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C-Cr Associates and Carbide Precipitation in Manet Steel

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Abstract. Internal friction (IF) data show that the evolution of C-Cr associates distribution of MANET steel is connected to the Cr-rich carbides (\(M_6C\) and \(M_23C_6\)) precipitation. Carbides extracted from the matrix have been investigated by X-ray diffractometry and EDS microanalysis measurements. It is discussed the hypothesis that the \(M_6C\) carbides form by aggregation of C-Cr associates.

1. INTRODUCTION

Phenomena of solute segregation induced by thermal treatments and/or irradiation have been extensively investigated in Fe-Cr based alloys by means of different experimental techniques: small angle neutron scattering [1,2], Mössbauer spectroscopy [3,4], TEM [5] and field ion microscopy [6,7]. The presence of C in these alloys strongly influences the segregation processes and in addition gives rise to the precipitation of carbides.

IF experiments made by Gondi et al. [8,9] on Cr martensitic steels showed that C-Cr associates are present in the as-quenched materials with a distribution mainly depending on the Cr content and on the cooling rate from the austenitic phase. Different types of associates correspond to a different number \(n\) (from 0 to 6) of Cr atoms, which occupy the corners of the octahedron around the C atom. C-Cr associates are characterized by different binding energies for the C atom and the IF spectrum can be considered as sum of seven Snoek-type peaks with relaxation strengths \(\Delta\), depending on the associate distribution.

Investigations on MANET steel have shown that the C-Cr associates play a fundamental role on the austenite \(\rightarrow\) martensite transformation [10] and influence the mechanical stability, in particular the fracture behaviour and the ductile to brittle transition, when the material is subjected to thermal treatments [11]. Therefore, C-Cr associates have to be considered microstructural features of the utmost importance for the mechanical behaviour of MANET steel and in general of Cr martensitic steels, candidate materials for structural applications in future fusion reactors [11].

The aim of the present work is to determine whether the C-Cr associates affect the precipitation of Cr carbides and, in this case, to assess which is their specific role in the process.

2. EXPERIMENTAL

The investigated MANET steel has the following chemical composition: 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%).

After the austenitization treatment (1.8 x 10\(^3\) s at 1348 K), the material has been cooled down to room temperature with a rate \(\dot{T}=150\) K min\(^{-1}\) and then subjected to a thermal treatment consisting of successive heating steps of 3.6 x 10\(^3\) s at 373, 473, 573, 673, 773 and 873 K.

IF and dynamic modulus \((\nu)\) measurements have been carried out after each heating step. IF tests were made using the method of frequency modulation in the T range 300-873 K with a nearly constant heating rate (2 K min\(^{-1}\)). The Q\(^{-1}\) values were determined from the logarithmic decay of flexural vibrations with resonance frequency \(f=250\) Hz. The strain amplitude was kept below 1x10\(^{-6}\).

After each step of thermal treatment the carbides have been extracted from the metal matrix by using an electrochemical method, then they have been investigated by X-ray diffractometry (XRD) and SEM observations with EDS microanalysis. The electrochemical method employed a cell operating at room temperature with a solution of HCl (10%) in methanol, cathod of INOX steel, tension 1.5 V and current 0.5 A. The filtering was made using Durapore membrane filters with pores of 0.1 \(\mu\)m. XRD spectra of carbides have been recorded using MoK\(_\alpha\) radiation in the 2\(\theta\) range 5-50\(^\circ\). Precision line profiles were obtained by step-scanning with 2\(\theta\) intervals of 0.005\(^\circ\) and counting times of 20 s for each step.
3. RESULTS

Fig. 1 shows the $Q^1$ curves after the heating steps at 673, 773 and 873 K.

![Graph showing $Q^1$ curves after heating steps at different temperatures.]

The IF spectra have been fitted (solid line) using as reference the activation energies $H_a$ given for ternary Fe-Cr-C alloys by the theoretical model of Tomilin et al. [12]:

$$Q^{-1} = \sum_{n=0}^{6} Q_{n}^{-1} = \sum_{n=0}^{6} \frac{\Delta_n}{2} \text{sech}(\frac{H_n}{R}(\frac{1}{T} - \frac{1}{T_o}))$$  \hspace{1cm} (1)

$$H_n = H_0 + n \Delta H$$  \hspace{1cm} (2)

$H_0 = 8.37 \times 10^4 \text{ J/mole}$ is the activation energy when only Fe atoms are present at the corners of the octahedron and a contribution $\Delta H = 1.30 \times 10^4 \text{ J/mole}$ has to be added to $H_0$ for every Cr atom that substitutes an Fe atom. The central temperatures $T_o$ of the $Q^1$ peaks calculated for the experimental resonance frequency $f = 250 \text{ Hz}$ are in Tab. 1. Some difficulties to fit IF spectra arise since MANET steel is more complex than a Fe-Cr-C alloy: it contains other alloying elements (Nb, Mo, Mn, V etc.), which cause shifts of peak positions respect the theoretical $T_o$ values. Furthermore these elements are present in minor concentration in Nb-rich and Cr-rich carbides and EDS microanalysis measurements show that their percentages present some variations depending on the temperature of thermal treatment. Since it is not possible to take into account all these effects and thus determine exactly the central temperatures of $Q^1$ peaks, shifts of the peak positions around the calculated values $T_o$ have been considered to get the best fit curve of experimental data.

As reported in detail in ref. [13], the IF spectrum presents components due to N relaxation processes. The N components correspond approximately to the IF peaks observed in Fe-Cr-N alloys by Ritchie and Rawlings [14] and attributed to N/Cr-Cr, Fe-N and N/Fe-Cr interactions.
The total N contribution is indicated in fig.1 by a dotted line. The heights of the $Q'$, Snoek-type peaks due to C relaxation processes are given in Tab.1.

Table 1- Heights of the $Q'$, Snoek-type peaks due to C relaxation processes after the heating steps at 673, 773 and 873 K. The central temperatures $T_c$ of the peaks are reported.

<table>
<thead>
<tr>
<th>Peak</th>
<th>$T_c$ (K)</th>
<th>673 K step</th>
<th>773 K step</th>
<th>873 K step</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{10}'$</td>
<td>380</td>
<td>$1.8 \times 10^4$</td>
<td>$3.0 \times 10^4$</td>
<td>$6.0 \times 10^4$</td>
</tr>
<tr>
<td>$Q_{11}'$</td>
<td>453</td>
<td>$2.3 \times 10^4$</td>
<td>-</td>
<td>$4.4 \times 10^4$</td>
</tr>
<tr>
<td>$Q_{12}'$</td>
<td>500</td>
<td>$1.0 \times 10^4$</td>
<td>$2.7 \times 10^4$</td>
<td>$5.8 \times 10^4$</td>
</tr>
<tr>
<td>$Q_{13}'$</td>
<td>560</td>
<td>$1.7 \times 10^4$</td>
<td>$3.0 \times 10^4$</td>
<td>$5.0 \times 10^5$</td>
</tr>
<tr>
<td>$Q_{14}'$</td>
<td>621</td>
<td>-</td>
<td>-</td>
<td>$1.9 \times 10^4$</td>
</tr>
<tr>
<td>$Q_{15}'$</td>
<td>650</td>
<td>$3.0 \times 10^4$</td>
<td>-</td>
<td>$9.0 \times 10^5$</td>
</tr>
<tr>
<td>$Q_{16}'$</td>
<td>710</td>
<td>$1.0 \times 10^4$</td>
<td>$1.0 \times 10^4$</td>
<td>$3.5 \times 10^5$</td>
</tr>
</tbody>
</table>

The XRD patterns of the extracted carbides indicate that only Nb-rich carbides (MC and M$_2$C) are present after the 673K heating step. These carbides, which were already present in γ-field, are retained after quenching and are scarcely affected by treatments in the temperature range of our tests.

The heating step at 773 K induces the precipitation of the M$_7$C$_3$ Cr-rich carbides (hexagonal $a=1.398$ nm, $c=0.452$ nm) whereas the M$_2$C$_6$ carbides (cubic $a=1.066$ nm) start to form only after the 873 K step. The relative intensities of XRD reflections of M$_2$C$_6$ and M$_7$C$_3$ carbides confirm a well known phenomenon, i.e. the precipitation of the former ones takes place at expenses of the latter ones. The average chemical composition of Cr-rich carbides is shown in Tab.2.

Table 2- Average chemical composition of Cr-rich carbides extracted from MANET steel.

<table>
<thead>
<tr>
<th>Cr (at.%)</th>
<th>Fe (at.%)</th>
<th>Nb (at.%)</th>
<th>Mo (at.%)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>45</td>
<td>3</td>
<td>2</td>
<td>M$_7$C$_3$</td>
</tr>
<tr>
<td>63</td>
<td>28</td>
<td>4</td>
<td>5</td>
<td>M$_2$C$_6$</td>
</tr>
</tbody>
</table>

4.DISCUSSION

The IF spectrum evolution following successive heating steps (see fig.1) shows that C-Cr$_{10}$ associates are not stable structures. This phenomenon, which is observed in samples cooled from the γ-phase with a relatively slow rate ($\dot{T}=150$ K min$^{-1}$), has been extensively discussed in other papers [10,11,13]. In this work the attention is focussed on an aspect connected to the precipitation of M$_7$C$_3$ carbides. The comparison of IF spectra in fig.1 (a) and (b) (see also Tab.1) shows that the most intense peak after the 673 K heating step, i.e. the $Q_{11}'$ peak, disappears after the successive step at 773 K. M$_7$C$_3$ carbides form after this treatment (773 K) and EDS microanalysis results (Tab.2) indicate that Cr atoms are 50% of the total metal atoms. From the stoichiometric composition it is derived that the ratio between C and Cr atoms present in M$_7$C$_3$ carbides is about 1:1. Therefore, the formation of M$_7$C$_3$ carbides occurs when the C-Cr$_{10}$ associates, structures with the same ratio between C and Cr atoms, cease to give their contribution to relaxation processes.

These results suggest that the formation of M$_7$C$_3$ carbides may take place by aggregation of C-Cr$_{10}$ associates. Following the 873 K heat step M$_2$C$_6$ carbides form at expenses of M$_7$C$_3$ carbides but nucleate on different sites [15]. When M$_7$C$_3$ carbides solve, C-Cr$_{10}$ associates are released in the matrix, can thus participate again to relaxation processes and the $Q_{11}'$ peak is observed in the IF spectrum (c). On the other hand the hypothesis that these carbides form by C-Cr$_{10}$ aggregation is consistent with the M$_7$C$_3$ structure described by Dyson and Andrews[16]. The positions occupied by metal and C atoms in the M$_7$C$_3$ carbide cell are represented in fig.2 where different symbols indicate different atomic layers. The complex structure is formed by distorted octahedra having a C atom at the centre (one of them is indicated).
5. CONCLUSIONS

The present work has evidenced that remarkable changes in IF spectrum of MANET steel take place when the material is subjected to thermal treatments in the temperature range of Cr-rich carbide precipitation (773-873 K). The formation of $M_7C_3$ carbides is accompanied by the disappearing of the peak due to C-Cr$_1$ associates, which re-appears when these carbides solve.

On the basis of IF results, of the chemical composition of the extracted carbides and of their crystal structure it is suggested that $M_7C_3$ carbides may form by C-Cr$_1$ associate aggregation.

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REFERENCES