JOURNAL OF MATERIALS SCIENCE 16 (1981) 1999–2002

Layer-by-layer analysis of the chemical state of iron in carburized steel surfaces by conversion electron Mössbauer spectrometry

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Conversion electron Mössbauer spectra revealed that the uppermost surface layer of a carburized and quenched steel was almost γ-austenite and that the surface layer of this sample consisted of α'-martensite and γ-austenite. Iron carbide was expected to have been formed in the surface layer of a carburized and annealed steel but, in fact, no iron carbide could be recognized in the sample. This may be due to the de-carburization or the re-diffusion of carbon into the steel. However, conclusive evidence supporting this explanation was not obtained.

1. Introduction

Compound layers formed on steel surfaces during hardening treatment are typically between 10 and 100 μm thick. Several methods are in common use to investigate the chemical composition of surface layers of this thickness. Of these X-ray diffractometry (XRD) is one of the most popular techniques, but the depth resolution of XRD is greater than 10 μm due to the penetration depth of X-rays into steel.

ESCA, low energy electron diffractometry (LEED) or Auger Electron Spectrometry (AES) have very high depth resolutions of a few layers (1 to 3 Å), but these methods are too sensitive to analyse layers several hundred nanometers thick.

In constrast, conversion electron Mössbauer spectometry (CEMS), through detecting conversion electrons (7.3 keV) and Auger electrons (5.5 keV), which are thrown out from ^{57}Fe atoms in the relaxation process of excited nuclei, has a depth resolution of about 0.1 μm, since the range of these electrons in solid materials is less than 0.1 μm [1, 2].

Electron probe microanalysis (EPMA) also has appropriate depth resolution, but is not suitable for studying the physico-chemical states of iron atoms. Therefore CEMS provides unique and useful information for the characterization of the hardened layers.

Nitriding and carburization are well-known methods used to obtain hardened surfaces. Though a lot of work has been carried out concerning the effects of treatment conditions or alloy compositions, it would appear that only metallographic or electrolytic approaches have been published concerning the structures of hardened surfaces.

Surface layer analysis by means of CEMS has only been started recently, and the usefulness of CEMS was demonstrated in the previous studies of nitrided and Parkerized steel surfaces [3–5]. In the present paper, CEMS was applied to the layer-by-layer analysis of the chemical state of iron in the carburized steel surface.

2. Experimental procedure

Two samples, Samples A and B, were prepared

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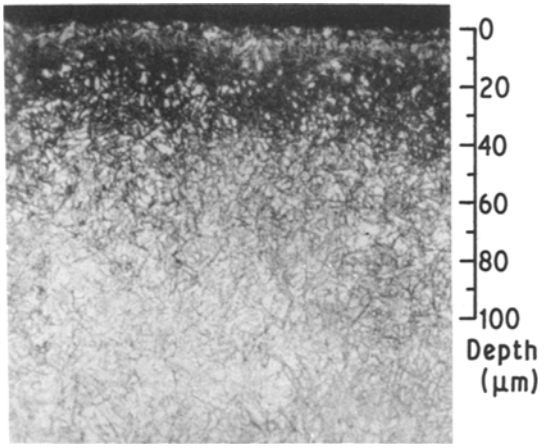

Figure 1 The metallographic cross-section of a carburized and quenched steel, Sample A (× 300).

by the following procedures. The surfaces of the two H-2 steels (C: 0.97 at %; Cr: 1.02 at %; Fe: 96.63 at %) were carburized in a mixed gas atmosphere of propane and air at 930° C for 2 h using nickel as a catalyst [6]. During the process the carbon potential was adjusted so as to maintain the carbon content of the uppermost surface at 1.0 wt %.

One sample was quenched in oil and then re-heated at 880° C for 15 min to remove strain in the steel (Sample A). The other sample was taken out of a furnace after the carburizing process, wrapped with asbestos and cooled gradually (Sample B).

The carburized steel surfaces were ground with SiC 800 powder in several micrometer steps and the CEM spectrum of each exposed layer was measured at room temperature.

The conversion and Auger electron spectra were detected by the back-scatter type proportional counter (Austin Science Associates BSD-2400) to which was connected the Mössbauer spectrometer. The γ-ray source was 50 mCi ^{57}Co(Rh). The microstructures of the surface and substrate layers were also observed by microscope.

3. Results and discussion

3.1. Carburized and quenched steel (Sample A)

Fig. 1 illustrates a metallographic cross-sectional view of the surface layer of Sample A, the carburized and quenched steel. The needle-like black phases are α′-martensite and the white areas are γ-austenite and α-iron phases.

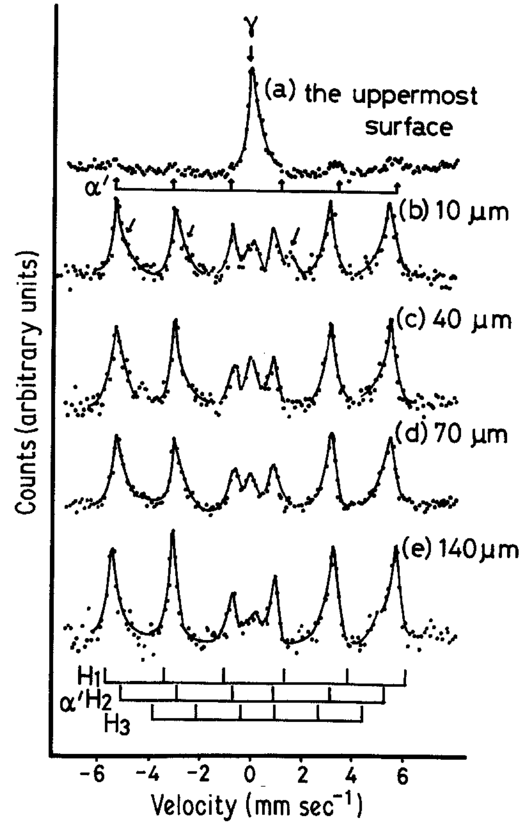

Figure 2 CEM spectra of a carburized and quenched steel, Sample A.

The CEM spectra and the X-ray diffraction pattern of the uppermost surface of Sample A are shown in Figs 2 and 3. From the X-ray diffraction pattern, the uppermost layer seems to be composed of γ-austenite and α′-martensite and α′-martensite cannot be distinguished from α-iron. In the CEM spectrum of the uppermost surface, however, the singlet peak of γ-austenite is prevalent and the sextet peak of α′-martensite, as is indicated by the arrows, is only weakly observed

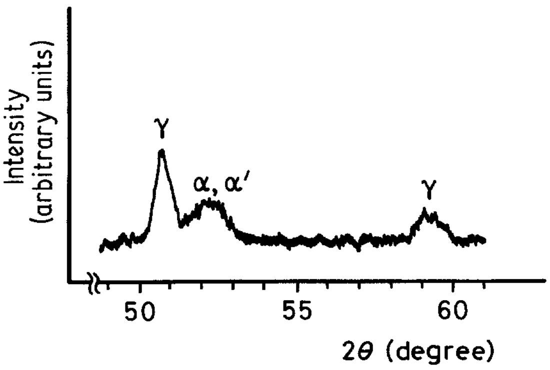

Figure 3 X-ray diffraction pattern of the uppermost surface of a carburized and quenched steel, Sample A.

TABLE I Mössbauer parameters observed for α'-martensite and γ-austenite and the ratio of the peak area of α'-martensite to that of γ-austenite. The parameters were calculated from the least-square fit of the spectrum which was assumed to be composed of a singlet peak of γ-austenite and a prevalent sextet of α'-martensite. These parameters support Conclusion b, Section 3.1

Depth (μm)	α'-phase		γ-phase	α'/γ
	Internal magnetic field, H (Tesla)	Isomer shift, δ (mm sec^{-1})	Isomer shift, δ (mm sec^{-1})	
40	31.864 ± 0.030	0.045 ± 0.009	− 0.076 ± 0.011	10.2/1.0
70	31.851 ± 0.051	0.071 ± 0.013	− 0.066 ± 0.015	10.6/1.0
140	33.052 ± 0.053	0.066 ± 0.013	0.132 ± 0.041	19.8/1.0

(Fig. 2a). The differences in the information obtained by CEMS and XRD methods with regard to the structure of the uppermost surface are due to the difference of depth resolution of CEMS and XRD.

According to the relationship between the carbon content and the volume of retained austenite reported by Fletcher and Cohen [7], 15 to 20 vol% retained austenite should correspond to 1.0 wt% carbon content. However, the proportion of γ-austenite on the uppermost surface of Sample A seen in this work was not found to agree with their results.

The CEM spectrum of the exposed layer at 10 μm-depth, spectrum b, showed the superposition of peaks corresponding to α'-martensite and γ-austenite. It has been reported that the spectrum of α'-martensite has three components [8]: $H_1 = 34.5$ T, $H_2 = 32.0$ T and $H_3 = 27.5$ T. The three sub-spectra should be seen at the values indicated by the key at the foot of Fig. 2. The sextet ($H = 31.8$ T) of spectrum b has shoulders and small peaks, which are indicated by arrows, proving that the phase is α'-martensite.

When the surface was ground to 40 μm, 70 μm and 140 μm, the superposed peaks of α'-martensite and γ-austenite were seen, in spectra c, d and e, respectively. By analysing these spectra the following conclusions were derived.

(a) The uppermost surface has the highest γ/α' ratio. The decrease of γ-austenite content is very steep in the range between the uppermost surface and the 10 μm-depth layer. This result indicates that the uppermost surface cooled down extremely rapidly during the quenching process and that rapid transformation to α'-martensite (within 10^{-7} sec) was inhibited.

(b) As the depth increased, the carbon content of the surface layer decreases and the spectrum of α'-martensite gradually approaches that of α-iron (see Table I).

(c) Every layer was composed of two phases: α'-martensite and γ-austenite. No evidence of the iron carbide phase (cementite, ζ-Fe_3C) was found.

Carbon or nitrogen atoms get into interstices of the iron lattice and form a hard solid solution [9]. Previous studies of the surface analyses of nitrided steel by CEMS have revealed that the surface layers consist of single-phase iron nitride [3, 4]. In spite of the similar diffusion rates for carbon and nitrogen atoms in the iron lattice there were distinct differences in the surface layer structures formed. These differences may be due to the different heat-treatment conditions, i.e., nitrided steel was heated to 520° C and cooled gradually in the furnace but Sample A was quenched after carburization.

If the treatment cycle is responsible for this difference, iron carbide will be formed in the surface of a sample which has been carburized and finally annealed (Sample B).

3.2. Carburized and annealed steel (Sample B)

Fig. 4 shows a metallographic cross-sectional view of Sample B. A comparison of Fig. 1 and Fig. 4

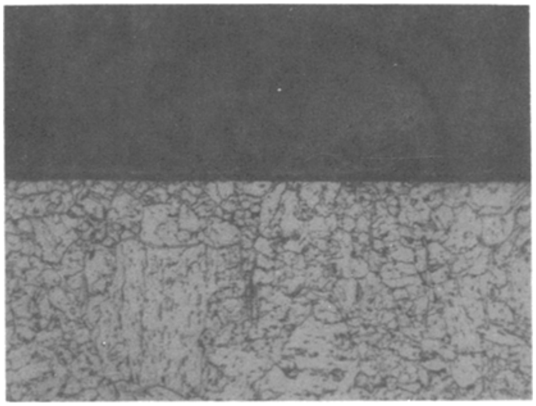

Figure 4 The metallographic cross-section of a carburized and annealed steel, Sample B (× 300).

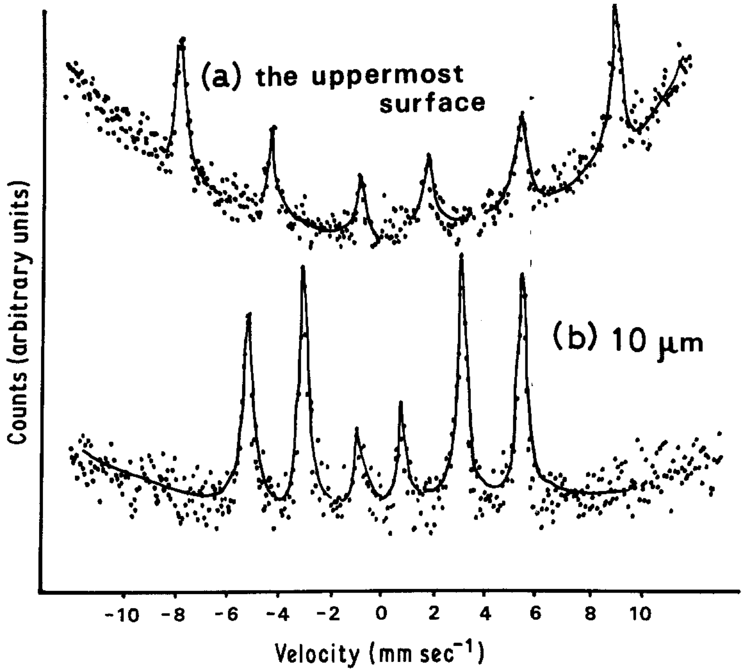

Figure 5 CEM spectra of a carburized and annealed steel, Sample B.

indicates that the grain size of Sample B is greater than that of Sample A.

The uppermost surface was a black layer. The CEM spectrum (Fig. 5, spectrum a) has the sextet peaks indicating a strong internal magnetic field (about 51 T), which is attributed to α-haematite [10]; the uppermost surface seems to have been oxidized.

Beneath the oxidized layer is α-iron (Fig. 5, spectrum b). The peaks attributed to iron carbide are not observed. This result indicates that there were no carbon atoms interacting with iron atoms. The fact that cementite cannot be identified from the spectrum taken from the surface is interpreted to result from either the decarburization of steel surface or the penetration of carbon atoms into the bulk.

4. Conclusion

CEMS has given information on the chemical state of iron present at the surface of steels. The information obtained using this method could not have been obtained either by XRD or by any other method. An extremely high ratio of γ/α' at the uppermost surface of the carburized and quenched steel and a gradual change of α'-martensite to α-iron in the surface layer of Sample A were observed. The CEM spectra also revealed the absence of iron carbide on the surface layer of the carburized and annealed steel.

Acknowledgements

We thank Associate Professors S. Tsujikawa and O. Ogawa, the Department of Material Science, University of Tokyo, for their helpful advice and encouragement.

References

1. J. J. SPIJKERMAN, "Mössbauer Effect Methodology" Vol. 7, edited by I. J. Gruverman, C. W. Seidel and D. K. Dieterly (Plenum Press, New York and London, 1971) p. 85.
2. F. E. WAGNER, *J. Phys. C* 37 (1976) 673.
3. Y. UJIHIRA, A. HANDA, Y. ABE and I. OKABE, *Nippon Kagakukaishi* (1979) 234.
4. Y. UJIHIRA and A. HANDA, *J. Phys. C* 40 (1979) 586.
5. K. NOMURA, Y. UJIHIRA, Y. MATSUSHIMA, R. KOJIMA and Y. SUGAWARA, *Nippon Kagakukaishi* (1980) 1372.
6. S. WADA and K. OGIWARA, *Met. Eng.* 17 (1977) 18.
7. S. G. FLETCHER and M. COHEN, *Trans. Amer. Soc. Metals* 32 (1944) 333.
8. H. INO, S. NASU and U. GONSER, *J. Phys. C* 41 (1980) 377.
9. K. H. JACK, *Proc. Roy. Soc.* A195 (1974) 34.
10. N. N. GREENWOOD and T. C. GIBB, "Mössbauer Spectrometry" (Chapman and Hall Ltd. London, 1971) p. 241.

Received 26 September 1980 and accepted 2 February 1981.