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THE STRUCTURES OF MARTENSITE AND BAINITE

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Résumé. — Les spectres Mössbauer du $^{57}$Fe dans la martensite et ses structures de recuit ont été analysés en six contributions, classées suivant le nombre et la distance des atomes de carbone les plus proches. Sur cette base, les configurations atomiques locales et la nature des liaisons ont été décrites dans Fe$_{3}$C et le carburé $\epsilon$ ; on a confirmé également la validité du modèle d'occupation des sites tétraédriques pour la phase martensitique à basse température.

Les spectres Mössbauer de la bainite montrent que la structure du carburé formé à 200°C est proche du carburé $\epsilon$, contrairement à la cémentite formée à 250°C.

Abstract. — The Mössbauer spectra of $^{57}$Fe in martensite and its aged structures were throughout resolved into six components, classified by the number and the distance of the nearest carbon atoms. On this basis, we analyzed the local atomic configuration and bonding nature in Fe$_{3}$C and $\epsilon$ carburé, and also confirmed the validity of the tetrahedral site occupation model for the low temperature martensite phase.

The Mössbauer spectra of lower bainite showed that the carbide structure formed at 200°C are close to $\epsilon$ carbure, in contrast to cémentite at 250°C.

1. Sample preparation. — High purity (>99.99%) iron foils were carburized in a mixture of H$_{2}$ and CO (or CH$_{4}$) gases at 900-950°C. To obtain fresh martensite, the carburized specimen was quenched into iced water and immediately transferred to a liquid nitrogen bath. The carbon content of the specimen (0.6-1.3 wt%) was estimated from the tetragonality measurements by X-ray diffraction. The lower bainite structure was obtained by quenching and austempering the carburized specimen in a silicon oil bath at 200-250°C.

2. The structure of martensite. — In figure 1, the spectrum A of as-quenched martensite was resolved into three ferromagnetic components a, b and c. By aging at 20°C, the intensity of the "b" component rapidly decreased but that of the "c" increased. The internal magnetic field of the main component "a" decreased. The results are similar to those of previous reports /1/-/6/. The components denoted as "d" and "e" appeared after aging at 20°C and were intensified by aging at 80°C and 90°C. The "b" component completely disappeared at 80°C.

Figure 2 shows the spectrum after aging at 140°C, together with that of the specimen aged at room temperature and of pure iron (solid line), normalized in absorption area. The "d" component disappeared after ageing at 140°C. The "e" and probably "c", too, remained, of which the values of internal field are very close to each other. A component "f" also appeared, which has a much smaller internal magnetic field. The intensities of central paramagnetic peaks were unchanged, meaning that the $\epsilon$ carbure phase formed at 140°C was not superparamagnetic in contradiction to previous works /1/-/7/-/8/.

![Fig. 1: Mössbauer spectra for the same specimen of Fe-1.2wt%C, as quenched and aged up to 80°C.](http://dx.doi.org/10.1051/jphyscol:19792224)
Fig. 2: Mössbauer spectra for the specimen of Fe-1.2 wt% C after ageing at room temperature and 140°C (measured at 300 K).

Fig. 3 is the spectrum of the same specimen measured at 4.2 K under an effective external magnetic field of 3.4 T (34 kOe) parallel to the direction of γ rays to erase out the 2nd and 5th peaks (±1/2 + ±1/2 transition). The spectrum is clearly resolved into three components "d" and "e" (plus "c") and "f", with the values of internal field \( H_i \) of 33.8, 27.1 and 18.6 T, respectively. A similar measurement for the specimen aged at 90°C for 1 hr showed that the "f" component with \( H_i = 19.2 \) T exists even at 90°C.

In our previous paper /9/, we examined the relation between the reduction of internal magnetic field from that for pure iron \( H_{10} \) and the number of the 1st nearest carbon atoms \( n \) in various Fe-C alloys and compound, and derived the rule that the reduction \( \Delta H_{1} = H_{10} - H_{1} \) is nearly proportional to \( n \) and that \( \Delta H_{1}/H_{10} \) is about 0.2. The rule is based on the nature of localized characters of bonding, and thereafter has been widely applied to other metal-metalloid systems /10/, /11/.

From this point of view, present results can be thoroughly explained. Both the "c" and "e" components having \( H_{1}/H_{10} \approx 0.8 \) are related to iron atoms neighboured by one nearest octahedral carbon atom, and the "f" component with \( H_{1}/H_{10} \approx 0.6 \) is related to those surrounded by two nearest carbon atoms. The "b" component having \( H_{1}/H_{10} \approx 0.95 \) can be identified as the absorption arising from four 1st neighbouring iron atoms of the tetrahedral by co-ordinated carbon, where the distance between iron and carbon is longer than that when carbon occupies octahedral positions. The tetrahedral site occupation model for low temperature martensite /2/, /3/, /12/ is, therefore, consistent with the above consideration.

The "a" and "d" components arise from iron atoms without 1st nearest carbon atoms. Considering from the effect of the 2nd and 3rd nearest carbon atoms, the enhancement of internal field /13/ may be assumed to result in \( H_{1}/H_{10} \approx 1.14 \) for "d".

By considering experimental evidences of the superlattice of Fe-C /14/ and of its long period structure /15/ formed after ageing around 80°C, it is concluded that the "d" component arises from the corner iron atoms of Fe-C lattice and "f" from the face centre iron atoms surrounded by two carbon neighbours. Quadrupole coupling (\( e_{Q} \approx 0.08 \) mm/s) of "e" is about a half of the value of "c" and opposite in sign. The "c" and "e" components are, therefore, identified as due to face-centred iron atoms surrounded by one carbon atom, spin directions of which are parallel and perpendicular, respectively, to the principal axis \( q \) of electric field gradient.

The "e" (including "c") and "f" components exist after ageing at 140°C (in Fig 3), where hexagonal \( \varepsilon \) carbide (or slightly distorted to orthorhombic \( \eta \) carbide) is formed. The local atomic configuration and bonding nature in this coherent precipitates are almost unchanged. Our spectrum analysis for \( \varepsilon \) carbide agrees well with that by Focct et al. /16/, but inconsistent with those by others /8, 17/.

3. The structure of bainite.— The Mössbauer effect and X-ray diffraction measurements showed that carbide formed in bainite at 250°C is surely cementite (Fe3C) from early stage of tempering. While, in contrast, the Mössbauer spectrum observed for the specimen austempered at 200°C was similar to but slightly different from that of \( \varepsilon \) carbide.

No one have examined by diffraction the carbide structure in bainite formed at such a low temperature, probably because of its small size beyond observation. In the present experiments, it is clarified...
that even in the case of Fe-C binary system without Si, carbide formed at low temperature is close to ε carbide in its local atomic configuration.

References