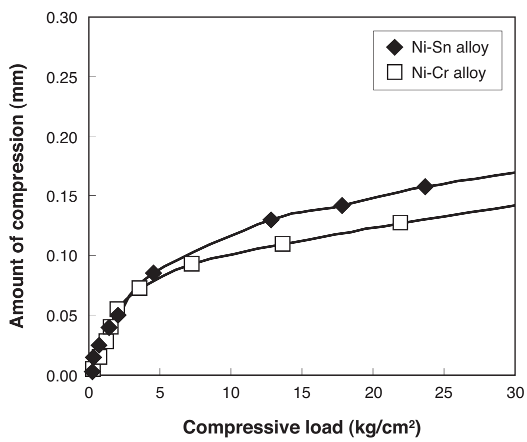

Fig. 2. Effects of compressive load on amount of compression of Ni-Sn alloy Celmet (20% Sn) and Ni-Cr alloy Celmet (20% Cr)

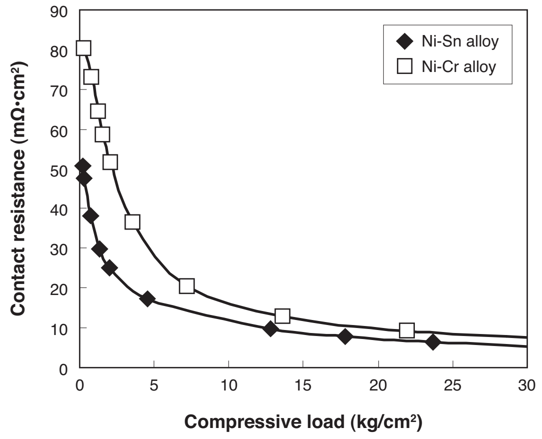

Fig. 3. Effects of compressive load on contact resistance of Ni-Sn alloy Celmet (20% Sn) and Ni-Cr alloy Celmet (20% Cr)

Figures 2 and 3 show results of thickness and electrical resistance changes under compression. Ni-Sn alloy Celmet differs little in compression characteristics from Ni-Cr alloy Celmet and is believed to be usable in a similar manner as conventional Ni-Cr alloy Celmet is used. On the other hand, the contact resistance of Ni-Sn alloy Celmet is lower than that of Ni-Cr alloy Celmet. A possible reason is that tin oxide films exhibit lower electrical resistance than chromium oxide films. Consequently, in its functionality as a current collector, Ni-Sn alloy Celmet is superior to Ni-Cr alloy Celmet.

3-2 Corrosion resistance evaluation

Since potentials are applied in an oxidizing atmosphere in a fuel cell, currents resulting from potentials applied on the anode and cathode sides need to be significantly smaller than the amount of fuel cell current. **Figure 4** shows current values resulting from typical potentials of 0 V and 0.8 V (versus standard hydrogen electrode) on the anode and cathode sides, respectively, determined through anodic polarization evaluation. Large currents in the case of nickel, especially on the cathode side, make the material unusable. In comparison, for both the Ni-Cr and Ni-Sn alloys, current values were lower than 3 mA/cm^2, three orders of magnitude smaller than common fuel cell currents. Consequently, they are usable as an excellent current collector.

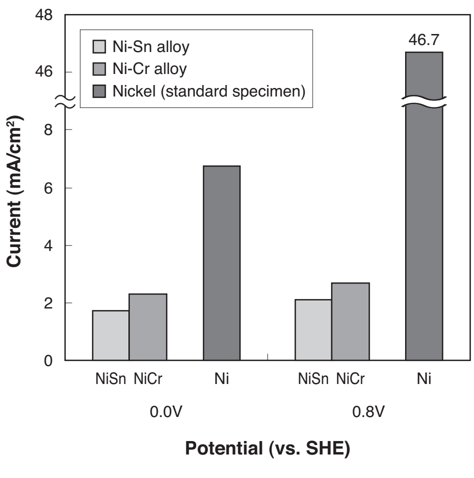

Fig. 4. Corrosion current evaluation at different potentials

Regarding the heat resistance of these materials, **Fig. 5** shows their rate of weight gain due to oxidation determined after heating at 600°C and 860°C for 10 hours. Ni-Cr and Ni-Sn alloys are lower than nickel in rate of weight gain. Moreover, being lower in rate of weight gain due to oxidation than the Ni-Cr alloy, the Ni-Sn alloy exhibits excellent heat resistance. Their resistance to heat and electrolyte is believed to come from oxide films of chromium and tin alloyed with nickel. The difference in rate of weight gain due to oxidation suggests the presence of a mechanism that oxide films on Ni-Sn alloy Celmet surfaces are denser than those on the Ni-Cr alloy and more effectively prevent the ingress of oxygen once the outermost surface is oxidized, thereby retarding the oxidation process.

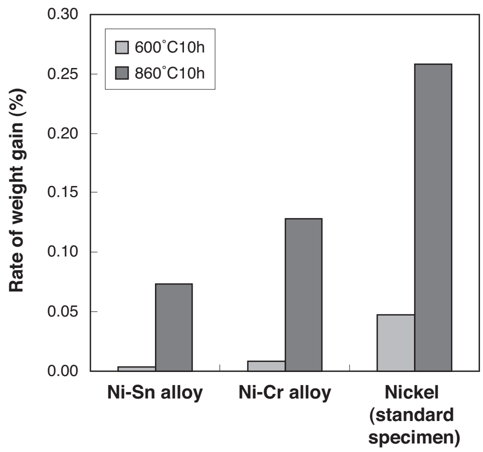

Fig. 5. Weight changes after heating at 600°C for 10 h and at 860°C for 10 h

Figure 6 shows results of compression characteristic testing conducted after the 860°C heat resistance test. The Ni-Sn and Ni-Cr alloys were about the same in behavior and retained some degree of strength even after heating at 860°C for 10 hours. **Figure 6** shows plateaus, which were not present before heating, suggesting the occurrence of structural buckling and deformation.

Additionally, **Fig. 7** presents results of electrical resistance measurements undergoing changes under heat. In the initial phase of heating, nickel was lowest in electrical resistance, followed by the Ni-Sn alloy and the Ni-Cr alloy. While the temperature increased to 600°C, the electrical resistance of the nickel steadily increased to a level similar to the Ni-Sn alloy. Meanwhile, at 600°C, the electrical resistance of the Ni-Sn alloy was half that of the Ni-Cr alloy,

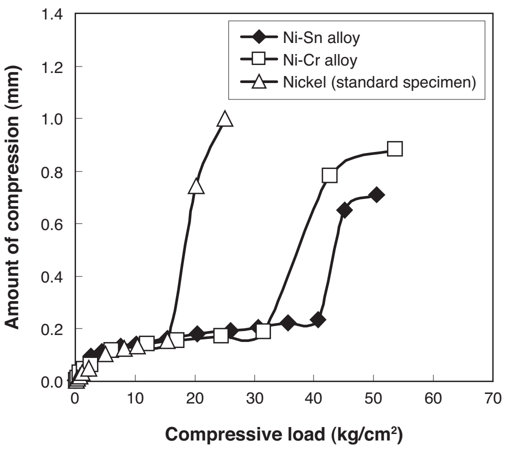

Fig. 6. Effects of compressive load on amount of compression of Ni-Sn alloy Celmet (20% Sn) and Ni-Cr alloy Celmet (20% Cr) after heating

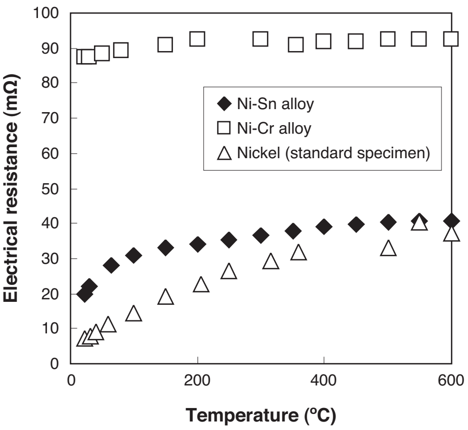

Fig. 7. Effects of heating temperatures on electrical resistance of test specimens

suggesting that the Ni-Sn alloy will exhibit excellent characteristics as a current collector for use at high temperatures.

4. Conclusion

Ni-Sn alloy Celmet was developed as a porous metal free of both environmental concerns and the use of chromium. The newly developed material was tested for resistance to electrochemical corrosion. Test results showed that the material exhibited superior characteristics to those of Ni-Cr alloy, with the corrosion current being less than 3 mA/cm^2 for samples with 20 wt% tin content at a potential of 0.8 V (versus standard hydrogen electrode).

The excellent heat and corrosion resistance of Ni-Sn alloy Celmet is expected to make the material suitable for applications in PEFCs and SOFCs. Moreover, Ni-Sn alloy Celmet is also promising for various filter applications where resistance to heat and chemicals is required.

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Contributors (The lead author is indicated by an asterisk (*).)

K. OKUNO*

• Electronics & Materials R&D Laboratories
Currently engaged in research and development of porous metals.

M. MAJIMA
• Ph.D. in Energy Science
Group Manager, Electronics & Materials R&D Laboratories

T. AWAZU
• Senior Assistant Manager, Electronics & Materials R&D Laboratories

K. TSUKAMOTO
• Engineering Department, Sumitomo Electric Toyama Co., Ltd.

H. TSUCHIDA
• Manager, Engineering Department, Sumitomo Electric Toyama Co., Ltd.

H. SAITO
• General Manager, Engineering Department, Sumitomo Electric Toyama Co., Ltd.