# Plasma Nitriding Properties of Sintered CoCrFeMnNi High-Entropy Alloy with Pure Ni Screen

Jiaxin Peng[1]and Akio Nishimoto[2]

[1]*Department of Chemistry and Materials Engineering, Graduate School of Science and Engineering, Kansai University,*
*3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan*
[2]*Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai*
*University, Osaka 564-8680, Japan*

Recently, reports have been made on the excellent tensile strength and ductility at low temperatures of the CoCrFeMnNi high-entropy alloy (HEA). The hardness of Cantor alloys (CoCrFeMnNi) produced by many methods tends to be lower than that of typical steel materials. Surface modification treatment is considered to be an effective method to improve the hardness of Cantor alloys. The purpose of this study is to vary the temperature using a Ni metal screen and search for optimal conditions for thickening the plasma nitrided layer in sintered Cantor alloys. Furthermore, this study aims to evaluate the properties of the nitrided layer by applying direct-current plasma nitriding (S-DCPN) treatment and varying the temperature of the sintered HEA using a pure Ni screen. The gas-atomized powder of CoCrFeMnNi HEA was processed through ball-milling for 10 h to prepare a sintered body. This sintered body then underwent S-DCPN treatment at 673-873 K for 15 h, at a gas pressure of 200 Pa with a composition of 75% $N_2$ and 25% $H_2$. During the plasma nitriding procedure, a pure Ni screen was installed as an auxiliary cathode to ensure uniform heating and an increased nitrogen supply. Furthermore, the nitrided sample underwent X-ray diffraction analysis, cross-sectional microstructure observation, surface morphology observation, surface hardness testing, glow discharge optical emission spectroscopic analysis (GD-OES), corrosion testing, and wear testing. The appearance observation shows that a black modified layer was observed on the surface of the sample after nitriding, and an edge effect was generated around the sample. The surface roughness and SEM images of the surface show that surface becomes rougher as the nitriding temperature increases. The XRD results show $Fe_2Ni_2N$, $FeNi_3$, $Cr_{0.25}Ni_{0.75}$, and NaCl-type (CoCrFeMnNi)N were identified in all samples, and expanded fcc was identified in the 673 and 723 K samples. The surface hardness of HEA samples significantly increased after nitriding. The GD-OES results showed that the depth of dissolved nitrogen increased with increasing nitriding temperature.

***Keywords:*** *plasma nitriding, high-entropy alloys, Ni screen, nitrided layer, spark plasma sintering*

## 1. Introduction

High-entropy alloys (HEAs) are defined as alloys with five or more constituent elements, nearly equiatomic composition ratios, and single-phase solid solutions. Cantor alloy (CoCrFeMnNi), a typical fcc type of HEAs, is known to have lower hardness than general steel materials. In recent years, attention has been focused on research on surface modification treatment of HEAs in order to improve such drawbacks1). Plasma nitriding, one of them, is used to enable the use of steel materials in harsher environments. Plasma nitriding does not use environmental pollutants and can be processed in a short time, so it has the advantage of consuming less gas and less energy. Although HEAs exhibit unique properties, there are few reports on their surface treatment. It has also been reported that dislocations can be introduced on the surface of atomized powder by ball milling2). In a previous study, direct current plasma nitriding (DCPN) treatment was performed on cantor alloy sintered compacts using a stainless steel screen with varying ball milling times. As a result, a thicker nitride layer was formed on the samples after ball milling for 10 h, and corrosion resistance and wear resistance were improved3). Plasma nitriding was also performed on three types of stainless steel, SUS304, SUS430, and SUS329J4L, using a Ni screen. A supersaturated N solid-solution S phase was detected on the sample surface after nitridation, and the amount of nitrogen diffusion was improved compared to the case of using the SPCC (Fe) screen4). In this study, S-DCPN treatment was applied to the sintered body of high-entropy alloy powder after ball milling using a Ni screen, and the properties of the nitride layer were evaluated.

## 2. Materials and experimental procedure

Atomized spherical powders of CoCrFeMnNi HEAs (particle size 53–150 μm) were used as samples. Regarding the conditions for producing the sintered body, the ball milling time was set to 10 hours, and spark plasma sintering was performed at 1073 K-20 min. The sintered sample was subjected to plasma nitriding treatment at a temperature of 673 to 873 K for 15 hours at a gas pressure of 200 Pa and a composition ratio of treatment gas $N_2:H_2=3:1$. A pure Ni screen was installed as an auxiliary cathode for the purpose of uniform heating and increased nitrogen supply during plasma nitridation. The distance between the screen and the sample was adjusted to 20 mm. An X-ray diffraction (XRD) test, cross-sectional structure observation, surface structure observation, surface hardness test, glow discharge optical emission spectroscopy (GD-OES), wear test, and corrosion test were performed on the plasma-nitrided samples.

## 3. Results

Figure 1 shows the surface appearance and surface roughness profile after nitriding. As shown in Fig. 1, it was confirmed from the appearance observation that a black modified layer was observed on the surface of the sample after nitriding, and an edge effect was generated around the sample. It is considered that the coloring becomes darker with the nitriding temperature increases. Figure 2 shows the

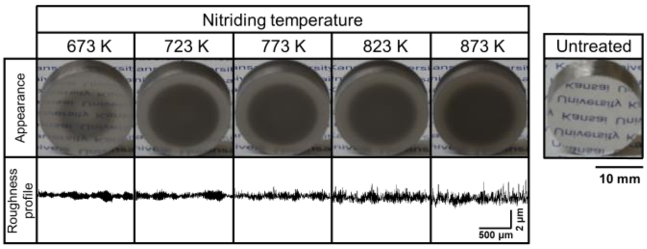

Fig. 1 Appearance observation and roughness profile of plasma-nitrided HEAs.

*R*a value of surface roughness. The *R*a values show that the surface becomes rougher as the nitriding temperature increases.

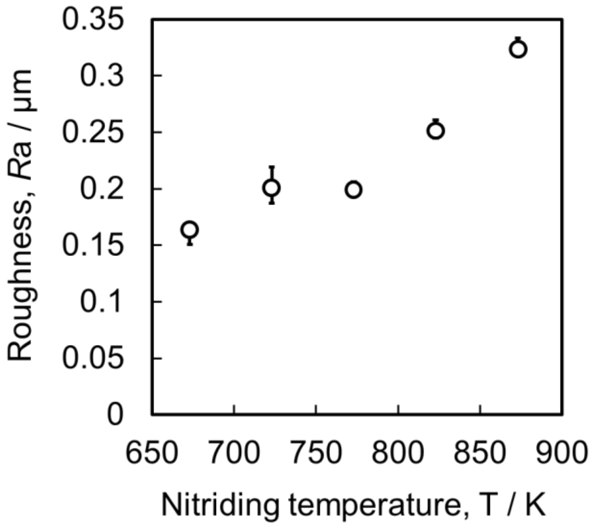

Fig. 2 Roughness *R*a value of plasma-nitrided HEAs.

Figure 3 shows the XRD results before and after nitriding. As shown in Fig. 3, $Fe_2Ni_2N$, $FeNi_3$, $Cr_{0.25}Ni_{0.75}$, NaCl-type (CoCrFeMnNi)N were identified in all samples, and expanded fcc was identified in the 673 and 723 K samples. It is considered that NaCl-type nitrides are likely to be formed instead of expanded fcc as the nitriding temperature increases. In addition, Ni in $Fe_2Ni_2N$, $FeNi_3$ and $Cr_{0.25}Ni_{0.75}$ produced at high temperature is thought to originate from the Ni screen.

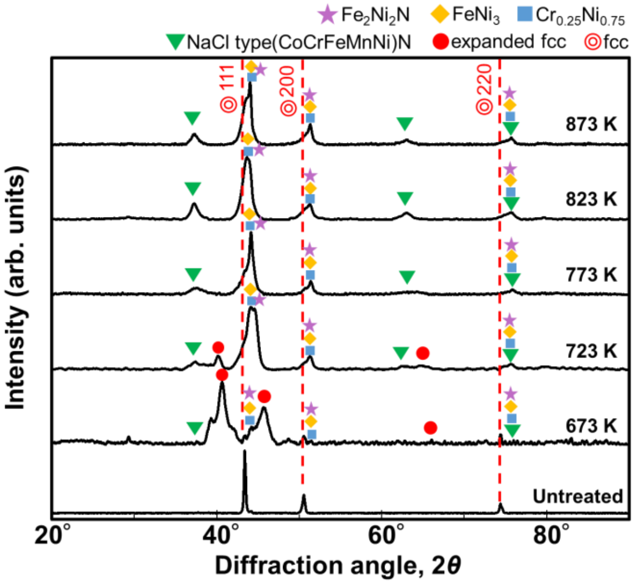

Fig. 3 XRD pattern of plasma-nitrided HEAs.

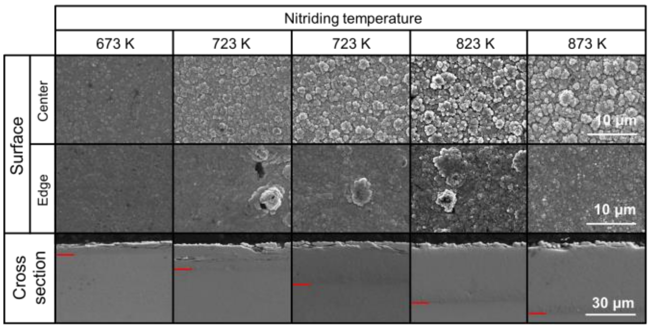

Fig. 4 Surface and cross-section SEM images of plasma-nitrided HEAs.

Figure 4 shows SEM images of the surface and cross section. Deposits were observed in the central part of all samples from SEM photographs of surface observation. In addition, no deposit was observed on the low temperature side of the edge portion, but deposits were observed on the high temperature side. It was found that the number and grain size of deposits increased with increasing nitridation temperature. A sediment layer and a nitride layer were observed in all samples from SEM photographs of cross sections. It was found that the thickness of the nitrided layer increased as the nitriding temperature increased.

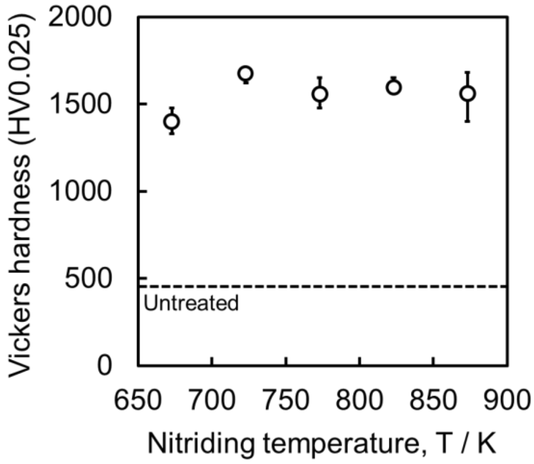

Fig. 5 Surface hardness of plasma-nitrided HEAs.

Figure 5 shows the surface hardness results before and after nitriding. As shown in Fig. 5, the surface hardness of the sample after nitriding was significantly improved compared to that before nitriding. The hardness of the 673 K sample is approximately 1400 HV, and the hardness of other samples approximately 1550 HV. It is believed that the thickness of the deposits layer and the nitride layer increases with increasing nitriding temperature, and the hardness does not increase with increasing thickness.

## References

1) A. Nishimoto, T. Fukube and T. Maruyama: Surf. Coat. Technol. **376** (2019) 52-58.
2) G. Li, M. Liu, S. Lyu, M. Nakatani, R. Zheng, C. Ma, Q. Li and K. Ameyama: Scr. Mater. **191** (2021) 196-201.
3) J. Peng and A. Nishimoto: BHM **168** (2023) 130-136.
4) S. Hamashima and A. Nishimoto: Mater. Trans. **63** (2022) 1170-1178.