

Investigation of low temperature diffusion of carbon in martensite by Mössbauer spectroscopy and X-ray diffraction

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Abstract Martensite containing 0.87 wt.% carbon was studied by Mössbauer spectroscopy at temperatures, $T = 10, 15, 25, 40$ and 78 K and by X-ray diffraction at $T = 78$ K in the course of 35 days. Samples in the form of $30 \mu\text{m}$ thick foil of pure carbon martensite with enhanced tetragonality were synthesized applying non-standard technology. The measured by X-rays ($c/a - 1$) ratio varies within the limits $0.044\text{--}0.055$ by pulsations with a period of few hours. According to Kurdimov's model any changes in tetragonality of martensite are fully related to the passage of carbon atoms from O_c to O_a and O_b octahedral sites or *vice versa*. Pulsations of the central and satellite sextets were observed by Mössbauer spectroscopy. In accordance with the conventional interpretation of satellites, these pulsations result from different spatial distribution of carbon around the Fe atoms in the diffusion process. The data of ($c/a - 1$) pulsations were used to determine the diffusion coefficient below 78 K. The measured diffusion coefficient of carbon in α -iron below 78 K contradicts the classical approach to the observed temperature dependence. As the temperature is lowered below 78 K, the diffusion constant approaches the nearly temperature-independent value. The low temperature branch is apparently characteristic of a quantum mechanical process dominated by tunnelling in the ground state.

Key words martensite • diffusion coefficients • Mössbauer spectroscopy • X-ray studies

Introduction

According to the Kurdimov's model [13], carbon atoms occupy octahedral sites O_a ($1/200$), O_b ($01/20$) and O_c ($001/2$) in the α -martensite lattice with preference to occupy O_c interstitial positions. From detailed calculations [10], it follows that the tetrahedral sites can be occupied only temporarily during the diffusion of carbon atoms between octahedral sites. The inequality occupation of the O_c sublattice in relation to O_a and O_b is the cause of tetragonality. According to the well-known empirical facts, the tetragonality increases linearly with the carbon concentration in the solution. However, the tetragonality also depends on the long-range order parameter η , [2, 13], which determines the carbon concentration in different sublattices: O_a , O_b and O_c . It was found by neutron diffraction that only 80% of the carbon atoms are situated in O_c sublattice, while the remaining 20% are distributed in O_a and O_b sublattices [7]. Following the definition of long-range order parameter η given elsewhere [13], as being $\eta = 0.7$. If all carbon atoms are in O_c sublattice, the martensite tetragonality will be considerably higher and η should be equal to 1. Using for calculation the formula given by Dąbrowski [2], the tetragonality should be about 45%. Such value is inherent to martensite with anomalous tetragonality [11]. For pure Fe-C martensite such high tetragonality is impossible. If some of the atoms of the iron matrix are replaced, for example by

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nickel atoms, the martensite phase will exhibit an anomalously high tetragonality.

In a study of Fe-Ni-C system [14], Pietrzyk and Kruk conclude that the interaction potentials between nickel and carbon are attractive and, as a consequence, the carbon atoms form a group around the nickel. This means that carbon atoms are bonded to nickel atoms, thus hampering the diffusion of carbon between O_c and O_a and O_b martensite sublattices. In this case all or almost all carbon atoms are left in the O_c sublattice ($\eta = 1$) and the tetragonality attains maximum value.

In pure Fe-C system, some of the carbon atoms, situated in O_c sublattice at the beginning of martensite transformation, proceed to O_b or O_a sublattices during the quenching process. Hence, if the cooling process is shortened, an anomalous or enhanced tetragonality of pure Fe-C martensite could be obtained. Therefore, a special technology was used in this work, to guarantee a considerable shortening of the quenching time.

Only isolated, non-clustered, carbon atoms take place in the diffusion process. In as-quenched martensite containing 9.5 at.% C, the fraction of separate carbon atoms determined experimentally by Mössbauer spectroscopy (MS), drops from 50% for as-quenched martensite to about 20% after aging at room temperature for 12 days and then remains at this level [8]. The theoretical investigation [3] shows that the influence of isolated C-atoms on the change of tetragonality in our case can be neglected.

It was observed [4] by MS and X-ray diffraction studies of a martensitic alloy subjected to thermal shock, that the process of tetragonality variation is not monotonous when heating from 78 K to room temperature. X-ray measurements show that the pulsations of $(c/a - 1)$ ratio (tetragonality) with a period of several hours are characteristic of this rearrangement. From the data of MS study, it was observed that the satellite sextets demonstrate analogous pulsations. According to the conventional interpretation of the intensity of satellites line [6, 9], these pulsations result from the different spatial distribution of carbon atoms in the neighbourhood of Fe atoms. Hence, the variation of the satellite intensities undoubtedly proves that the local arrangement of carbon atoms is changing.

Experimental

Samples for X-ray measurements, containing 0.87 wt.% C, were prepared from pure ARMCO iron in the form of 30 μm thick foil. They were sealed in an evacuated quartz tube, heated up to 950°C and quenched in aqueous solution of NaCl. After breaking the tube, the water, which was at atmospheric pressure, very quickly came into contact with the sample placed in vacuum. Immediately after cooling, the samples were immersed in liquid nitrogen. The intensities of $\langle 112 \rangle$ and $\langle 121+211 \rangle$ peaks were measured by X-ray diffraction. The measurements were carried out after increasing intervals of storage at liquid nitrogen temperature. The duration of each measurement was 20 min. Each sample was subjected to ten successive measurements. The same procedure was repeated six times with new

samples, immersed in liquid nitrogen in the interval of 35 days.

The sample for MS measurements was prepared by the same technology. A series of conventional measurements was carried out at constant external conditions. The duration of each sextet measurement was 30 min and the experiments at the same temperature were repeated in time interval from 50 to 100 h. The temperature, from the starting value of 78 K was step-like changed to 40, 25, 15 and 10 K. Simultaneously, the calibration spectrum was recorded using ARMCO absorber for each measurement. This permanent calibration excluded the influence of any uncontrollable apparatus instability. The numerical analysis reveals the presence of 2.9 at.% retained austenite, whereas carbide phases have not been detected.

Results

X-ray results

Successive $(c/a - 1)$ ratio pulsations, irregular in amplitude and period (of the order of few hours) were recorded. Their characteristics are identical with those, first observed by us for $(c/a - 1)$ ratio pulsations in martensite [4].

The observed variations of tetragonality are presented in Figs. 1 and 2. Their amplitudes are placed in the space between 'a' and 'b' curves in Fig. 2.

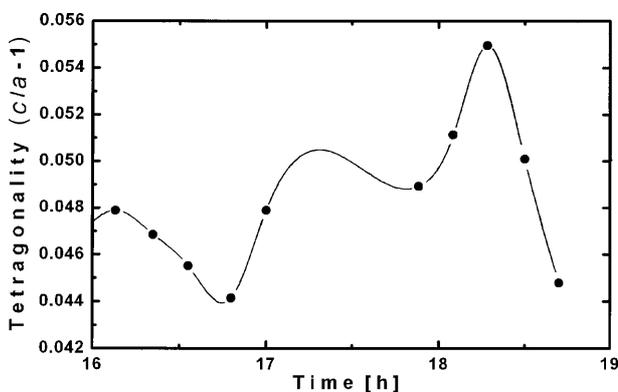


Fig. 1. Time dependence of tetragonality.

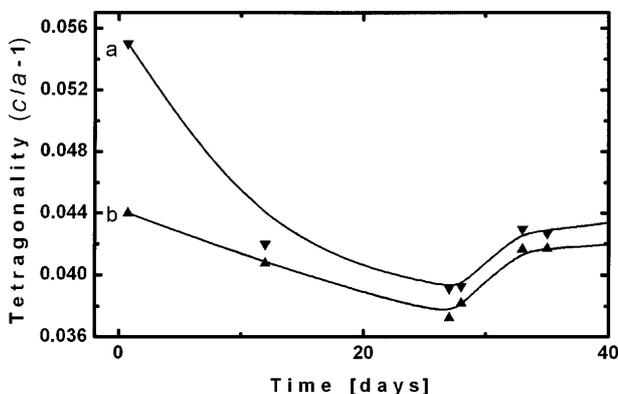


Fig. 2. Variation of maximal and minimal martensite tetragonality as a function of time: a – maximum; b – minimum of tetragonality registered by $(c/a - 1)$ pulsation effect.

A characteristic feature is the minimum observed in the interval 20–33 days after the storage of samples in liquid nitrogen.

A new effect is the increase of tetragonality during the aging at low temperature. This effect is most evident for the samples aged for a long time, e.g. more than 4 weeks at the liquid nitrogen temperature.

Mössbauer spectroscopy results

In the conditions described above we observed changes in the martensite phase, manifested by a change of the form of the spectral lines. Variations in carbon ordering affect reflected by the intensity of satellite sextets, lead to the effective broadening of the obtained spectral lines with accompanying reduction of the intensity or *vice versa*.

The dependence of amplitude of central sextet lines of the martensite vs. the time for different temperatures is presented in Fig. 3. Characteristic pulsations like that observed in [4] were recorded. An analysis of experimental error, taking into account both, statistical errors and possible spectrometer instability, results in a factor of data reliability in the range 10–20.

Comparison of X-ray and Mössbauer spectroscopy results

Two different experimental methods used in the present study reflect different aspects of the same physical process of C-microdiffusion in Fe-C samples. Interpretation of $(c/a - 1)$ pulsations observed by X-ray technique is obvious. The tetragonality pulsations are due to the migration of C atoms from O_c to O_a and O_b sites; and their returning to O_c sublattice. From the determined value of $(c/a - 1)$ ratio, the fraction of migrating C-atoms can be evaluated. In our case this fraction amounts to about 10% of total number. The observed phenomenon is difficult to be explained in other way than by the change of the local surrounding of iron atoms, situated in the nearest neighbourhood to the carbon atom; which is impossible without microdiffusion processes. The interpretation of MS data is very complicated and ambiguous, since the obtained spectra reflect the state of Fe nuclei and only indirectly – the location of C-atoms. Therefore, we can obtain the required information by comparison of tetragonality $(c/a - 1)$ pulsation with analogous pulsation of the Mössbauer sextet at 78 K.

Both experimental techniques provide comparable results. X-ray experiments at 78 K showed the pulsations with a very slow decrease of amplitude for quite a long period. After a period of 35 days they are still present. Another effect is the decrease of pulsations frequency with the decrease of temperature. Pulsations represented in Figs. 1 and 3 show a stochastic character. As their Fourier analysis shows [1], they exhibit a multi-wave character. Obviously, shortest-waves modes, are connected with a one-particle process. These modes were used to determine diffusion velocity. For better accuracy in determination of the amplitude and

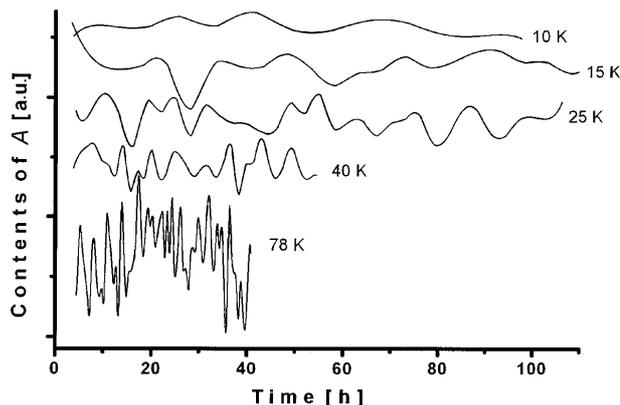


Fig. 3. Contribution A of central line in MS spectrum as a function of time at various temperatures.

frequency of the modes, we applied least squares method description of the curves, represented in Fig. 3, using Fourier modes for different periods. This fact we used for a numerical determination of the diffusion coefficient in the temperature range from 10 to 78 K. For the temperatures 10, 15, 25, 40 and 78 K, we obtained the diffusion coefficients D , equal to 6.15×10^{-25} , 7.135×10^{-25} , 1.37×10^{-24} , 2.635×10^{-24} and $5.9 \times 10^{-24} \text{ cm}^2 \cdot \text{s}^{-1}$, respectively.

Using the above experimental values of D and consolidating them with the literature data for the Arrhenius law, we obtained the dependence of D coefficient in the temperature range from 10 to 1100 K, represented in Fig. 4. As it is seen, when the temperature is lowered below 78 K, the plot diffusion constant bends to a nearly temperature-independent value rather than continuing its activated trend. It questions the classical approach to the observed temperature dependence.

Discussion

Assuming that carbon atoms occupy octahedral lattice sites, the components of the concentration expansion tensor are associated with the martensite lattice parameters by the following relations, [2]:

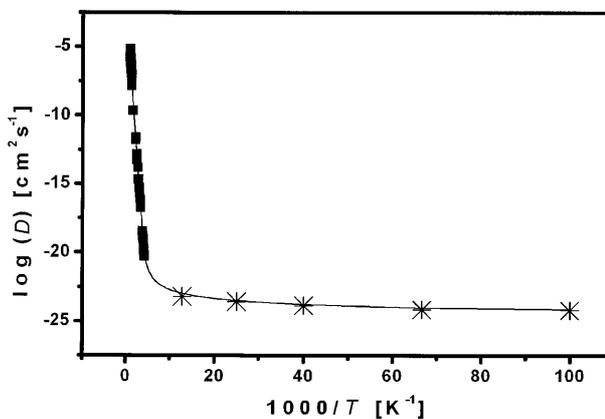


Fig. 4. Temperature dependence of the diffusion coefficient of carbon in α -iron.

$$(1a) \quad a = b = a_0(1 + \alpha n/3 - \beta \eta n/3)$$

$$(1b) \quad c = a_0(1 + \alpha n/3 + 2\beta \eta n/3)$$

where a , b , c are the lattice parameters of martensite unit cell, a_0 is the lattice parameter of α -Fe, n is the atomic concentration of carbon, η is the long-range order parameter, $\alpha = 2U_{11} + U_{33} = 1.02$, $\beta = U_{33} - U_{11} = 1.845$ [3], U_{11} and U_{33} are components of the concentration expansion tensor.

Applying the above equations to the experimentally observed $(c/a - 1)$ ratio, the value of η in the range of 0.8–0.94 is obtained. At $\eta = 0.94$, about 96% of carbon atoms are in O_c sublattice and only 4% in O_a and O_b . These values differ essentially from the quantities characteristic of martensite with normal tetragonality, namely 80% and 20%.

The pulsation mechanism could be explained as follows. In order to reach the energy minimum of the crystal structure, there exists a tendency for free carbon atoms located in the O_c sublattice to form clusters, which is advantageous from the internal energy point of view. Hence, independently of the final position, each carbon atom migrates first to O_a or O_b sublattices (this is the shortest and most probable way of microdiffusion). Consequently, the martensite tetragonality decreases. Because some of the carbon atoms return to the O_c in order to form clusters, the $(c/a - 1)$ value increases. Such a mechanism of carbon migration could explain the $(c/a - 1)$ ratio variation.

It is noteworthy mentioning that pulsations were registered in the same samples also at high temperatures in the region of $\alpha \Rightarrow \kappa$ martensite phase transition, [5]. An analogous effect was observed in the Pd-W-H system [12]. Katsnelson *et al.* have proposed another hypothesis to explain this fact by collective coherent microdiffusion, which include a large number of interstitial atoms. The concentration microgradient of interstitial atoms as well as long-range interactions are present in both systems; therefore, such an alternative for the processes in Fe-C martensite cannot be excluded *a priori*. The simultaneous action of both mechanisms is also realistic, i.e. the collective parameters will be superimposed on the individual motion. To make the final choice, additional investigations are needed.

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