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CHEMICAL STATE ANALYSIS OF NITRIDED STEEL SURFACE BY MEANS OF CONVERSION ELECTRON
MÖSSBAUER SPECTROMETRY

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Abstract.- CEMS was used to characterize the nitrided steel surfaces and chemical states of surfaces estimated layer by layer. Gas nitrided steel surface is composed of $c$-$Fe_2 N$, distorted $Fe_{3+x}N$ ($0 < x < 1$), $\gamma$'-$Fe_2 N$ martensite and $a$-$Fe$ layer slightly disturbed by intruded nitrogen. Tufftrided steel surface consists of $c$-$Fe_2 N$, intermediate $c$-$Fe_3 N$ and $\gamma'$-$Fe_2 N$, $\gamma$'-$Fe_2 N$ and disturbed $a$-$Fe$ layers. Ion nitrided steel surface has a 2–3 µm thickness of $\gamma_1$'-$Fe_2 N$ (magnetically randomly oriented), $\gamma_2$'-$Fe_2 N$ and distorted $a$-$Fe$ layers.

1. Introduction.- Though the potentiality of CEMS as an analytical tool for the characterization of oxidized iron surface or ion implanted semi-conductor material has been widely demonstrated, little attention is orientated to the layer by layer analysis of the surface layers. Development of depth sensitive CEMS apparatus may meet the above request, there still is need several years before depth sensitive spectrometer has come into practical use.

The present paper describes the results of chemical state analyses of nitrided steel surfaces achieved by the combination of careful grinding of surface layer and the CEMS detecting 7.3 keV conversion electron and 5.6 keV Auger electron of iron-57.

2. Experimental.- The polished surface of NT70H (Fe:95.97at.% C:0.56at.%; diameter:5cm, length: 0.5cm) was nitrided by the following three procedures.

(A) A sample was placed in the stream of ammonia gas and heated at 793 K for 30 hours. 30% of ammonia molecules were dissociated to feed nitrogen atoms ($2NH_3 \rightarrow 2N + 3H_2$) in the atmosphere /1/.

(B) A sample was dipped into fused salts bath of potassium cyanide and potassium cyanate and nitrided for 7 hours /2/.

(C) A sample was placed in the stream of nitrogen (0.35 l/min.) and hydrogen (0.5l/min.) mixture and ion nitrided for 4 hours at 793 K by the glow discharge of nitrogen /3/.

The nitride surfaces were ground to the desired depth utilizing the fine powder of Sic 500 and CEMS of the exposed layers were measured by the backscatter electron detector (Austin Science Associates BSD-2400). The ground thickness was monitored through the weighing of nitrided samples.

3. Results and discussion.-

3.1. Surface states of gas nitrided steel.- The CEMS of gas nitrided steel surface (30µm) are shown in figure 1, which indicates the presence of 4 distinct layers on the surface.

The uppermost surface material is identified to paramagnetic $c$-$Fe_2 N$, the thickness of which is more than 10µm.

The intensity ratio of the doublet peaks is 5:3. Although the conjecture that the efg of the layer could be oriented parallel to the surface is plausible, the idea that the doublet peaks are due to the superposition of several peaks of different iron species could not be ruled out.

CEMS of (b) reveals that the distorted $Fe_{3+x}N$ ($0 < x < 1$) layer exists between the $c$-$Fe_2 N$ austenite layer and $\gamma$-$Fe_2 N$ martensite.

CEMS of (c) indicates that the crystal structure of $\gamma$-$Fe_2 N$ is distorted considerably from that of pure $\gamma$-$Fe_2 N$ /5/, /6/. The CEMS of the layer has the magnetically split six peaks with the intensity ratio 3:4:1:1:4:3, indicating the magnetic domain of the exposed $\gamma$-$Fe_2 N$ layer to be oriented parallel to the surface.
CEMS of (d) shows that the crystal structure of α-Fe phase close to the γ'-Fe₅N is distorted to a considerable extent by the intrusion of nitrogen atoms into the lattice of α-Fe. Yamakawa and Fujita reported that ε-Fe₂₃N was also found besides ε-Fe₂-3N and γ'-Fe₅N in the nitrided steel obtained by nitriding pure iron in the ammonia gas for 20 minutes /7/. But we could not observe the peaks of ε-Fe₂N on the CEMS of gas nitrided steel surface. Our samples are produced by gas nitriding steel surface for 30 hrs, so that ε-Fe₂N might have already changed into ε-Fe₂-3N or γ'-Fe₅N.

3.2. Surface states of tufftrided steel.-- The CEMS' of tufftrided steel surface (40um) are shown in Figure 2.

CEMS of (a) suggests the existence of two chemical layers at the uppermost surface. The peaks are assigned to the mixture of ε-Fe₃C and ε-Fe₅N, referring to the information that carbon coagulates near the surface ε-Fe₂-3N phase /8/.

CEMS of 20um-30um layer from the uppermost surface indicates the gradual decrease of nitrogen atoms as the depth going on. CEMS of (d) is assigned as the broadened peaks of the distorted γ'-Fe₅N phase.

Magnetically split peaks of α-Fe is obtained at the 40um depth, the somewhat distorted profiles revealing the intrusion of nitrogen atoms in the α-Fe crystal lattice.

3.3. Surface states of ionitrided steel.-- The surface layer consists of 3 layers, γ'₁-Fe₅N, γ'₂-Fe₅N and α-Fe phase (Fig. 3).

The uppermost layer is γ'₁-Fe₅N. Relative intensities of magnetically split peaks of γ'₁-Fe₅N suggests that the magnetic domain of the uppermost 10-100nm layer is oriented at random. The unusual evidence can be explained by the evaporation of surface iron atoms by the impact of nitrogen ions, followed by the reaction of iron and nitrogen in the space and sputtering of produced iron nitride onto the surface /9/.

Relative intensities of CEMS of the layer 3um below the surface are 3:4:1:1:4:3, indicating the magnetic domain of the exposed γ'₂-Fe₅N layer to be
orientated parallel to the surface.

Fig. 3: CEMS of ion nitrided steel surface ground with SiC powder.

Non-equivalent three sites of iron atoms in γ′-Fe₄N are clearly separated in CEMS (lattice site iron (FeI) and face-center sites (FeII-A and FeII-B). Considerably discrepancy is observed in the quadrupole splitting of FeII-A or FeII-B between γ′-Fe₄N phase and γ′-Fe₄N phase (Fig. 3 (a) and (b)).

α-Fe phase prevails in the 10µm depth layer.

References

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