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Study of low-temperature redistribution of carbon interstitials in martensite

L. DABROWSKI
Institute of Atomic Energy, 05-400 Otwock-Swierk, Poland
E-mail: dab@cx1.cyt.gov.pl

S. NEOV
Institute for Nuclear Research and Nuclear Energy, Tzarigradsko chaussee 72, 1784-Sofia, Bulgaria.

Martensite containing 0.87 wt% carbon was studied by X-ray diffraction at 100 K. A sample of pure carbon martensite with enhanced tetragonality was synthesized applying non-standard technology. The measured *c/a* ratio was varied in the limits from 1.044–1.055 by pulsations with a period of a few hours. The highest value of tetragonality was about 35% greater than normal, and thus it approaches the anomalous value. Pure carbon martensite with such a high tetragonality has not been observed up to now. An explanation of the enhanced tetragonality and its time pulsations has been given on the basis of Kurdiumov's model. © *1998 Kluwer Academic Publishers*

1. Introduction

According to the Kurdiumov's model [1], carbon atoms occupy octahedral sites O_a $(1/2, 0, 0)$, O_b $(0, 1/2, 0)$ and O_c $(0, 0, 1/2)$ in the α-martensite lattice with a preference to fill O_c interstitial positions. From the calculations [2], it follows that the tetrahedral sites can be occupied only temporarily during the diffusion of carbon atoms between octahedral sites. The inequality of the O_c sublattice in relation to O_a and O_b is the cause of tetragonality. According to the well-known empirical law, the tetragonality increases linearly with the carbon concentration in the solution. However, the tetragonality also depends on the long-range order parameter, η [1, 3], which determines the carbon concentration in different sublattices: O_a, O_b, and O_c. It was found by the neutron diffraction method that only 80% of the carbon atoms are situated in the O_c sublattice, while the remaining 20% are distributed in O_a and O_b sublattices [4]. Following the definition of the long-range order parameter given elsewhere [1], we obtain $\eta = 0.7$. If all carbon atoms are in the O_c sublattice, the martensite tetragonality will be considerably higher and η would be equal to 1. Using for calculation the formulae given by Dabrowski [3], the tetragonality must increase by about 45%. Such a value is inherent to martensite with anomalous tetragonality [5]. For pure Fe–C martensite, it is not possible to obtain such a high tetragonality. When some of the atoms of the iron matrix are replaced, for example by nickel atoms, the martensite phase will possess an anomalously high tetragonality. The model proposed by Kurdiumov [1] gives a numerical description of this phenomenon. On the other hand, it is not able to explain why at the substitution of iron by nickel, all or almost all carbon atoms remain in the O_c sublattice and whether it will be possible to obtain an anomalous tetragonality in pure carbon martensite.

In a study of the Fe–Ni–C system [6], Pretrzyk 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 linked with the atoms of nickel, 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 remain in the O_c sublattice ($\eta = 1$) and the tetragonality is maximal. This is one of the alternative interpretations of the experimental data.

Bearing in mind the above considerations, we discuss the following thesis: in the pure Fe–C system, some of the carbon atoms, situated in the O_c sublattice at the beginning of the martensite transformation, go to the other 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 which guarantees a considerable shortening of the quenching time.

2. Experimental procedure

The sample for X-ray measurements, containing 0.87 wt % C, was prepared from pure Armco iron in the form of 30 μm thick foil. It was sealed in an evacuated, quartz ampoule heated up to 950 °C and quenched in an aqueous solution of NaCl. After breaking the ampoule, the water, which was at atmospheric pressure, very quickly comes into contact with the sample placed in a vacuum. Immediately after

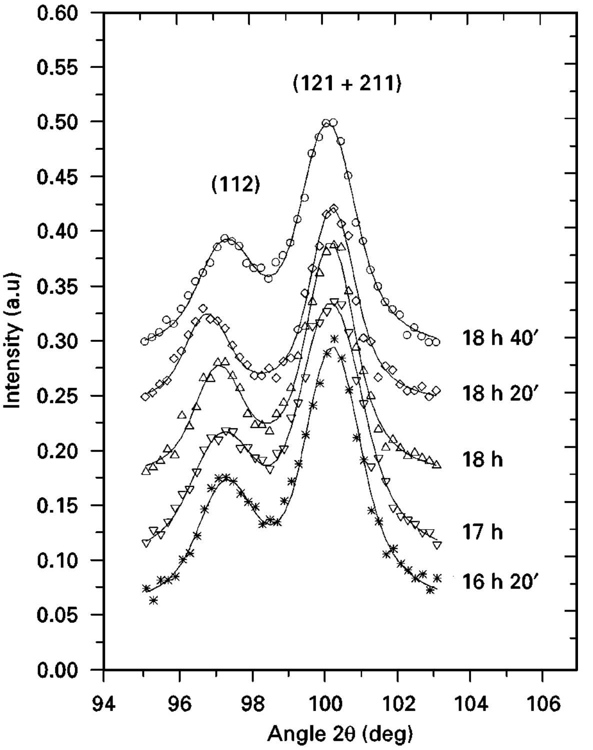

Figure 1 X-ray doublet intensity measured at $T = 100\,\mathrm{K}$ as a function of time after quenching.

cooling, the sample was immersed in liquid nitrogen for 10 min.

After removing from the liquid nitrogen, it was subjected to 10 successive X-ray measurements of (1 1 2) reflex by a CoK_α source, $\lambda = 0.178\,89$ nm and SiO_2 monochromator for K_β. The duration of each measurement was 20 min. At the end of the experiment, the sample was again immersed in liquid nitrogen. The same procedure was repeated every day for 4 day. Successive c/a ratio pulsations, irregular in amplitude and period (of the order of a few hours) were registered. Their characteristics are identical to those first observed by us for c/a ratio pulsations in martensite [7]. Five typical spectra, measured in a time sequence 16 h 20 min, 17 h, 18 h 20 min and 18 h 40 min after quenching, are presented in Fig. 1. The corresponding c/a ratios deduced from them are 1.046, 1.047, 1.048, 1.055 and 1.044.

Two well-expressed effects were registered on the experimental spectra, shown in Fig. 1: the first is the enhanced tetragonality of the martensite and the second is the characteristic time pulsations of the c/a ratio. From the observed spectra, it follows that the values of $(c/a - 1)$ are 10%–35% higher in comparison with the same expression for martensite with normal tetragonality. They are very close to the value for martensite with anomalous tetragonality, which is about 45% higher than the normal one.

3. Discussion

Assuming that carbon atoms occupy octahedral lattice sites, the components of the concentration expansion tensor are associated with the martensite lattice parameters by following relations [3]

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

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

where a, b, c are the lattice parameters of martensite, a_0 is the lattice parameter of α–Fe, n is the atomic concentration of carbon, η 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 ratio, we obtain a value of η in the limits 0.8–0.94. At $\eta = 0.94$, about 96% carbon atoms are in the O_c sublattice and only 4% in O_a and O_b. These values differ essentially from the analogous ones inherent to the martensite with normal tetragonality, namely 80% and 20%, respectively.

Unlike the study of diffusion kinetics [8, 9] which reveals an exponential process approaching the thermodynamic equilibrium in carbon martensite, our Mössbauer spectroscopy and X-ray diffraction investigations [7] show a distinct oscillatory course. These structure pulsations have been observed in samples prepared from pure Armco iron in the form of 30 μm thick foil. After gas carbonization, quenching in water and then in liquid nitrogen, the samples containing 0.87 wt% C were aged at room temperature for a period of 4 months. Prior to the measurements, they were immersed in liquid nitrogen for 3 wk. Immediately before the measurements, a thermal shock was applied to the samples by raising the temperature from 78 K to 300 K for 30 min. The oscillations were registered at fixed temperatures of 100, 200 and 300 K. Similar pulsations have been observed in the same samples at high temperatures in the region of $\alpha \rightarrow \kappa$ martensite phase transition [10].

The observed pulsations have the same characteristics as those reported elsewhere [7] but their amplitude is much higher. This is not surprising because in this case the samples investigated contain freshly quenched martensite, i.e. the system is very far from the equilibrium state, much more than in the previous case. The pulsation mechanism could be explained as follows. In order to reach the crystal structure energy minimum, there is 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), thus the martensite tetragonality decreases. Because some of the carbon atoms return to the O_c in order to form clusters, the c/a value increases. Such a mechanism of carbon migration could explain the c/a ratio pulsations [7].

Analogous pulsations were observed in the Pd–W–H system [11]. Katznelson *et al.* proposed another hypothesis ot explain this fact by the collective coherent effects of the micro-diffusion 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 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.

4. Conclusion

On the basis of X-ray experiments, the following conclusion can be drawn. By rapid quenching (much faster than the critical value), a martensite with enhanced tetragonality has been synthesized. According to the calculations carried out, the long-range order parameter, η, can exceed the normal value of 0.7, and reach 0.94. In this case, the number of carbon atoms passing from the O_c sublattice to O_a and O_b is five times less. The course of this process is not uniform, and is accompanied by a time pulsation with a period of a few hours at a temperature of 100 K.

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