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AGEING OF Fe-Ni-C MARTENSITE

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Résumé - Nous décrivons une étude, entreprise en collaboration, portant sur les étapes initiales du vieillissement de la martensite Fe-Ni-C à haute teneur de carbone, et utilisant les techniques combinées de microscopie ionique de champ (FIM) et de microscopie ionique de champ à haute résolution (TEM). Le matériau étudié est un alliage Fe-15%poids, Ni-1%poids, C, avec la température M_s inférieure à -35°C. L'alliage a été examiné à la fois avant et après vieillissement à 20°C pendant des durées atteignant 2000 hrs. Les micrographies FIM ainsi que TEM révèlent une microstructure modulée à très fine échelle. Les microanalyses par sonde à atomes révèlent des bandes riches en carbone contenant jusqu'à 11% (%at) de C. Ce travail fournit une caractérisation positive des changements chimiques surviennent durant ce que l'on nomme l'étape "zéro" de la trempe ou du vieillissement, c'est-à-dire précédant la transition où se produit la formation de carbone.

Abstract We report a collaborative study of the early stages of ageing of high-carbon Fe-Ni-C martensite, using the combined techniques of atom probe field-ion microscopy (FIM) and high-resolution transmission electron microscopy (TEM). The material used in this investigation was an Fe-15wt%Ni-1wt%C alloy, with M_s temperature below -35°C. The alloy was examined in both the unaged condition and after ageing at 20°C for times up to 2000 hours. Both FIM and TEM micrographs revealed a very fine scale modulated microstructure. Atom probe microanalyses revealed carbon-rich bands containing up to 11at%C. This work provides a positive characterization of the chemical changes that occur during the so-called "zeroth" stage of tempering or ageing - i.e. preceding transition carbide formation.

I - INTRODUCTION

Ageing of high-carbon martensite has been of considerable interest in physical metallurgy for many years [1-12]. Due to the complicated microstructure of martensite, there are widely differing interpretations of results obtained from several techniques and a wide range of materials. The atom probe technique has been shown to be very powerful for the determination of local carbon atom concentrations in martensites [8,10], although its ability to reveal information about crystallographic parameters is very limited. In order to clarify the structural evolution during ageing, therefore, a collaborative research programme has been initiated, using a range of different techniques, to study one material from the unaged state to the stage before transition carbide formation. In this paper we report some preliminary results obtained by TEM and atom probe FIM.

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2 - EXPERIMENTAL

The material used in this investigation was an Fe-15wt%Ni-1wt%C alloy (Fe-14at%Ni -4.5at%C), with an M_s temperature below -35°C. Heat treatment consisted of austenization for 1 hour at 950°C, water quench and further cooling in liquid nitrogen. Ageing treatment was done at room temperature (20°C) for various periods up to 2000 hours.

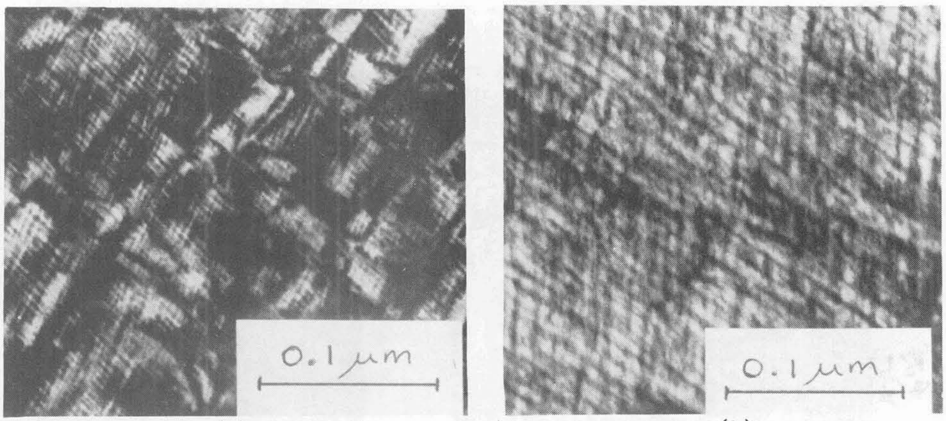
TEM and FIM specimens were prepared from aged material by standard electropolishing techniques. Atom probe analyses were done at liquid nitrogen temperature, and in random area mode. The probe aperture varied between approximately 1.5 and 3 nm, depending on tip voltage.

3 - RESULTS

TEM micrographs of thin foils prepared after 3h and 1150h ageing treatments, Figs.1a and 1b, show a tweed morphology consisting of very fine striations roughly along the traces of (012) and (01$\bar{2}$) planes. The coarse, dark features are contrast from screw dislocations lying along 111 directions. The TEM micrograph of a FIM tip prepared after 1440h ageing is shown in Fig.2a. The FIM image in Fig.2b also revealed the fine striations. The dark bands containing high-carbon regions were observed in a sequence of FIM, carbon and iron images using the imaging atom probe technique, Fig. 3a. Another example of high-carbon bands with ~2nm width and inter-band distance of ~6nm is shown in Fig.3b. The composition profile, Fig.4, obtained by probing down through the (011) pole of a specimen aged for 1580 hours revealed quite regular variations of carbon concentrations with an average maximum amplitude of about 11at% and wavelength of roughly 30 atomic layers (50 ions ≈1 layer). Fig.5 shows the composition profile after 1870h ageing, together with a diagram of autocorrelation analysis in which the size of high-carbon region of 2000 ions and the wavelength of 4000 ions are clearly demonstrated. To show the variation of carbon concentration, every point in Fig.5 was averaged over 200 ions. Averaging over smaller numbers of ions only increases the noise on the background. The periodicity of the composition profiles shows one of the characteristics of a modulated structure. The frequency distribution which can reveal the progress of the decomposition during ageing [14] is shown in Fig.6. The sample size in each case is 100 ions. The distribution in the unaged condition is similar to the calculated binomial distribution of a homogeneous solid solution. The frequencies at 0 and 1%C are increased with ageing time, and also high carbon concentration regions become progressively more abundant. This provides evidence that the alloy is undergoing continuous phase decomposition. Strikingly, there is a peak at 11at%C on the frequency distribution curve after 1580h ageing, which may represent the carbon content of the high-carbon region. There is no evidence of Fe_4C composition (20at%C) during the period of ageing up to 2000h examined in the present study.

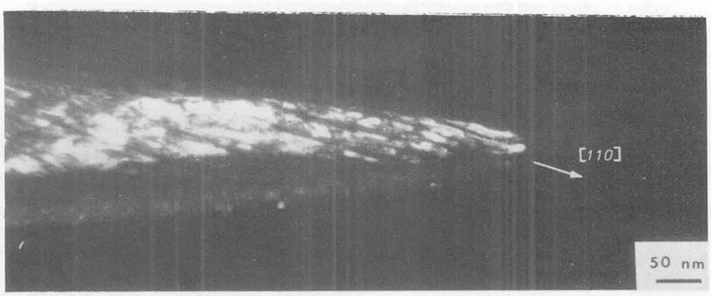
4 - DISCUSSION

Both the TEM and FIM atom probe results described above support the deduction from previous TEM studies [7,11,15] that a modulated structure is formed during the early stages of ageing. A FIM atom probe study by Miller et al. on a Fe-23wt%Ni-0.42wt%C martensite with M_s temperature -50°C [10] also demonstrated that at the early stages of ageing the maximum carbon concentrations of high-carbon regions were of the order of 10at%C, consistent with the present results. To explain the occurrence of the modulated structure the most likely model is that of spinodal decomposition [16]. The hypothetical spinodal region on the phase diagram is shown schematically in Fig.7. The solid lines are the phase boundaries and the dashed lines represent the coherent spinodal. The composition figures are based on the atom probe results from the 0.42wt%C alloy [10], and the 1wt%C alloy used in the present study, together with evidence from Mossbauer studies by Choo and Kaplow [4] which indicate that Fe-1.86wt%C alloys also undergo decomposition. The slopes of the lines are uncertain at present. When virgin martensite decomposes in spinodal mode, the carbon concentrations in high-carbon regions increase with ageing time as the frequency distribution implies. After reaching a metastable

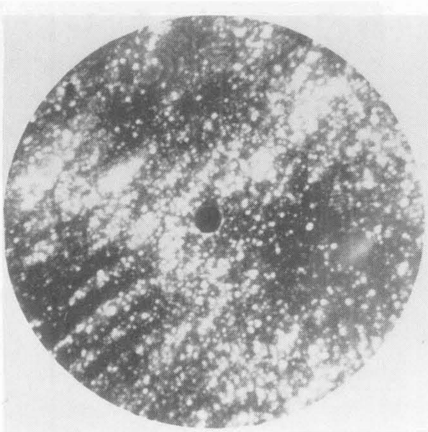


(a) (b)

Fig.1 - Electron micrographs of martensite aged at room temperature (a) for 3h; and (b) for 1150h.
Both are bright field images taken with the incident electron beam nearly along [100], but with the foil tilted slightly about [010]

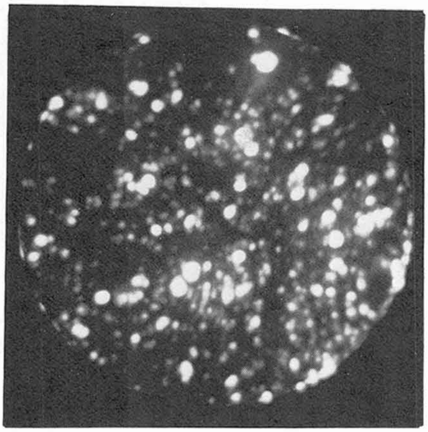


(a)

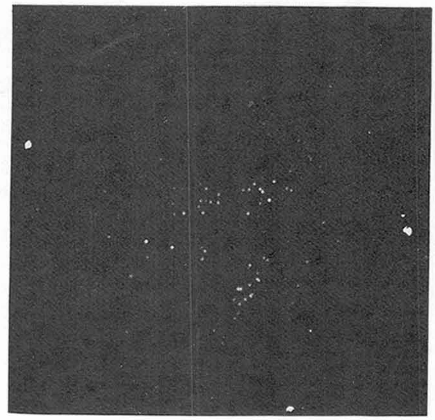


(b)

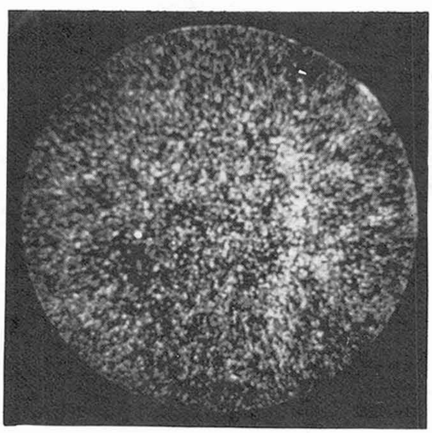
Fig.2 - (a) Electron micrograph of a FIM specimen after 1440h ageing.
(b) FIM image of the same specimen taken at 10 kV.



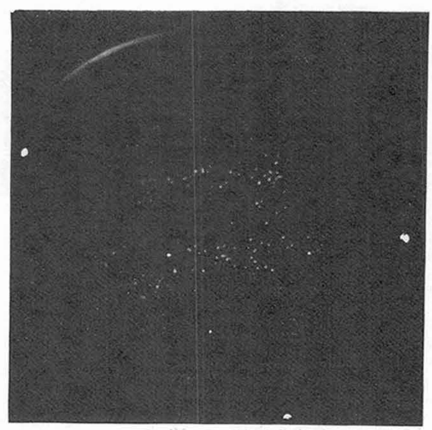
(a) (i)



(a) (ii)



(a) (iii)



(b)

Fig.3 - (a) Sequence of (i) FIM image, (ii) gated carbon and (iii) gated iron images after 1680h ageing, taken at 11.5 kV. (b) Another gated carbon image taken at 10.9 kV.

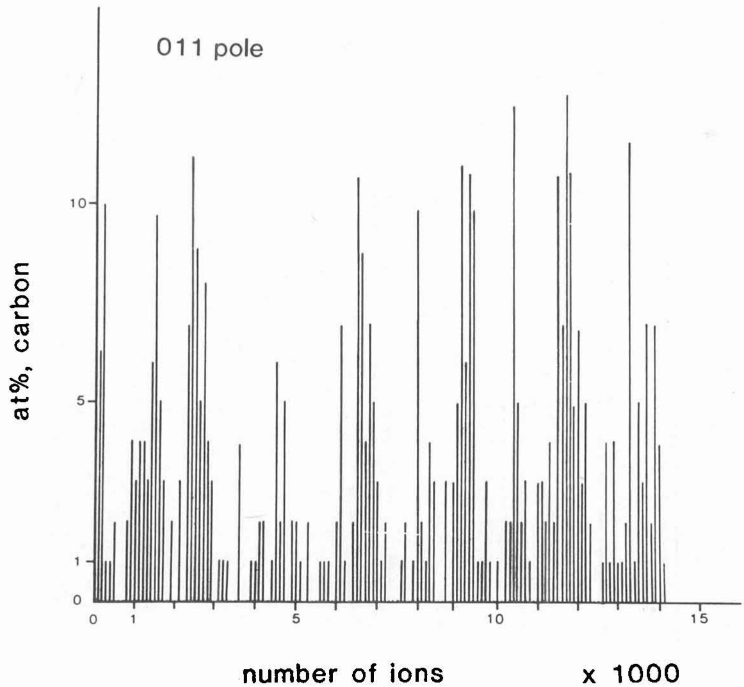


Fig.4 - Composition profile probing through (011) pole with each date point averaged over 100 ions. The specimen was aged for 1580h.

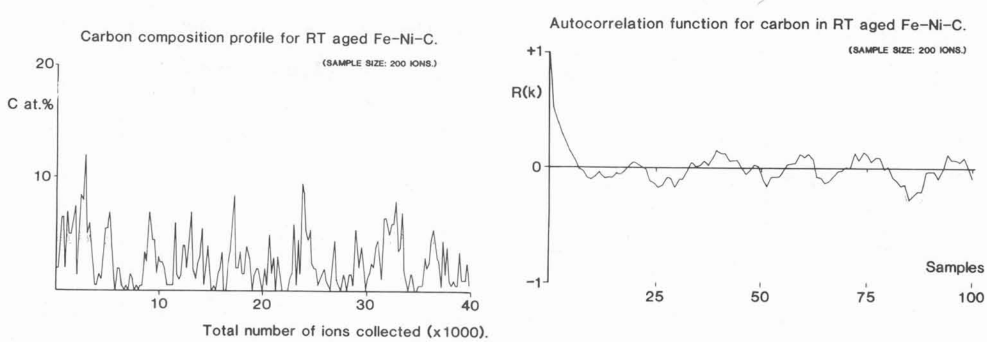


Fig.5 - Composition profile and diagram of autocorrelation analysis after 1870h ageing with original data points averaged over 200 ions.

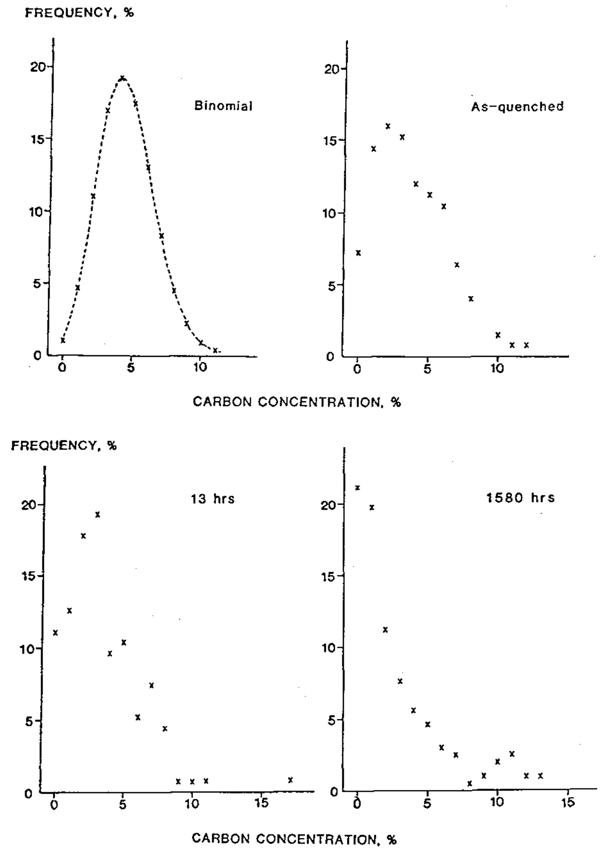


Fig.6 - Frequency distribution of carbon content in 100 ions blocks. Total number of ions collected in each ageing condition was over 10000.

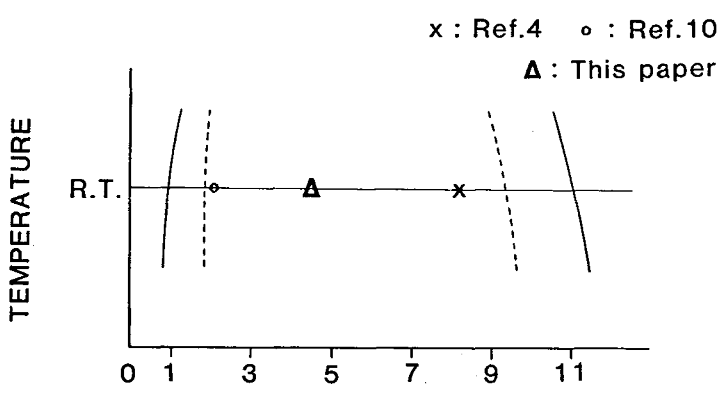


Fig.7 - Schematic phase diagram of spinodal region of martensite. The solid lines are phase boundaries and the dashed lines represent the coherent spinodal.

equilibrium stage of decomposition at ~2at% and 11at%C it would appear to proceed into the conventional first stage of tempering by a process of nucleation and growth.

The occurrence of an average maximum carbon concentration of 11at%C can tentatively be interpreted in terms of the development of a coherent phase of composition $Fe_{16}C_2$. This composition corresponds to that of the first intermediate precipitate formed during the low-temperature ageing of iron-nitrogen martensites, $Fe_{16}N_2$ (b.c.t. structure) [17]. There appears to be no other evidence in the literature suggesting the existence of an iron carbon phase at this composition. X-ray and electron diffraction and Mossbauer data have conventionally been interpreted in terms of the Fe_4C phase (fcc structure), although it has been recognised that this may be below stoichiometry in carbon content [18]. A close relationship exists between the two unit cells, since the removal of 50% of the interstitial atoms from the Fe_4C structure in an ordered manner produces the $Fe_{16}N_2$ structure [17]. The absence of any separate diffraction evidence for a $Fe_{16}C_2$ phase suggests that the carbon atoms may not be fully ordered in this structure. If only partial ordering of the interstitial atoms occurred, then the main diffraction observed would be that from the Fe_4C structure. However, weaker features due to the higher order structure might be observable with care. It would be of interest to investigate this point further.

Further work over a wider range of ageing times and temperatures is currently being undertaken, with the intention of fully establishing the limits of carbon concentration reached in the coherent phase, before nucleation of transition carbides occurs.

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