Conversion electron Mössbauer spectra of heated ion nitrided steel surfaces

Conversion electron Mössbauer spectrometry (CEMS) has proved to be one of the most useful techniques for the physico-chemical state analysis of iron located at chemically-treated steel surfaces, such as a borided surface [1], a nitrided surface [2–4], a carburized surface [5], a galvanized surface [6] and a Parkerized surface [7–9]. It is fairly difficult to obtain decisive results from the CEM spectra measured only at room temperature and, therefore, a proportional counter, capable of working at elevated temperatures, was designed in our laboratory [10].

The detector was effectively used to study the chemical compositions of iron nitrides, which have similar internal magnetic field strengths and isomer shifts, by analysing the change of the magnetic properties of the surface products upon heating up to Curie temperature.

It has been reported, hitherto, that ϵ-$Fe_{2-3}N$ and γ'-Fe_4N were present at the surface of nitrided steel [2–4], and, in order to obtain conclusive evidence we investigated this report in more detail. In this work the CEM spectra near the Curie points were observed and the relationship between the Curie temperature and the nitrogen contents of iron nitride reported by Mekata *et al.* [11], and Decristofaro and Kaplow [12] was applied to the results.

The sample was prepared by the following process. NT-70H steel (C : 0.56 at %, Mn : 1.21 at %, Cr : 0.85 at %, Si : 0.59 at %, Mo : 0.40 at %, V : 0.33 at %, S : 0.14 at %, Fe : balance, about 96 at %, manufactured by Mitsubishi Steel Co. Ltd) was used as a substrate for the ion nitridation. The steel surface was nitrided in a chamber by operating glow electric discharge for 4 h at 790 K. During the operation, nitrogen ($0.25\ l\ min^{-1}$) and hydrogen ($0.25\ l\ min^{-1}$) gases flowed into the chamber. The surface of the ion-nitrided steel was ground by the same way as reported previously [2, 3].

The CEM spectra of the exposed layers were measured by using the high-temperature proportional counter described in [10].

The CEM spectrum obtained at room temperature indicated that two phases of iron nitrides existed at the uppermost surface.

The one phase was seen to be distorted and paramagnetic: an extremely wide singlet peak was seen on the spectrum. This peak was estimated to result from the formation of ϵ-Fe_xN, where $2.0 < x < 2.3$, since the phase had a Curie point well below room temperature. The other magnetically-split peaks seen on the spectrum showed the existence of ferro-, ferri- or antiferromagnetic iron nitride. Since the magnetically-split peaks were also present on the CEM spectrum taken at 507 K, the peak was attributed to γ'-Fe_4N, the Curie temperature of which was reported as 760 K by Nozik *et al.* [13].

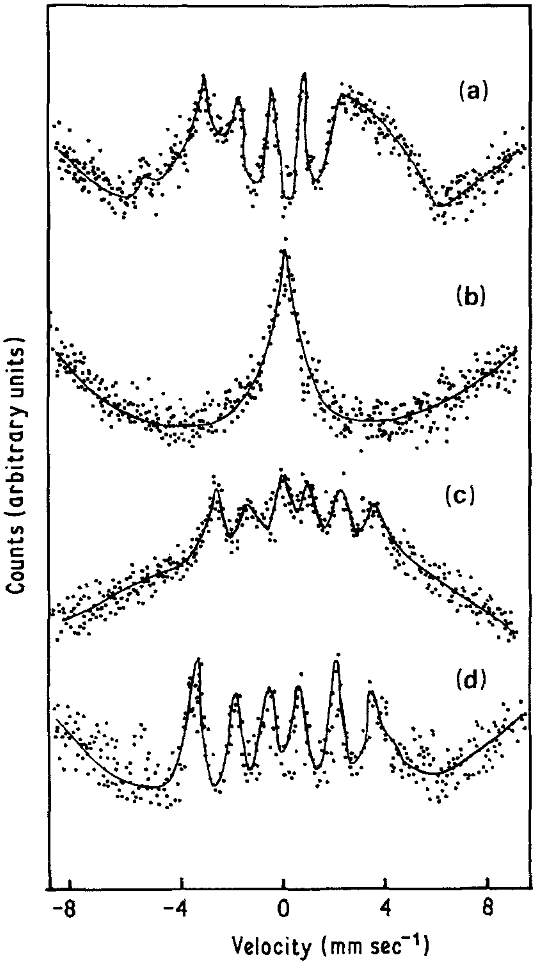

Figure 1 CEM spectra of ion nitrided steel ground to a depth of 5 μm taken from the top surface. (a) Measured at room temperature (before heating); (b) measured at 507 K; (c) measured at 363 K; (d) measured at room temperature (after heating). Note: The baselines of (a), (b) and (d) are concave in shape whereas that of (c) is convex in shape.

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The CEM spectrum was observed for the same sample ground to a depth of $1\,\mu$m. Both singlet and sextet peaks were seen on the spectrum measured at 363 K, suggesting that two phases existed; the Curie point of one phase was below 363 K. Only the paramagnetic peak was observed when the CEM spectrum was measured at 507 K, indicating that the second iron nitride had a Curie temperature between 363 K and 507 K.

It was concluded that ϵ-$Fe_{2.3-2.4}N$ and ϵ-$Fe_{2.4-2.7}N$ deposited stably at a depth of $1\,\mu$m below the top surface.

The CEM spectra of the sample ground to a depth of $5\,\mu$m are shown in Fig. 1.

Only the paramagnetic peak appeared on the CEM spectrum taken at 507 K, whereas the sextet peaks were seen at 363 K as shown in Fig. 1b and c. The iron nitride was identified as ϵ-Fe_xN ($2.4 < x < 2.7$), since the Curie point was found to lie between 363 K and 507 K.

The nitrogen content decreased gradually with increasing distance from the top surface of the sample. If the surface layer is ground still further the phase corresponding to γ-Fe_4N is disclosed.

The distinct magnetically-split peaks were seen on the CEM spectrum after the heated sample was cooled to room temperature (see Fig. 1d). The spectrum indicated that the distorted and quadrupole-split phases were relaxed to the strainless crystal form by the thermal treatment up to 507 K. Comparison of Fig. 1a and d indicated that the iron nitride located at the exposed layer was well annealed. Nitrogen atoms combined with iron atoms were estimated to migrate slowly along the crystal to coalesce the distorted structure.

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Thermal expansion of spinel-type $AgIn_5S_8$ by the X-ray method

The Ag–In–S system is currently of much interest because of the particular semiconductive properties of the ternary compound $AgInS_2$, a potentially suitable material for opto-electronic devices [1]. The crystals prepared by normal freezing from the melt of stoichiometric mixtures, with $AgInS_2$ composition, crystallize in the chalcopyrite structure [2]. When an $AgInS_2$ sample was quenched from above its melting point, crystals with the $AgIn_5S_8$ composition, crystallizing in the spinel structure, were obtained by Roth *et al.* [3].

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