C-Cr Associates and Carbide Precipitation in Manet Steel

P. Gondi, R. Montanari and M.E. Tata

Dip. Ingegneria Meccanica, Università di Roma "Tor Vergata", Via della Ricerca Scientifica s.n.c., 00133 Roma, Italy

Abstract. Internal friction (IF) data show that the evolution of C-Cr_n associate distribution of MANET steel is connected to the Cr-rich carbides (M₇C₃ and M₂₃C₆) precipitation. Carbides extracted from the matrix have been investigated by X-ray diffractometry and EDS microanalysis measurements. It is discussed the hypothesis that the M₇C₃ carbides form by aggregation of C-Cr₁ 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_n 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_n 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 Δ_r, depending on the associate distribution.

Investigations on MANET steel have shown that the C-Cr_n associates play a fundamental role on the austenite → 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_n 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_n 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 × 10³ 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 × 10³ s at 373, 473, 573, 673, 773 and 873 K.

IF and dynamic modulus (*M_d*) 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 1 × 10⁻⁶.

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 μm. XRD spectra of carbides have been recorded using MoKα radiation in the 2θ range 5-50°. 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

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

Figure 1- IF spectra of MANET steel after the heating steps at 673 K (a), 773 K (b) and 873 K (c). The markers indicate the central positions of the Q_n^{-1} peaks.

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

$$Q^{-1} = \sum_{n=0}^6 Q_n^{-1} = \sum_{n=0}^6 \frac{A_n}{2} \cdot \text{sech} \left[\left(\frac{H_n}{R} \right) \cdot \left(\frac{1}{T} - \frac{1}{T_n} \right) \right] \quad (1)$$

$$H_n = H_0 + n \cdot \Delta H \quad (2)$$

$H_0 = 8.37 \times 10^4$ J/mole is the activation energy when only Fe atoms are present at the corners of the octahedron and a contribution $\Delta H = 1.30 \times 10^4$ J/mole has to be added to H_0 for every Cr atom that substitutes an Fe atom. The central temperatures T_n of the Q_n^{-1} peaks calculated for the experimental resonance frequency $f \approx 250$ 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_n 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_n^{-1} peaks, shifts of the peak positions around the calculated values T_n 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^{-1}_n Snoek-type peaks due to C relaxation processes are given in Tab.1 .

Table 1- Heights of the Q^{-1}_n Snoek-type peaks due to C relaxation processes after the heating steps at 673, 773 and 873 K. The central temperatures T_n of the peaks are reported.

Peak	T_n (K)	673 K step	773 K step	873 K step
Q^{-1}_0	380	1.8×10^{-4}	3.0×10^{-5}	6.0×10^{-4}
Q^{-1}_1	453	2.3×10^{-4}	-	4.4×10^{-4}
Q^{-1}_2	500	1.0×10^{-4}	2.7×10^{-4}	5.8×10^{-4}
Q^{-1}_3	560	1.7×10^{-4}	3.0×10^{-4}	5.0×10^{-5}
Q^{-1}_4	621	-	-	1.9×10^{-4}
Q^{-1}_5	650	3.0×10^{-5}	-	9.0×10^{-5}
Q^{-1}_6	710	1.0×10^{-4}	1.0×10^{-4}	3.5×10^{-5}

The XRD patterns of the extracted carbides indicate that only Nb-rich carbides (MC and M_2C) 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_7C_3 Cr-rich carbides (hexagonal $a=1.398$ nm, $c=0.452$ nm) whereas the $M_{23}C_6$ carbides (cubic $a=1.066$ nm) start to form only after the 873 K step. The relative intensities of XRD reflections of $M_{23}C_6$ and M_7C_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.

Cr (at.%)	Fe (at.%)	Nb (at.%)	Mo (at.%)	Type
50	45	3	2	M_7C_3
63	28	4	5	$M_{23}C_6$

4.DISCUSSION

The IF spectrum evolution following successive heating steps (see fig.1) shows that C-Cr_n 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_7C_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^{-1}_1 peak, disappears after the successive step at 773 K. M_7C_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_7C_3 carbides is about 1:1. Therefore, the formation of M_7C_3 carbides occurs when the C-Cr₁ 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_7C_3 carbides may take place by aggregation of C-Cr₁ associates. Following the 873 K heat step $M_{23}C_6$ carbides form at expenses of M_7C_3 carbides but nucleate on different sites [15]. When M_7C_3 carbides solve, C-Cr₁ associates are released in the matrix, can thus participate again to relaxation processes and the Q^{-1}_1 peak is observed in the IF spectrum (c). On the other hand the hypothesis that these carbides form by C-Cr₁ aggregation is consistent with the M_7C_3 structure described by Dyson and Andrews[16]. The positions occupied by metal and C atoms in the M_7C_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).

Figure 2- Unit cell of the M_7C_3 carbide [16]: C atoms occupy the centre of a distorted octahedron.

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-Cr₁ 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-Cr₁ associate aggregation.

ACKNOWLEDGMENTS

The authors are grateful to Mr. P. Plini and Mr. B. Iacovone for the assistance in sample preparation.

REFERENCES

- [1] Spooner S., Brundage W.E., Scripta Metall. **17** (1983) 573-574.
- [2] Vintaykin Ye.Z., Kolontsov V.Yu, Phys. Met. Metallogr. **26** (1968) 97-100.
- [3] Chandra D., Schwartz L.H., Trans. AIME **2** (1971) 511-519.
- [4] De Nys T., Gielen P.M., Trans AIME **2** (1971) 1423-1428.
- [5] Ha K.F., Zhang H.M., Jing K.L., Metall. Trans. **20A** (1989) 2563-2567.
- [6] Zhu F., Wendt H., Haasen P., Scripta Metall. **16** (1982) 1175-1182.
- [7] Haasen P., Metall. Trans. **16A** (1985) 1173-1184.
- [8] Gondi P., Montanari R., Physica Stat. Sol. (a) **131** (1992) 465-480.
- [9] Gondi P., Montanari R., Coppola R., J. of Nuclear Mater. **191-194** (1992) 1274-1278.
- [10] Gondi P., Montanari R., Sili A., Z. für Metallkd. **85** (1994) 664-669.
- [11] Gondi P., Montanari R., Sili A., Tata M.E., J. of Nuclear Mater. (in print).
- [12] Tomilin I.A., Sarrak V.I., Gorokhova N.A., Suvorova S.O., Zhukov L.L., Phys. Metall. Metallogr. **56-3** (1983) 74-79.
- [13] Gondi P., Montanari R., Tata M.E., Materials Letters **25** (1995) 249-255.
- [14] Ritchie I.G., Rawlings R., Acta Metall. **15** (1967) 491-496.
- [15] Honeycombe R.W.K., Steels Microstructure and Properties (Edward Arnold, London 1990) pp.158.
- [16] Dyson D.J., Andrews K.W., J. of The Iron and Steel Institute (1969) 208-219.