JOURNAL OF MATERIALS SCIENCE 14 (1979) 1961–1967

Autoradiographic evidence of carbon clustering in Fe–Ni–C martensite

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The distribution of carbon in the microstructure of the twinned martensite of Fe–23 Ni–0.4 C, has been studied by microautoradiography of radioactive carbon 14. A statistical analysis of the autoradiographs, observed in the scanning electron microscope for massive specimens or in the transmission electron microscope for thin foils, show that: (i) clustering of carbon in the twin boundaries of the martensite plates occurs rapidly by ageing at room temperature; (ii) two twinning systems may be active sites for carbon clustering in the same plate; (iii) carbon segregation seems more pronounced in twin boundaries than in martensite–martensite, martensite–austenite, or mid-rib interfaces; (iv) the precipitation of ϵ-carbide by ageing at 100 and 150° C is confirmed.

1. Introduction

Tempering of martensite has been the object of a large number of investigations. Resistivity, hardness, internal friction and Mössbauer effect measurements [1–4], have shown that the mobility of carbon is noticeable above −60° C.

Segregation of carbon atoms occurs rapidly at room temperature [4]. Moreover, Kurdjumov [2] has shown that the decomposition of the saturated solid solution of carbon in martensite with the precipitation of ϵ-carbides takes place at a slow rate at room temperature and that the introduction of nickel accelerates the decomposition process. There exists a temperature range between −60° C and + 60° C in which carbon segregation occurs on the defects of the martensite. The formation of very small clusters cannot be observed by the classical methods of X-rays or electron diffraction, but can be confirmed by indirect methods like resistivity or hardness measurements or by more specific methods like Mössbauer effect measurements [1–4]. It is thus difficult to demonstrate directly the decomposition of the supersaturated solid solution at room temperature and localization of carbon atoms during segregation processes, in the form of isolated atoms or clusters of small dimensions.

This paper reports an application of a simple method of introducing radioactive carbon into a metallic specimen [5–7] to study the localization of this element in the microstructure during tempering between 20 and 150° C with the help of high-resolution autoradiography. The technique of high-resolution microautoradiography on thin foils can, in fact, demonstrate directly very small segregations of carbon with respect to the microstructure on a very minute scale considering its sensitivity and resolution (resolution of the order of 1500 Å).

2. Material and experimental procedure

The material was an Fe–Ni–C alloy of following chemical composition*: 0.40% C, 0.48% Mn, 0.42% Si, 0.012% P, 0.30% S, 23.39% Ni. All specimens were austenitised at 1050° C in a sealed quartz capsule under argon atmosphere followed by air-cooling. Immediately after quenching to −196° C (liquid nitrogen) different heat-

*This material was kindly supplied by Professor J. Galland, Ecole Centrale, Chatenay-Malabry, for the purpose of collaborative study.

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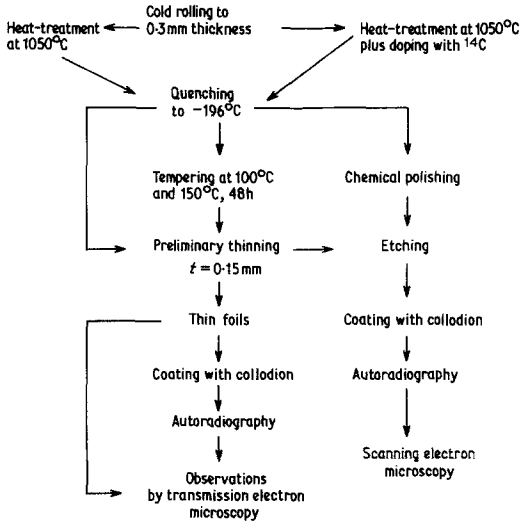

Figure 1 Experimental procedure.

treatments were carried out on the as-quenched martensite: 20 days at room temperature, 48 h at 100° C, or 48 h at 150° C.

The experimental procedure differs slightly depending on whether the autoradiographs are obtained on massive specimens (observed on SEM) or on thin foils (observed by TEM) (Fig. 1) [5, 6]. As the principle of high resolution autoradiography (autoradiography H.P.R.) has already been discussed elsewhere [5–8] we shall describe here only the experimental conditions which have been adopted.

2.1. Introduction of radioactive carbon

The specimens were charged with radioactive carbon by cementation from a gas phase with the help of radioactive barium carbonate at 1050° C during 24 h in order to obtain a homogeneous distribution of carbon [7]. Carbon 14 is a low-energy β-emitter (155 keV) with a long half-life. The amount of carbon introduced into a specimen ($\simeq$ 10 p.p.m.) was negligible in comparison with the carbon content of the alloy and did not alter the characteristics of the material. Two types of observations were carried out: scanning electron microscopy and transmission electron microscopy.

2.2. Scanning electron microscopy and autoradiography

After suitable heat-treatment the specimens were chemically polished in a bath of 6 ml distilled water, 6 ml H_2O_2 and 2 ml HF and etched in 10% Nital. Finally, a very thin collodion layer was deposited on the surface of each specimen in order to avoid chemical interation between the specimen and the photosensitive emulsion. The emulsion was then deposited in the form of a monolayer on the specimen surface, and irradiated at − 20° C for 3 days and under an atmosphere of argon to avoid any risk of oxidation, the emulsion was then developed *in situ* in a developer D 19 and fixed. It should be noted that the silver grains developed have dimensions of the order of 3000 Å. These grains appear bright under the scanning electron microscope.

2.3. Transmission electron microscopy and autoradiography

In order to detect and localize the segregation of atoms in the elementary state and on a very fine scale, a technique of obtaining autoradiographs on thin foils was developed [5]. The thin foils, obtained by using a "double jet" method (acetoperchloric bath) were coated with a thin layer of collodion and a monolayer of Ilford L4 emulsion successively. The conditions of irradiation and development of the emulsion are identical to those of massive specimens. The silver grains appear as dark images during observation by transmission electron microscopy.

3. Experimental results

3.1. As-quenched martensite

Observations on thin foils have shown that the martensite is acicular, consisting of partially twinned plates (Fig. 2). The martensite exhibits the usual feather-shaped morphology and the

Figure 2 Thin foil electron micrograph showing as-quenched structure containing plate martensite and retained austenite. Note the high dislocation density in the untransformed austenite.

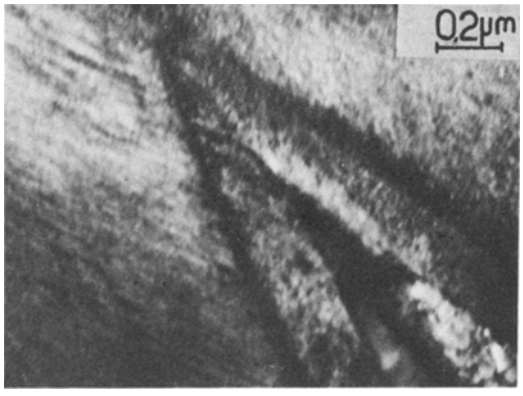

Figure 3 Thin foil electron micrograph showing as-quenched structure containing internal twins in martensite plate.

mid-rib is well defined. The zone in the vicinity of the mid-rib shows heavy twinning.

Transmission electron microscopy on thin foils has shown that the retained austenite is not free from defects and has, in fact, a very heavy density of dislocations. On the other hand, the observations by TEM of thin foils (Fig. 3) show that the martensite appears to be already aged at the moment of observation. High resolution autoradiography on massive specimens observed in a scanning electron microscope reveals that this is due to the segregation of carbon (see Section 4 and Fig. 13).

3.2. Martensite aged at room temperature

Observations by TEM show the presence of micro-precipitates on the martensite–martensite and martensite–residual austenite interfaces and on the micro-twins of the martensite. The micrograph obtained by dark-field illumination reveals these micro-precipitates. It was not, however, possible to identify these precipitates with the help of diffraction patterns (Fig. 4a to c).

Autoradiographic studies on massive specimens observed by SEM show a segregation of carbon in the grain boundaries and the matrix of the martensite plates (Fig. 5). In the case of thin foil autoradiography, statistical observations at high magnification show a tendency of the silver filaments to be aligned along the micro-twins (Fig. 6). As this tendency is not evident from a simple observation, and in order to detect such an alignment with precision, a statistical analysis of the distribution of silver filaments on an autoradiographic image was carried out (Fig. 7). The method consists in measuring on the electron micrographs the number of alignments of silver grains per unit length; an alignment is defined by the presence of at least three silver filaments on straight segments having a suitable length fixed arbitrarily ($\simeq 4\,\mu m$). The number of alignments per unit length is plotted as a function of the angle of the direction of analysis with respect to the reference direction (Fig. 7); in the present case, the refer-

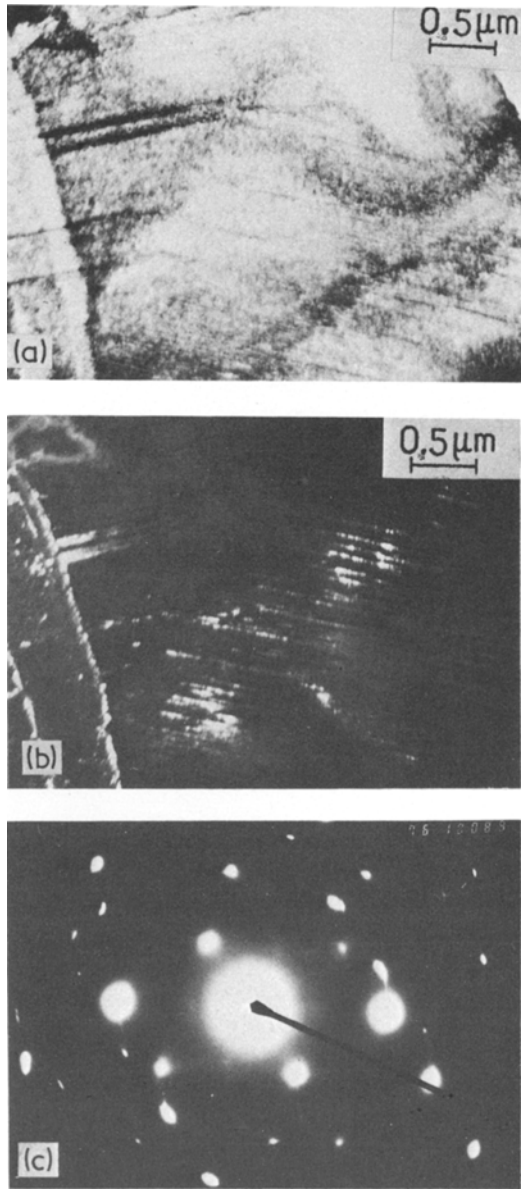

Figure 4 Thin foil electron micrograph showing precipitates at interfaces regions and twins regions: (a) bright field, (b) dark field, (c) diffraction pattern. Sample aged 20 days at room temperature.

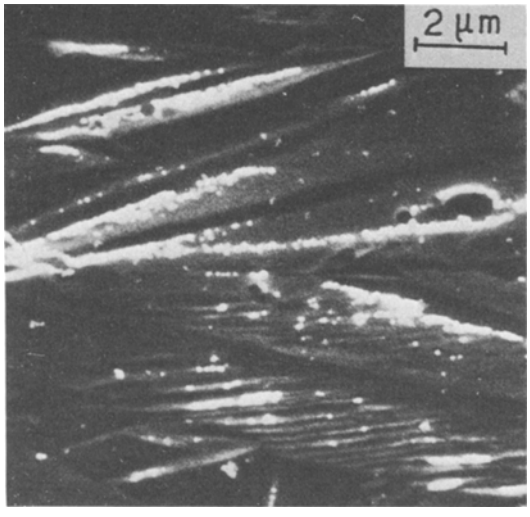

Figure 5 Observation of carbon segregation by ^{14}C autoradiography (SEM) in martensite aged 20 days at room temperature. The bright dots are the silver grains of the autoradiograph.

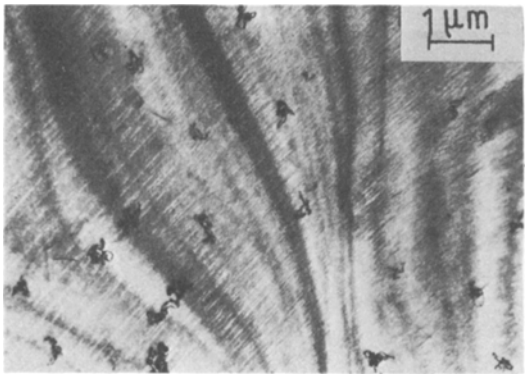

Figure 6 Observation of carbon segregation by high-resolution autoradiography (TEM) in martensite aged 20 days at room temperature. The dark filaments are the silver grains of the autoradiograph.

ence is chosen at an angle of 90° to the trace of the plane of twin of the micrograph.

A significant tendency for alignment is observed along directions parallel to the micro-twins ($\theta = 90°$ in Fig. 7). Alignments are also observed in another direction ($\theta = 55°$ in Fig. 7) which may correspond to another twinning system (see below). Finally, alignments perpendicular to the two previous directions are also observed with a smaller probability (Fig. 7).

3.3. Martensite tempered at 100 and 150° C

Observations by TEM reveal the presence of precipitation on the interfaces and particularly on

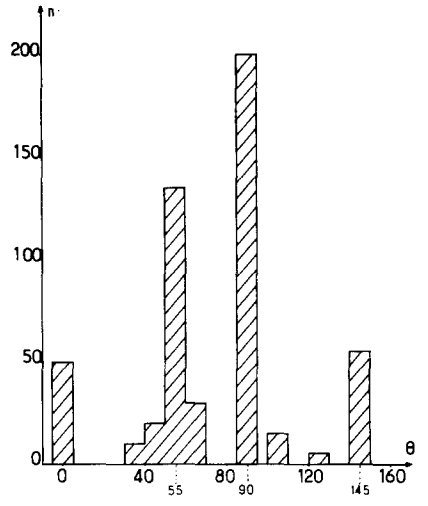

Figure 7 Statistical distribution of the silver grain alignments in the autoradiographs. An alignment is defined as a group of three or more silver grains aligned in a given direction. n = number of silver grains per unit length in the alignments, θ = angle of the alignments with a reference direction (the reference direction is normal to the visible twinning direction).

the micro-twins of the martensite (Fig. 8). Two directions of precipitation can be observed within the plates (Fig. 9). The electron diffraction patterns have shown that these precipitates are ϵ-carbides ($Fe_{2,3}C$) [10] having a hexagonal structure. On the other hand, the high-resolution autoradiographs on massive specimens also show the presence of carbon precipitation in these sites (Fig. 10).

4. Interpretation

Experimental evidence demonstrates that the martensite can evolve at room temperature or even at

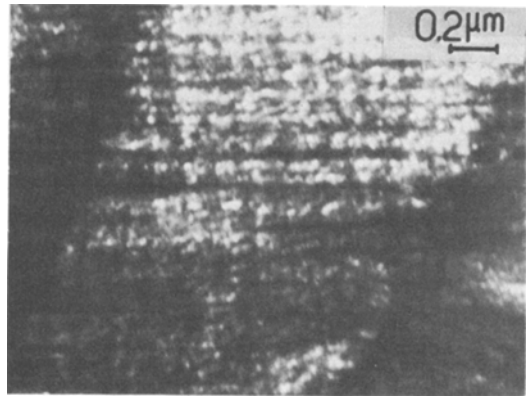

Figure 8 Transmission electron micrograph of ϵ-carbide and fine twins in martensite plate tempered 48 h at 100° C.

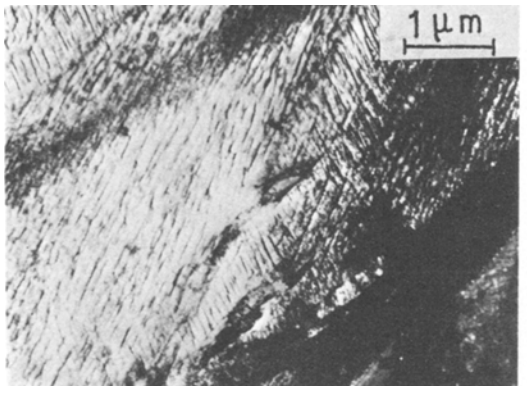

Figure 9 Transmission electron micrograph of ϵ-carbide and fine twins in martensite plate tempered 48 h at 150° C.

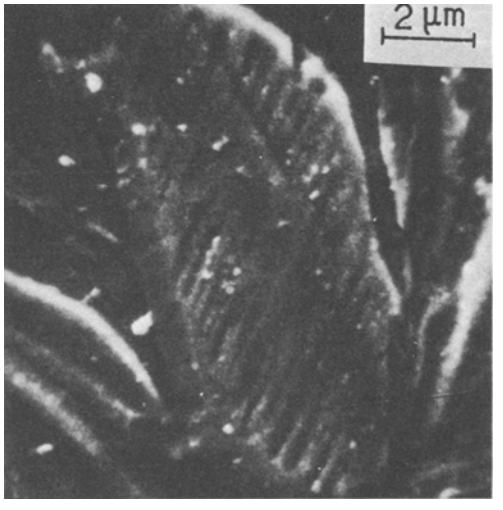

Figure 10 Observation of carbon segregations by ^{14}C autoradiography (SEM) in martensite plate tempered 48 h at 150° C.

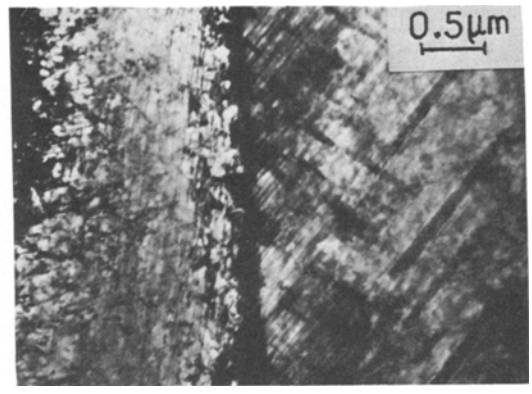

Figure 11 Transmission electron micrograph of Fe–33% Ni alloys showing two directions of internal twin, in martensite plate (as-quenched structure at 77 K).

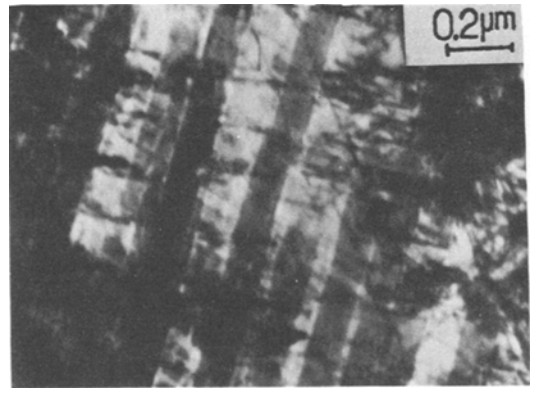

Figure 12 Transmission electron micrograph in Fe–33% Ni alloy showing dislocations lines in the twinned structure (as-quenched structure at 77 K).

much lower temperatures [3, 4]. Winchell and Cohen [3] have used Fe–Ni–C alloys and have demonstrated an increase in resistivity attributed to the first steps of precipitation of carbide which is, in fact, observed at higher temperature. Secondly, Genin [4] in the investigations carried out by Mössbauer spectroscopy in the Fe–C alloys has demonstrated the formation of clusters of carbon atoms and their rearrangement into nucleii of ϵ-carbides. The ϵ-carbide $Fe_{2.3}C$ [9, 10] with an h c p structure, precipitates preferentially on the micro-twins of the martensite [11]. Moreover, Hale and McLean [12] have found precipitates of ϵ-carbide in the Fe–C alloys (0.005% C) at room temperature. As far as we know, this phenomenon has never been observed in Fe–Ni–C alloys (twinned martensite).

From the results of high resolution autoradiography of martensite aged for 20 days at room temperature there is preferential clustering of carbon atoms in the micro-twins of the martensite, i.e. in the $(1\,1\,2)_{\alpha'}$ planes ($\theta = 90°$ in Fig. 7). Matauer and Schissler [13] have found in an Fe–Ni–C alloy (twinned martensite) the coexistence of two twinning systems $(1\,1\,2)_{\alpha'}$ and $(0\,1\,1)_{\alpha'}$, in the region near the mid-rib. In a complementary study of an Fe–33% Ni (40 p.p.m. C) alloy with a martensite structure similar to the Fe–Ni–C of the present study, but easier to resolve on the electron microscope scale, two twinning directions have been evidenced (Fig. 11). Furthermore, the microstructure of the Fe–Ni alloy contains dislocation lines pinned perpendicular to the twin planes (Fig. 12). As the structures of the two alloys are of the same type, the

second direction of carbon segregation ($\theta = 55°$ in Fig. 7) observed on autoradiographs can be associated with this second system of twinning $(0\,1\,1)_{\alpha'}$ plane. Similarly, the reported alignments perpendicular to both principal directions ($\theta = 0°$ and $\theta = 145°$, Fig. 7) could correspond to a preferential localization of carbon segregated on the dislocations; the usual direction of the dislocation lines is indeed perpendicular to the twinning planes of the martensite (Fig. 12).

A detailed analysis of the micrographs shows, in fact, that many of the silver grains corresponding to alignment $\theta = 0°$ also belong to alignments $\theta = 90°$. It may be assumed that, due to the energy stabilization requirements, the dislocations adopt such a configuration that they are in prolongation with one another, passing from one micro-twin to the next.

The autoradiographic technique is not adapted to the investigation of as-quenched martensite, as the time necessary for the preparation of thin foils and the autoradiographic exposure is long (of the order of 10 days) which leads to the ageing of the structure at room temperature. This inconvenience can be reduced by adopting massive specimens (total time for obtaining autoradiographs reduced to about 2 days) without, however, completely eliminating the possibility of appreciable ageing of the microstructure. In these conditions, we have observed in the as-quenched martensite (aged 24 h before application of autoradiographs) a segregation of carbon on the interfaces and within the needles, (Fig. 13). It is not, however, possible to define its exact localization in the needles, for the fine structure cannot be revealed with this technique.

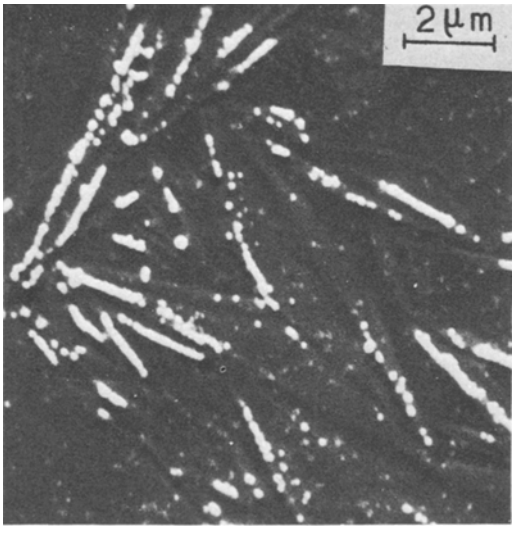

Figure 13 Observation of carbon segregation by ^{14}C autoradiography (SEM) in martensite plate aged for 24 h at room temperature.

In the case of specimens tempered at 100 and 150° C, ϵ-carbide precipitation was observed on both twinning systems, i.e. the $(1\,1\,2)_{\alpha'}$ and $(1\,1\,0)_{\alpha'}$ planes.

5. Conclusions

Segregation or clustering of carbon atoms in micro twins i.e. along the $(1\,1\,2)_{\alpha'}$ and $(1\,1\,0)_{\alpha'}$ planes, of martensite aged at room temperature has been demonstrated directly with the help of autoradiographs on thin foils. Segregation was also observed on the martensite–martensite and martensite–residual austenite interfaces. The clustering appeared to be more prominent on the micro-twins. Although it was not possible to identify directly the clustering using electron diffraction studies, when considering the earlier results, carbon seems to be present in the form of ϵ-carbide or nucleii of such a phase. It was later observed that in as-quenched martensite, the carbon segregates on the martensite interfaces and within the martensite plates. Finally, in specimens tempered at 100 and 150° C, the presence of precipitation of ϵ-carbide in the micro-twins of martensite has been confirmed.

Acknowledgements

The authors would like to thank International Atomic Energy Agency, French Gouvernment and Comision Nacional de Energia Atomica Argentina, for support of one of the authors (J.O.G.).

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Received 15 November and accepted 23 November 1978.