Q^{-1} spectra connected with C under solute atom interaction

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Abstract

Internal friction, dynamic modulus (M_d), microhardness measurements and X-ray diffraction analyses have been used to study the characteristics of C–Cr associates in 11% Cr martensitic steel MANET.

On the basis of a preferential bond between C and Cr atoms, we discuss a statistical model which may explain the formation and stability of C–Cr associates for $T < T_C$ and their dissolution for $T > T_C$. The model is illustrated by snapshots obtained by Monte Carlo simulations. Q^{-1} results show that the temperature T_c, critical for associate stability, is about 1450 K. The characteristics of C–Cr associates in as-quenched material depend on cooling rate: with slower rates it was found that diffusive motions of solute atoms take place for $T > 1270$ K playing a fundamental role on martensitic transformation.

1. Introduction

Segregation and precipitation in Fe–Cr alloys have been widely studied for their consequences on mechanical properties, in particular, the ductile-to-brittle transition, and on swelling resistance during radiation damage. Deviations from the random distribution of solute Cr atoms have been examined by Mössbauer spectroscopy [1, 2], small angle neutron scattering (SANS) [3, 4], internal friction (IF) measurements [5, 6] and have been observed directly by field ion microscopy [7, 8].

IF experiments made by us [9–11] on the 11% Cr martensitic steel MANET showed that C–nCr associates are present in the as-quenched material. Different types of associates correspond to a different number n of Cr atoms (from 0 to 6), which occupy the corners of the octahedron around a C atom, and are characterized by different binding energies for the C atom. As discussed in ref. 9, IF spectra can be considered as the sum of seven Snoek-type peaks with relaxation strengths Δ_n depending on the distribution of C–Cr associates.

It was found that the characteristics of C–nCr associates present in MANET steel after quenching and their evolution after thermal treatments depend on the cooling rate from the austenitization temperature T_a. C–Cr associates form in an austenitic field and are then inherited by a martensitic structure if diffusion processes have no time to produce, during slow cooling, a transformation of these structures. The role played by C–Cr associates in martensitic transformation and

specific mechanisms have been discussed in another paper [12].

The aim of the present work is to determine the temperature range where diffusive processes are effective and cause the occurrence of different structures in samples cooled at different rates. Another problem is to find out the temperature limit T_C above which the C–Cr associates are not stable and dissolve.

2. Experimental details

The chemical composition of the investigated Cr martensitic steel (MANET) is: C 0.17, Cr 10.5, Mo 0.50, Ni 0.85, Mn 0.60, Nb 0.20, V 0.25, Si 0.32, Al 0.05, N 0.003, P 0.005 and Fe to balance (wt.%). Before quenching, all the samples underwent thermal treatment at high temperature for 1800 s: a batch of MANET steel was heated at 1348 K (γ field) whereas another batch was heated at 1473 K ($\alpha + \gamma$ field). After high T treatments, MANET samples were quenched at different cooling rates (from 150 to 3600 K min^{-1}).

Experiments were also carried out on samples cooled with T profiles characterized by two different cooling rates: $\dot{T} = 150$ K min^{-1} from the austenitization temperature $T_a = 1348$ K to T_X and then $\dot{T} = 3600$ K min^{-1} from T_X to M_S with 1000 K $\leqslant T_X \leqslant 1300$ K.

IF tests were made using the method of frequency modulation in the range of temperatures from 300 to 773 K with nearly constant heating rate (2 K min^{-1}). The IF coefficient Q^{-1} was determined from the logarithmic decay of flexural vibrations with resonance frequency $f \approx 250$ Hz. The strain amplitude was kept below 1×10^{-6}.

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The MANET steel microstructure was also investigated by microhardness tests and X-ray diffraction (XRD) analysis. XRD spectra were recorded using MoKα radiation; precision line profiles were obtained by step-scanning with 2θ intervals of $0.005°$ and counting times of 20 s for each step.

3. Results

Figure 1 shows Q^{-1} and M_d/M_0 curves of MANET samples quenched from the γ field ($T_a = 1348$ K) with different cooling rates: $\dot{T} = 3600$ K min^{-1} (a) and $\dot{T} = 150$ K min^{-1} (b). In both IF spectra the highest peaks are those at high T corresponding to C–4Cr for the faster cooling rate (a) and to C–4Cr and C–6Cr for the slower one (b). The dynamic modulus shows decrements corresponding to the observed Q_n^{-1} peaks with the attribution of distinct relaxation times to each peak. The markers on the figure top indicate the position of Q_n^{-1} peaks for n varying from 0 to 6 in the case of $f = 250$ Hz and activation energies H_n calculated using the model of Sarrak and co-workers [5, 6] as explained in detail later on (see eqn. (1)).

To find the T range where diffusive processes take place causing the occurrence of different structures in samples cooled with different rate, we have investigated the behaviour of samples cooled with T profiles such as that in the sketch of Fig. 2. The cooling rate is $\dot{T} = 150$ K min^{-1} from T_a to T_X and then $\dot{T} = 3600$ K min^{-1} from T_X to M_S (645 K).

Fig. 2. XRD results of MANET samples cooled from 1348 K to T_X with $\dot{T} = 150$ K min^{-1} and then from T_X to M_S with $\dot{T} = 3600$ K min^{-1} as shown in the sketch. Half-height widths β of {110} XRD lines and ratios between {110} and {211} line intensities, which indicate texture variations, are plotted vs. T_X.
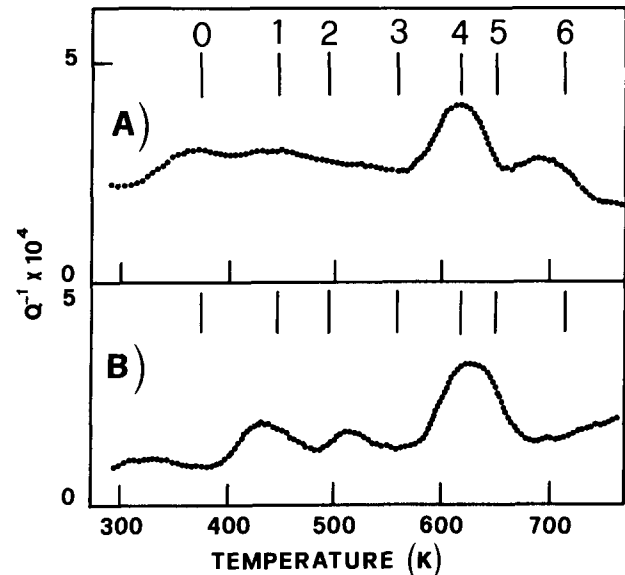
Fig. 3. Q^{-1} curves of MANET steel samples cooled from 1348 K with T profiles sketched in Fig. 2 with $T_X = 1073$ K (A) and $T_X = 1173$ K (B).

The results of XRD analysis on MANET samples cooled with values of T_X varying from 1000 to 1348 K show that significant variations take place only for $T_X > 1270$ K, whereas when $T_X < 1270$ K the values of β_{110} (half-height line width) and of I_{110}/I_{211} (ratio between the reflexion intensities) are nearly constant. Some Q^{-1} spectra of samples, which underwent this particular quenching, are shown in Figs. 3(a) and (b) with T_X equal to 1073 and 1173 K respectively.

To determine the temperature T_C, above which C–Cr associates are not more stable and dissolve, we have carried out tests on samples fast-quenched from temperatures higher than $T_a = 1348$ K. Figure 4 shows Q^{-1}
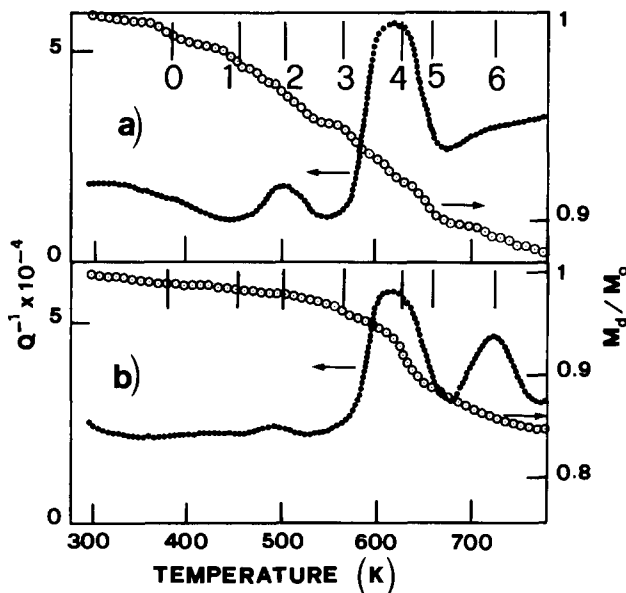

Fig. 1. Q^{-1} and M_d/M_0 curves of MANET steel after quenching from 1348 K with cooling rate $\dot{T} = 3600$ K min^{-1} (a) and $\dot{T} = 150$ K min^{-1} (b).
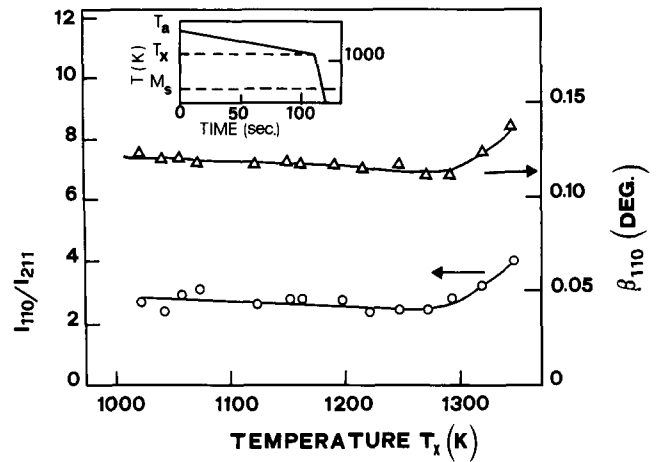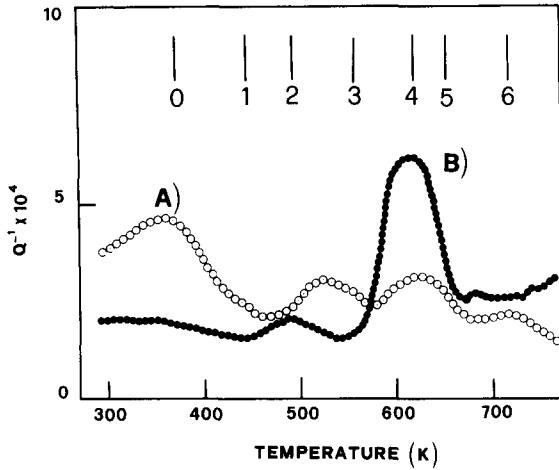
Fig. 4. Q^{-1} spectra of MANET samples quenched from $T_1 = 1473$ K (A) and $T_2 = 1443$ K (B), which are in $\gamma + \alpha$ and γ fields respectively.

curves of MANET samples quenched from $T_1 = 1473$ K and $T_2 = 1443$ K with $T_2 < T_D < T_1$ (T_D is the temperature dividing γ and $\gamma + \alpha$ fields). The two Q^{-1} spectra are quite different. The sample quenched from T_2 shows an IF spectrum with a Q^{-1} peak at $n = 4$ and is similar to the spectrum of Fig. 1 (a) (quenching from T_a in γ field) whereas the other IF curve relative to the sample quenched from T_1 shows the highest Q^{-1} peak at low T corresponding to $n = 0$.

MANET samples quenched from the biphasic field (1473 K) have a structure with martensite and ferrite. The martensitic zones have a mean hardness of 450 HV, a value comparable with that of MANET quenched from 1348 K, whereas the ferritic zones have a hardness of $\simeq 350$ HV.

4. Discussion

IF results are discussed on the basis of theoretical considerations due to Sarrak and co-workers [5, 6] regarding the effects of Cr atoms on the Snoek peak. A C atom in an octahedral interstice is surrounded by six next-neighbours, which may be either Fe or Cr atoms. According to Sarrak and co-workers it is supposed that the activation energy H_0 for an atom is 20 Kcal mol^{-1} when only Fe atoms occupy the octahedron corners and that a contribution of $\Delta H = 3.1$ Kcal mol^{-1} has to be added for every Cr atom which substitutes an Fe atom. So we can write:

$$H_n = H_0 + n\,\Delta H \tag{1}$$

with n varying from 0 to 6.

Neglecting background contribution, the IF spectrum is thus given by:

$$Q^{-1}(T) = \sum_{n=0}^{6} Q_n^{-1}(T)$$

$$= \sum_{n=0}^{6} \frac{\Delta_n}{2} \, \text{sech}\left[\left(\frac{H_0 + n\Delta H}{R} \right) \cdot \left(\frac{1}{T} - \frac{1}{T_n} \right) \right] \tag{2}$$

where T_n is the temperature of the nth peak.

Relaxation times τ_n can be expressed as:

$$\tau_n = \tau_0 \cdot \exp(-H_n/kT) \tag{3}$$

with $\tau_0 = 5 \times 10^{-15}$ s. Relaxation strength Δ_n can be assumed to be proportional to the C concentrations C_n in different types of octahedra. As discussed in ref. 9, jumps are taken into account for their contribution to IF only when they occur between equivalent interstices, i.e. interstices surrounded by the same number of Cr atoms. In general there is good correspondence between calculated and measured Q_n^{-1} peak positions even if, in some cases, we observed small shifts.

Figure 1 shows that after fast cooling ($\dot{T} = 3600$ K min^{-1}) the clusters of C–4Cr associates are predominant whereas with slow cooling ($\dot{T} = 150$ K min^{-1}) a comparable number of clusters with C–6Cr is present in MANET steel. To understand at which temperature the diffusive processes take place, we have to consider the XRD and IF results illustrated in Figs. 2 and 3.

IF spectra of samples quenched slowly at $\dot{T} = 150$ K min^{-1} to $T_X = 1073$ K and to $T_X = 1173$ K are substantially similar to the IF spectra obtained from samples cooled slowly to M_S with main Q_n^{-1} peaks at $n = 4$ and $n = 6$. This result means that the processes responsible for the differences observed in samples cooled at different rates occur at $T > 1100$ K and is in agreement with XRD analysis, which shows changes of texture and of half-height line width β only for T_X values higher than 1270 K.

The temperature range between $T_a = 1348$ K and $T = 1270$ K is critical for the cooling rate: cooling profiles with different slopes in this T range produce martensite with different C–Cr clustering and thus with different properties and stability as shown in refs. 9, 11 and 12.

The existence of C–Cr associates in the γ field may be related to the energy ΔH^*, which favours C to Cr aggregations. The effect of ΔH^* on C and Cr distributions has been examined by means of Monte Carlo simulations, for which reference is made to books of Binder and Hermann [13, 14]. Since C and Cr have quite different diffusivities in Fe lattice, two stages are considered:

(a) the first is one of rapid diffusion of C atoms with the formation of C–Cr associates (Fig. 5(a));

(b) the second is one of slower diffusion of the free Cr atoms with the formation, at C–Cr associates, of Cr aggregates (Fig. 5(b)).
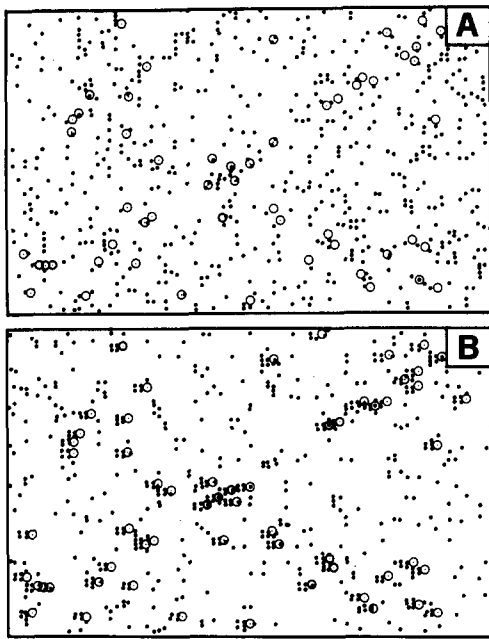
Fig. 5. Snapshots representing Cr (●) and C (○) distributions after 1000 random walk jumps of interstitial C with immobile Cr (A) and after 2000 random walk jumps of Cr with non-mobile C-Cr associates (B). The lattice sites occupied by the Fe atoms are not marked. The results of computer simulation by Monte Carlo method for the probability of jumping for neighbouring C-Cr atoms show it is proportional to exp $(-T_C/T) = $ exp (-1.15) with periodic boundary conditions (taken from ref. 9).

The snapshots were obtained with periodic boundary and probability of jumping from bound positions proportional to exp$(-\Delta H^*/kT)$, i.e. exp$(-T_C/T)$ being $T_C = \Delta H^*/k$.

Figure 4 shows that IF spectra of samples quenched from γ and $\gamma + \alpha$ fields are quite different, in particular, the Q^{-1} curve of a sample quenched from $T_2 = 1473$ K is characterized by a high peak at low T ($n = 0$), which is the classical Snoek peak exhibited by Fe-C alloys. This result indicates that C-Cr associates are no longer present when $T = 1473$ K and thus the temperature T_C is in the range 1445–1473 K, very close to the separation point between γ and $\gamma + \alpha$ fields.

Confirmation comes also from XRD analysis, which shows that the value of β_{110} is greater for samples quenched from a γ field ($\simeq 0.13°$) than for samples quenched from an $\alpha + \gamma$ field ($\simeq 0.11°$). Of course, the higher value of β is connected with the inhomogeneities of Cr atom distribution. Taking $T_C = 1450$ K, we obtain $\Delta H^* \simeq 2.9$ Kcal mol^{-1}, a value comparable with the value of ΔH considered for the different Q_n^{-1} peaks.

5. Conclusions

The results of the present work can be summarized thus:

(1) At the temperature used for austenitization treatment ($T_a = 1348$ K) the MANET steel shows a structure with non-random distribution of Cr atoms, which is characterized by the presence of stable C-Cr associates. Computer simulations based on the Monte Carlo method show that the formation of C-Cr associates is a preliminary step to the formation around them of more extended aggregates of Cr atoms.

(2) The cooling rate plays a role in the characteristics of C-Cr associates present in as-quenched material; the diffusive processes occurring with slower cooling take place for temperatures higher than $\simeq 1270$ K.

(3) The temperature T_C, which is the stability limit for C-Cr associates, is $\simeq 1450$ K.

Acknowledgments

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