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Internal Friction Study on Manet Steel: Effects of Cooling Rate from Austenitic Domain

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: Snoek type Q^{-1} peaks observed in Fe-Cr-C alloys are related to jumps between equivalent octahedra or tetrahedra with n Cr atoms at the corners, with n up to 6 or 4. The effects of high T and cooling treatments are considered on the characteristics of the C-Cr $_n$ associates and in consequence of martensite. The results are interpreted in terms of C-Cr $_n$ associates acting as embryos for the nucleation of martensite with stability depending on tetrahedrality or octahedrality of the associates.

1. INTRODUCTION

The basic references are two papers, of Tomilin et al. [1] and of Gondi et al. [2]. In Fe-Cr-C alloys Tomilin et al. observed the occurrence of seven Q^{-1} vs. T peaks considered of Snoek type, that is due to interstitial C jumping between neighbouring octahedra with Cr atoms, in number n from 0 to 6, substituting Fe at the corners in the body centered structure. The height of the observed peaks was interpreted [1,3] in terms of Poisson distribution of single C-Cr $_n$ associates with account for the energies of binding of C to the Cr atoms. In the Cr martensitic steel MANET Gondi et al. observed that the height of these peaks depends on thermal treatments and their results were interpreted by assuming that reversible jumps between equivalent sites, i.e. C-Cr $_n$ cells with the same n and with common face, have to be considered as contributing to each peak. Following results presented previously [4], the effects of austenitising temperature and cooling rate on martensite characteristics are considered in this paper in connection with the martensite properties due to the presence of the Cr atoms in solution.

2. EXPERIMENTAL

The material used is a MANET1 steel with the following composition in wt%:

C 0.17, Cr 10.5, Ni 0.85, Mn 0.60, Mo 0.50, Nb 0.20, V 0.25, Si 0.32, Al 0.05, N 0.003, P 0.005.

After cold rolling to 0.5 mm thickness and cutting, the samples were austenitised at $T_a=1348K$; batch A of samples was cooled from T_a with a rate of 150 K/min, batch B quenched with a rate of 3600 K/min, batch C with a two stage cooling, first with 150 K/min down to 1073 then with 3600 K/min to RT.

Internal friction Q^{-1} measurements were done using frequency modulation with amplitudes $< 10^{-6}$, with frequencies ~ 250 Hz and temperatures increasing from RT to 773 K with a rate of 2 K/min. Together with Q^{-1} the dynamic modulus was also measured; the dynamic modulus variations were consistent with Q^{-1} peaks depending on anelasticity.

3. RESULTS

Fig.1-a shows the Q^{-1} vs T data as measured with the samples of batch A with cooling rate of 150 K/min, in fig.1-c the trend due to subsequent heating for 1 hr at 373K. In fig.1-b the Q^{-1} vs T data after fast cooling (3600 K/min -batch B) with effects of subsequent heating for 1 hr at 373 K in fig.1-d are presented.

As mentioned in the introduction these peaks have been related to jumps between octahedra with n corners occupied by Cr atoms, with n up to 6. The Q^{-1} spectrum is thus considered as corresponding to

$$Q^{-1} = \sum_{n=0}^{n=6} \frac{\Delta_n \omega \tau_0 \exp(H_n / kT)}{1 + [\omega \tau_0 \exp(H_n / kT)]^2}$$

$H_n = H_0 + n\Delta H$, $\Delta H = 13$ kJ/mole binding energy of C to Cr [1,2], $H_0 = 83.7$ kJ/mol and $\tau_0 = 5.0 \cdot 10^{-15}$ s respectively activation energy and pre-exponential factor of the Snoek peak, $\Delta_n/2$ the height of peaks connected to C-Cr $_n$ associates.

The markers at the top of the figures correspond to the position of the different peaks for the n values in labels, of course on account of the corresponding binding energy, as used in the bibliography.

After slow cooling the measurements show two Q^{-1} peaks corresponding to C-Cr $_6$ and C-Cr $_4$ and after fast cooling two peaks corresponding to C-Cr $_4$ and C-Cr $_2$ associates.

As shown in fig.1-c, the situation after slow cooling appears unstable and transforms after heating at 373K in conditions giving rise to a strong peak corresponding to C-Cr $_4$ associates plus a broad peak in the region C-Cr $_0 \Leftrightarrow$ C-Cr $_1$.

Figure 1: Q^{-1} vs. T trends of MANET samples first austenitised at 1348 K and then cooled with rates of 150 K/min down to room T (1-a), 3600 K/min down to RT (1-b), first 150 K/min down to 1073 K and in sequence 3600 K/min to RT (1-e). In fig.s 1-c-d-f effects of subsequent heating at 373 K respectively for the samples of fig.s 1-a-b-e. Numbers n at the top of fig.s represent positions of peaks related to octahedra with n Cr atoms at the corners.

Greater structural stability does instead occur after fast cooling since the Q^{-1} spectra remains approximately unchanged by heating up to relatively high temperatures (fig.1-d).

Always referring to treatment A the C-Cr₄ peak accompanying the C-Cr₆ one may find an explanation by considering interlaced octahedra obtained by displacements of 1/2 of the cube side; as shown in fig.2-b a base octahedron with 6 Cr atoms (A) appears thus connected with octahedra labelled B and C with only 4 corners occupied by Cr and with common face, thus explaining the C-Cr₄ peak.

Jumps between equivalent tetrahedral sites in the interior of single octahedra with all corners occupied by Cr appear instead of better consistency with peaks C-Cr₄ and C-Cr₂ coming about after treatment B. As shown in fig.2-c, in the case of tetrahedral jumps there are in fact two sets of couples for jumping, with 4 and with 2 Cr atoms into and at the boundary of the octahedron with the corners occupied by Cr.

As shown by fig.2-b, the peak C-Cr₄ might be also due to jumps between the octahedra interlaced with the basic one; in this case however they occur at the boundaries octahedra with 3 corners occupied by Cr and with common face, not agreeing with the occurrence of only peak C-Cr₂ which is instead consistent with the tetrahedral jumps.

The absence of a C-Cr₃ peak after the A treatment is on the other hand a negative aspect for the explanation considered with respect to this treatment, since groups of octahedra with all corners occupied by Cr are accompanied at the boundaries by C-Cr₃ equivalent octahedra; the absence of the related C-Cr₃ peaks might be due the low probability of formation of C-Cr₃ associates, depending on the tetrahedrality of C.

Diffusion of the Cr atoms to form the associates is assumed on account of the high temperatures and of the binding energy of Cr to C [2].

Consistently with the results it may be assumed that the different C-Cr_n associates act as embryos for martensite nucleation.

5. Conclusions

The Q⁻¹ measurements have put into evidence the occurrence, in martensitic steels, of C-Cr_n associates with different characteristics depending on high T treatments leading, before fast cooling to room T, to absence or presence of groups of bcc cells with the fcc ones.

The different martensite properties resulting after the high T treatments appear thus referable to the C-Cr_n associates, higher or lower stability of martensite depending on C-Cr₄ tetrahedral and on C-Cr₆ octahedral associates respectively.

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