# THE NITRIDING OF FINE METALLIC POWDER IN A LOW-PRESSURE RF DISCHARGE

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## ABSTRACT

The ion nitriding of fine electrolytic iron powder in an electrically floating state was carried out for 2,4 or 8 h in an rf discharge of pure nitrogen or nitrogen-hydrogen mixture at 27 to 133 Pa. The nitrided powder was examined with SEM, chemical analysis and X-ray diffraction. The formation of $\gamma'$-$Fe_4N$ was confirmed in those experiments, but the formed nitride seemed to be decomposed with a prolonged nitriding time, and the nitriding was affected considerably by hydrogen in the gas mixture.

## 1. INTRODUCTION

In earlier study of rf ion nitriding of small half-columnar electrolytic iron sample ( Ref.1 ), we made it clear that the temperature of the sample was affected variously with gas variety, pressure, rf input and the distance between the sample and rf coil region. Moreover we found that the ion nitriding of the sample in an electrically floating state proceeded in a pure nitrogen rf discharge, and both $\gamma'$-$Fe_4N$ and $\varepsilon$-$Fe_{2-3}N$ formed in its surface layer.

The purpose of this study is to investigate the possibility of ion nitriding of electrolytic iron powder and the effect of hydrogen addition to nitrogen.

## 2. EXPERIMENTAL

The discharge was generated in a cylindrical quartz tube reactor 26.4 mm i.d. and approximately 1 m long, both ends of which were connected to stainless steel caps sealed with O-rings. Fig.1 shows the schematic diagram of the reactor.

The gas pressure was lowered to 1 atm at the outlet of each gas cylinder, and each flux of gas into the reactor tube was measured with float type flowmeter calibrated at 1 atm, and controlled with teflon needle valve. To prevent the nitriding sample from contamination by impurities, e.g. water vapour contained in gases and hydrocarbon oil from

the vacuum pump, two liquid-nitrogen traps were used at both sides of the reactor tube. The gas pressure in it was measured by MacLeod gauge at the outlet of it. To generate discharge, an rf generator operated at a maximum output of 500 W and a frequency of 13.56 MHz. An rf induction coil, 5 turns solenoid, was made of 5 mm o.d. cupper tube and water-cooled during the oparation.

Commercial grade electrolytic iron powder which was screened to -200 mesh ( Photo.1 ) was used as a sample, and its nitrogen content was determined to be 0.0078 wt% in our analysis. A quartz boat filled with the sample ( approximately 5 g ) was put in the place which is shown in Fig.1. The guaranteed purity of nitrogen and hydrogen gases used was 99.9995 % and 99.999 % respectively. The sample was flushed twice by hydrogen gas in the reactor, then hydrogen discharge was generated at 27 Pa pressure and 140 W rf input for purification and pre-heating of the sample. The nitriding was subsequently done at 130 to 140 W rf input. The gas pressure was controlled under continuous gas flow during the discharge. Both pure nitrogen gas and 50% nitrogen - 50% hydrogen mixture gas were used as reacting gases at pressure of 27 to 133 Pa.

## 3. RESULTS AND DISCUSSION

The morphology of sample powder surface was observed with a scanning electron microscope ( SEM ), and its nitrogen content was determined by chemical analysis ( C.A. ) using Kjeldahl method. X-ray diffraction ( X.D. ) permitted identification and semiquantitative analysis of iron nitride formed during the nitriding experiment. A portion of each sample powder ( 20 mm long ) near the rf coil region, as shown by the shade in Fig.1, was slightly sintered. This phenomenon was probably due to inductive heating in the rf field.

Photo.2 to 5 are some SEM photographs showing upper surface of each sintered powder sample. Photo.2 shows the morphology of it after a pre-treatment by hydrogen discharge for 1 h. Photo.3, 4 and 5 show them after ion nitriding with pure nitrogen gas at 133 Pa for 2, 4 and 8 h respectively. On comparing them with Photo.1, it is obvious that iron particles grew and they reached the maximum size in ion nitriding for 2 h, then shrinked with ion nitriding time. Moreover, Photo.5 shows that their surfaces were in melting condition. Hence, the shrinking of particles seems to be due to thermal evaporation besides sputtering.

X.D. from the surface of sintered sample, as shown by the mark ※ in Fig.1, was examined. This analysis revealed that an ion nitride, $\gamma'$-$Fe_4N$, formed in all samples. Based on these data, semiquantitative analysis of $\gamma'$-$Fe_4N$ was tried. The hight of two peaks corresponding to the intensity of diffraction lines from both $\gamma'$-$Fe_4N$ (111) plane and $\alpha$-Fe (110) plane was determined and its ratio R was obtained; i.e., $R = [\gamma'\text{-}Fe_4N\text{-}(111) / [\alpha\text{-}Fe\text{-}(110)$. The chemical analysis of the upper sintered surface layer by a depth of about 0.5 mm, the lower sintered surface layer, the inner part and non-sintered part of sample was carried out.

The results in X.D. and C.A. on the upper surface of sintered samples are shown in Fig.2,3 and 4. In the case of ion nitriding with 100% nitrogen gas for 4 h, R and nitrogen content $C_N$ both increase with nitrogen pressure, as shown in Fig.2. Fig.3 shows that both decrease with increasing the pressure in the case of 50% nitrogen - 50% hydrogen mixture gas. Fig.4 shows that $C_N$ increases and R decreases with

nitriding time in the nitriding using 100% nitrogen gas at 133 Pa. These phenomena were well understood by assuming the following process: during the nitriding, the sample was sintered by heating, therefore the surface area decreased and the rate of nitriding of each iron particle gradually decreased. So, the rate of decomposition of iron nitride from thermal evaporation and sputtering overcomes it, and the nitrogen atoms produced by decomposition diffuse into each particle. The fact that surface of particle was in the melting state ( Photo.5 ) supports the above-mentioned assumption.

The lower surface layer and the inner part of sintered sample both contained about 0.06 wt% nitrogen and the non-sintered sample did about 0.10 wt% nitrogen. These values were not affected very much by experimental conditions.

REFERENCE

(1) Y.Taniguchi and K.Akashi, Denki Kagaku ( J. Electrochem. Soc. of Japan ) 46, 560 (1978).

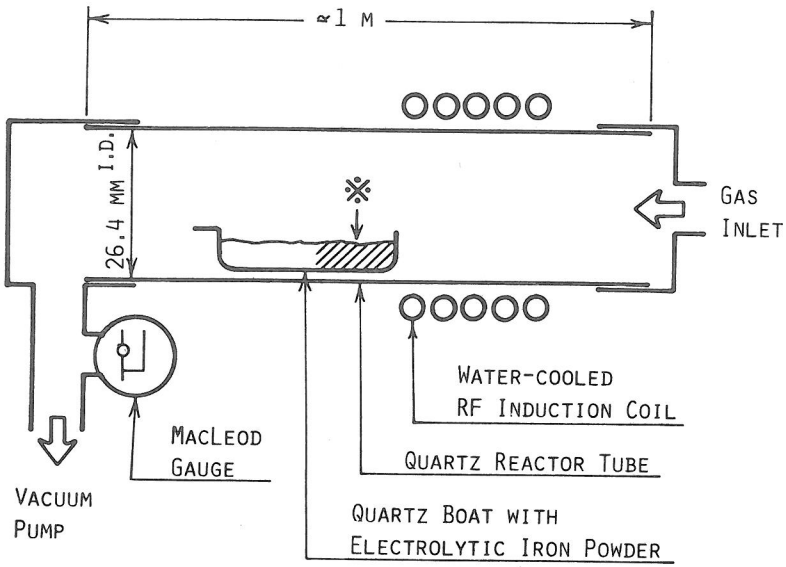


FIG.1 THE SCHEMATIC DIAGRAM OF ION NITRIDING REACTOR.

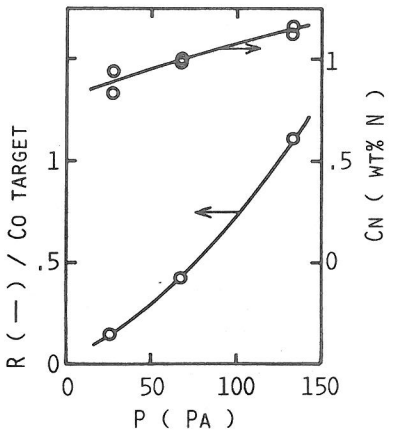


FIG.2

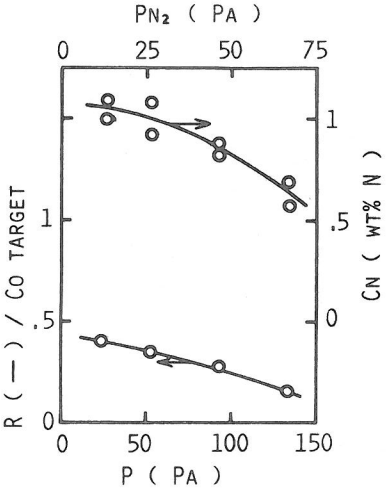


FIG.3

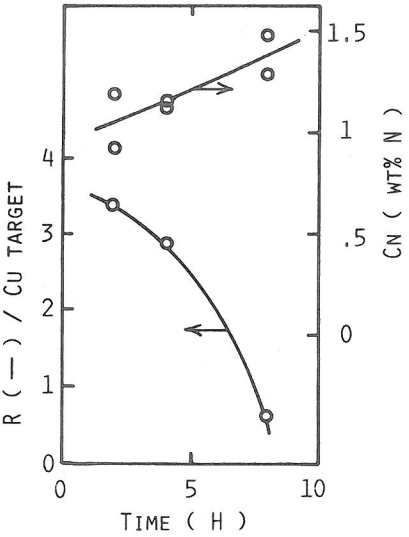


FIG.4

FIG.2 R AND CN VS. P CURVES FOR ION NITRIDING, 100% $N_2$ GAS, 4 HOURS.

FIG.3 R AND CN VS. P CURVES FOR ION NITRIDING, 50% $N_2$ – 50% $H_2$ MIXTURE GAS, 4 HOURS.

FIG.4 R AND CN VS. TIME CURVES FOR ION NITRIDING, 100% $N_2$ GAS, 133 PA.

## SEM PHOTOGRAPHS

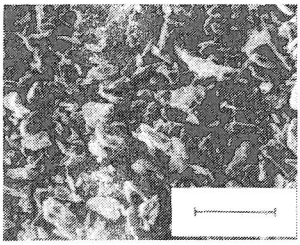

Photo.1 Electrolytic iron powder.
( bar = 100μm )

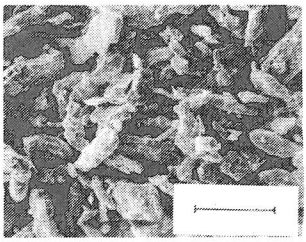

Photo.2 Upper surface of sintered sample in hydrogen discharge at 27 Pa for 1 H.
( bar = 100μm )

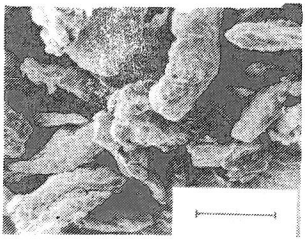

Photo.3 Upper surface of sintered sample, ion nitrided in 100% nitrogen gas at 133 Pa for 2 H.
( bar = 100μm )

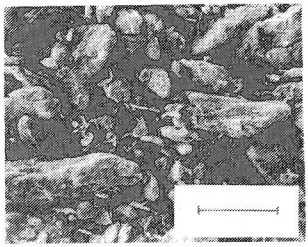

Photo.4 Upper surface of sintered sample, ion nitrided in 100% nitrogen gas at 133 Pa for 4 H.
( bar = 100μm )

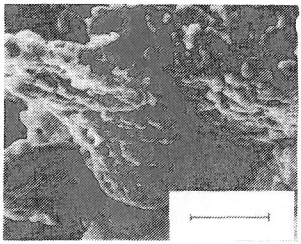

Photo.5 Upper surface of sintered sample, ion nitrided in 100% nitrogen gas at 133 Pa for 8 H.
( bar = 10μm )