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Distribution of C–Cr associates and mechanical stability of Cr martensitic steels

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Abstract

Structural and mechanical stability of two martensitic steels with different Cr content (MANET and modified F82H) has been studied by means of internal friction (IF) and dynamic modulus (M_d) measurements, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) observations with EDS microanalysis and mechanical tests (hardness, Charpy). Following thermal treatments at 700°C, MANET samples cooled from the austenitic field at a rate of 150°C/min, exhibit Cr segregation both inside the grains and in the zones near grain boundaries. The Cr segregation induces internal stresses, which influence the mechanical properties, in particular the fracture mode, ductile–brittle transition temperature (DBTT) and upper shelf energy (USE). The material is not stable: DBTT changes depending on the time of the treatment and after 20 h at 700°C a mixed fracture mode (quasi-cleavage plus intercrystalline) is observed. Cr segregation is very weak in modified F82H steel submitted to the same treatments and a greater mechanical stability has been observed. The different behaviour of MANET and modified F82H is discussed on the basis of IF and M_d results, which show that the stability of the distribution of C–Cr associates in as-quenched materials is a factor of great importance to avoid the Cr segregation. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

After neutron irradiation Cr-containing martensitic steels exhibit different structural evolution and mechanical behaviour in dependence of the Cr content: when Cr is in the range 7–9% the best combination of mechanical properties has been observed; in particular, the DBTT shift is lower than in 10–12% Cr steels and also USE undergoes minor variations. Reviews are in Refs. [1–3]. The α' phase, observed only in irradiated steels with a Cr content exceeding 10%, is considered one of the most important factor affecting embrittlement [4,5].

Recently, Wanderka et al. [6,7] showed that decomposition takes place in MANET steel after dual beam irradiation (Fe^+ 300 keV, He^+ 15 keV): long range pseudo-periodic variations of Cr concentration (wavelength ~10 nm, amplitude 2.2–2.8 at.%) were observed in samples irradiated in the temperature range 400–425°C, whereas Cr-rich clusters (diameter ~4 nm, concentration 18–25 at.%) were present after irradiation at 450–500°C.

Therefore, a better understanding of the physical processes leading to Cr segregation is important to improve the performances of Cr martensitic steels, foreseen as structural and first wall materials in future fusion reactors. Previous IF results [8–10] on MANET steel indicated the presence of elementary structures, the C–Cr associates, formed by one C atom at the centre and by six (Cr or Fe) atoms at the corners of an octahedron. The C–Cr associates differ for the number of Cr atoms and their initial distribution after quenching strongly influences the evolution of Cr segregation processes and the fracture behaviour of the material treated at 700°C. The aim of the present work is to compare the distributions of C–Cr associates in MANET and modified F82H (F82H mod.) steels subjected to the same treatments and thus to ascertain the influence of Cr content on these elementary structures and their evolution.

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2. Experimental

The experimental tests have been carried out on MANET and F82H mod. with the following chemical compositions: MANET – Cr 10.37, C 0.10, Mo 0.58, Ni 0.65, Mn 0.76, Nb 0.16, V 0.21, Si 0.18, Al 0.007, N 0.032, P 0.004, S 0.005, B 0.0075, Co 0.005, Cu 0.01, As 0.01, Sb 0.0002, Sn < 0.01, Fe (wt%) to balance; F82H mod. – Cr 7.68, C 0.09, Mo 0.003, Ni 0.02, Mn 0.16, Nb 0.0001, V 0.16, Si 0.11, Al 0.003, Ta 0.02, Ti 0.01, Cu 0.01, N 0.007, P 0.002, S 0.002, B 0.0002, W 1.95, Fe (wt%) to balance [11]. The values reported for F82H mod. steel are averages of values measured in different ingot positions.

MANET and F82H mod. samples of different shape (bars $70 \times 7 \times 0.6$ mm^3, sheets $40 \times 25 \times 4$ mm^3 and V-notched Charpy specimens) have been subjected to an austenitization treatment for 30 min at 1075°C and quenched in Ar atmosphere with a cooling rate of 150°C/min. The samples were then heated at 700°C for successive times up to 20 h. After each step of heating, IF and M_d measurements, XRD analysis, SEM observations with EDS and mechanical tests (hardness and Charpy) have been performed.

Bar-shaped samples were employed for IF measurements, which were carried out using the method of frequency modulation. The Q^{-1} value was determined from the logarithmic decay of flexural vibrations with resonance frequency $f \cong 250$ Hz. The maximum strain amplitude was about 1×10^{-6} . During IF tests the temperature was increased from room temperature to 500°C at a constant rate (~2°C/min).

XRD patterns were recorded in the 2Θ range 15–70 deg. using Mo-Kα radiation. High precision line profiles of {1 1 0}, {2 0 0}, {2 1 1} reflexions were collected by step scanning with 2Θ angular intervals of 0.005 deg and counting time of 20 s for each step.

Charpy tests were made in the temperature range from −180°C to +150°C and the DBTT was determined as the temperature corresponding to (USE − LSE)/2, where USE and LSE are upper and lower shelf energies, respectively. The reported data are averages of 3 tests performed at each temperature. Full size V-notched specimens of MANET and 1/2 size specimens of F82H mod. were used for the Charpy tests.

3. Results

Fig. 1 shows the results of mechanical tests carried out on the materials after increasing times of tempering at 700°C. The DBTT trend of MANET steel (Fig. 1(a)) is discontinuous: the value is +12°C in as-quenched condition, decreases at −45°C after 2 h, increases at +10°C after 6 h and then decreases again remaining nearly constant around −20°C for longer times of treatment. F82H mod. exhibits a different behavior because DBTT decreases after the first heating steps, but it is scarcely affected by the successive treatments. The hardness trends are similar for the two Cr martensitic steels (Fig. 1(b)).

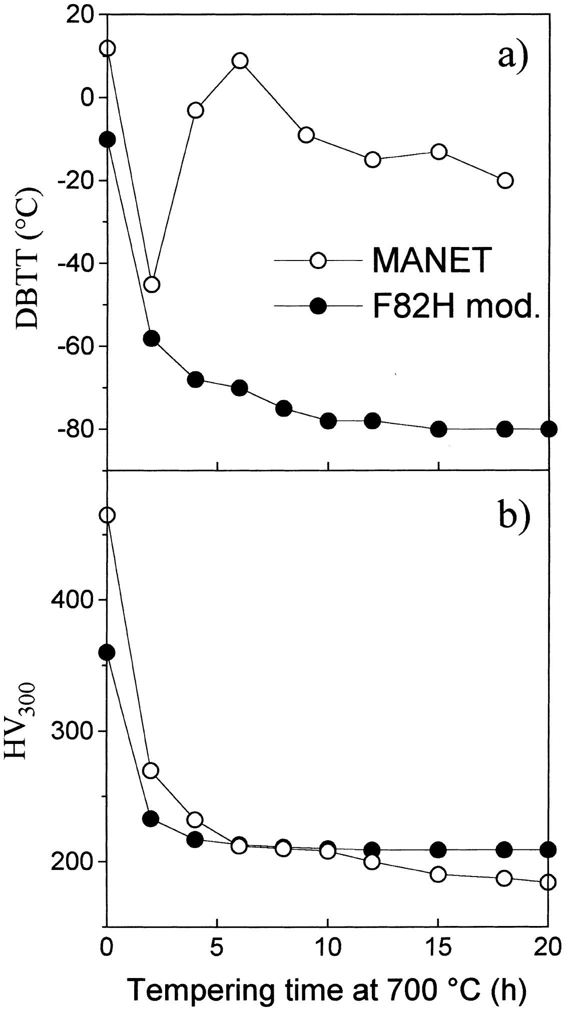

Fig. 1. Trends of DBTT (a) and hardness (b) of MANET and F82H mod. steels vs. the tempering time at 700°C.

SEM observations show that after the first step (2 h) of thermal treatment the martensitic structure of both steels is completely recovered, and carbides decorate the boundaries between previous laths. After prolonged times of treatment the morphology of the materials does not change substantially, but EDS microanalysis reveals that Cr segregation occurs only in MANET. Cr concentration profiles along a direction (white line) are shown in Fig. 2 for MANET (a) and F82H mod. (b) after 20 h at 700°C. In Fig. 2(a) the Cr content exhibits fluctuations higher than those in Fig. 2(b); further, the mean signal level is not constant but increases in correspondence with the zones near grain boundaries.

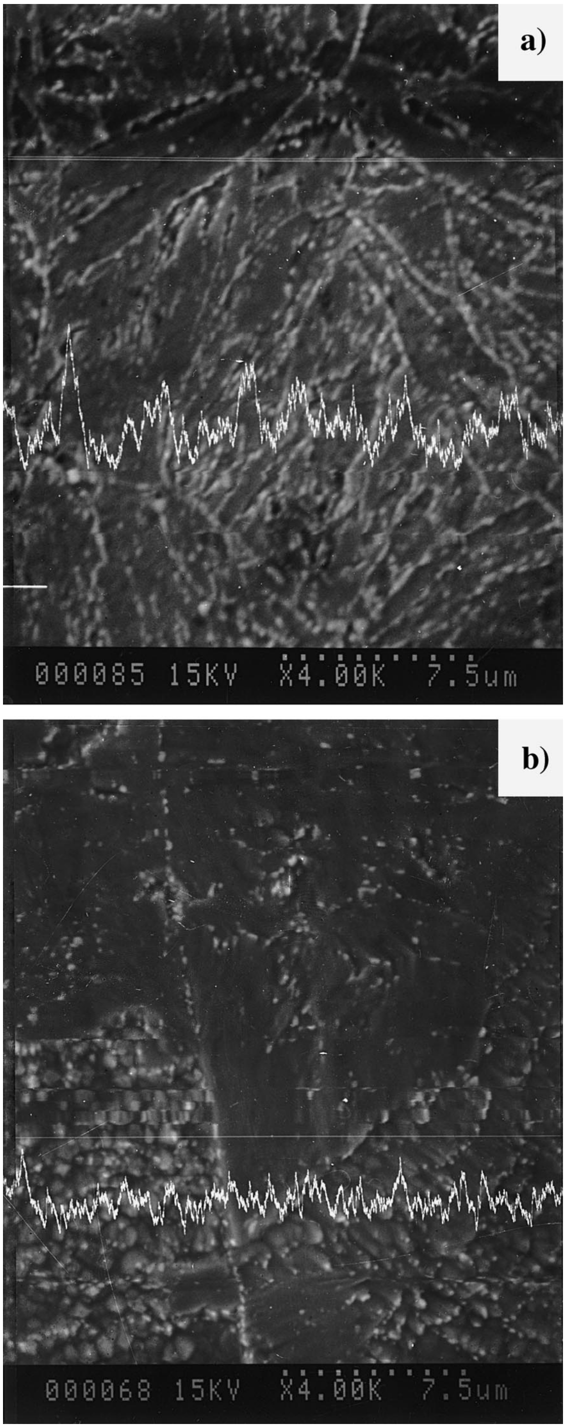

Fig. 2. SEM micrographs of MANET (a) and F82H mod. (b) steels heated 20 h at 700°C. The Cr microanalytical profiles refer to the points along the indicated white line.

Fracture surfaces obtained from Charpy tests in the ductile field show that the dimple size distribution undergoes a slight shift to larger dimensions for longer tempering times, but no significant differences between MANET and F82H mod. have been observed. In the brittle field, as-quenched MANET steel shows the typical features of quasi-cleavage fracture; more details have been reported in Refs. [9,10]. The structures exhibited by F82H mod. are similar and also remain unchanged in samples subjected to thermal treatments up to 20 h. The fracture surface morphology of MANET steel instead shows evidence of a mixed mode of fracture (quasi-cleavage plus intercrystalline) after prolonged times of heating at 700°C. Fig. 3(a) shows a zone where intercrystalline fracture occurred. To verify whether correlations do exist between fracture morphology and Cr distribution, EDS microanalytical maps of Cr have been collected by scanning the same zones examined by SEM (Fig. 3(b)–(e)). The comparison between the micrographs in Fig. 3(b) and (c), relative to MANET steel, shows a good correspondence between Cr enriched zones and zones where fracture occurred in the intercrystalline mode. In the case of F82H mod. Fig. 3(d) and (e), Cr appears to be homogeneously distributed.

The XRD halfheight linewidths β of the strongest reflexions of the materials are plotted in Fig. 4 : in MANET the β value decreases up to approximately 6 h of treatment and then shows a progressive increase, which is very weak or absent at all in F82H mod. Since the analysis of peak profiles shows that the size contribution to line broadening is negligible except for the first minutes of tempering, the halfheight linewidth β can be taken as an indication of internal strains. Therefore, the β increase indicates that internal stresses arise in MANET but not in F82H mod.

IF and M_{d} curves of both the steels, as-quenched and treated 20 h at 700°C, are shown in Fig. 5. The M_{d} trends are consistent with Q^{-1} relaxation peaks. The contribution from C relaxation processes to IF spectra of Cr martensitic steels is the sum of seven Snoek-type Q_n^{-1} peaks and can be analyzed using the model of Tomilin et al. [12]. Each Q_n^{-1} peak is due to a relaxation process involving C–Cr associates with n Cr atoms (n varying from 0 to 6), and the peak height is proportional to their number. The central positions of the seven Q_n^{-1} peaks are indicated on the top of Fig. 5. Also, relaxation processes involving N give a contribution to IF spectra; more details on the analysis of IF spectra can be found in Refs. [8,13].

4. Discussion

A complete recovery of the martensitic structure takes place in MANET and F82H mod. steels after the first step of treatment at 700°C. The observed softening (Fig. 1(b)) and halfheight linewidth β decreases (Fig. 4) are due to the reduction of lattice defects and to the disappearing of martensitic laths.

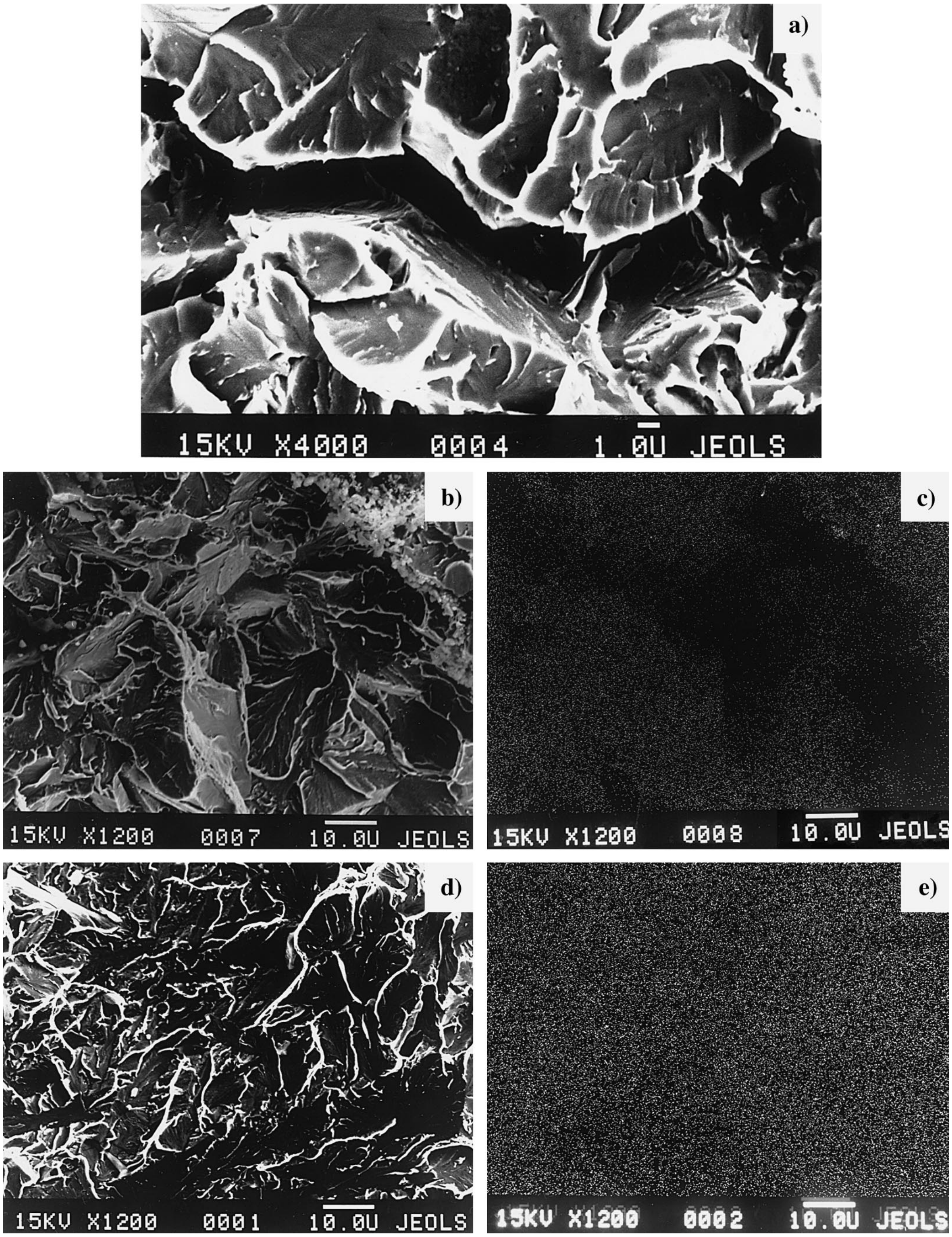

Fig. 3. Fracture surfaces of MANET (a, b) and F82H mod. (d) samples heated 20 h at 700°C and broken in the brittle field. Microanalytical Cr maps in (c) and (e) refer to the same zones shown in (b) and (d), respectively.

The Cr concentration profile in Fig. 2(a) confirms the results of previous works [9,10]: prolonged heating at 700°C induces the formation of zones with different Cr content inside the grains and of concentration gradients with Cr enrichment near grain boundaries in MANET steel cooled with a rate of 150°C/min from the austenitic field. The Cr segregation gives rise to internal strains evidenced by the increase of β values after 6 h of treatment [9,10]. In F82H mod. steel, where Cr remains near homogeneously distributed, β values show small variations after the initial decrease.

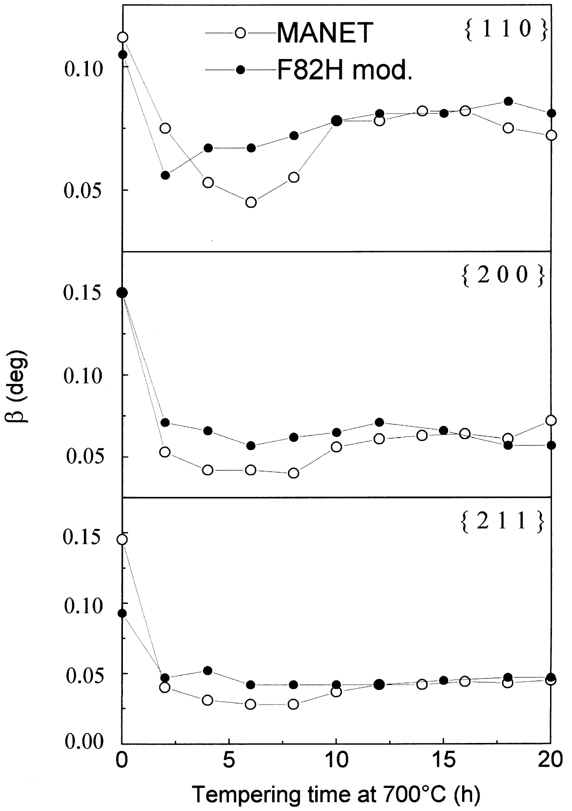

Fig. 4. Halfheight linewidths β of the higher intensity XRD reflexions of MANET and F82H mod. vs. the tempering time at 700°C.

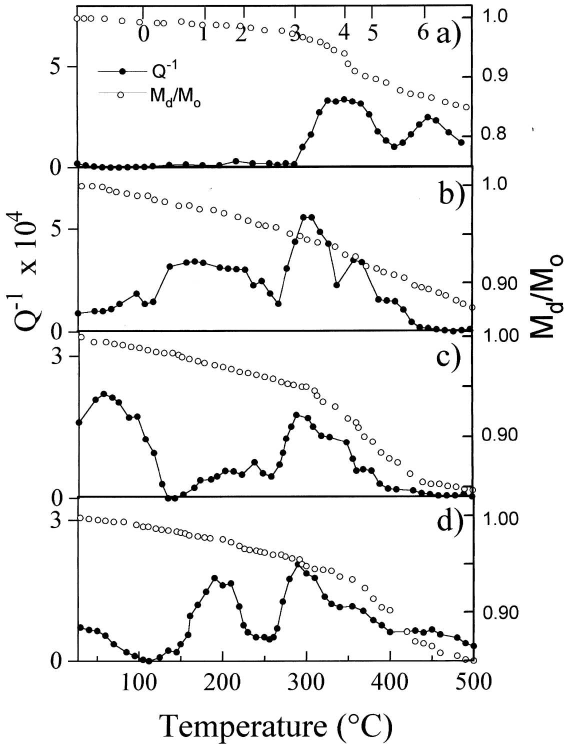

Fig. 5. IF spectra and M_d/M_0 trends of MANET (a, b) and F82H mod. (c, d) steels in as-quenched condition (a, c) and after 20 h at 700°C (b, d). M_0 is the initial modulus value.

Cr segregation phenomena give rise to internal stresses and influence the mechanical stability of MANET, in particular the fracture behaviour. The correspondence between the zones where the rupture occurs in the intercrystalline mode and the zones with Cr enrichment (Fig. 3 (b) and (c)) indicates that the progressive Cr segregation is responsible for the transition from the quasi-cleavage mode of fracture to a mixed one and thus for the discontinuous DBTT trend (Fig. 1(a)). In F82H mod. heated 20 h at 700°C the fracture occurs in the quasi-cleavage mode, and Cr segregation is not observed (Fig. 3(d) and (e)).

The examination of the IF spectrum of as-quenched MANET steel shows that the Q^{-1} peaks of higher intensity are those relative to C–Cr associates with four and six Cr atoms (Fig. 5(a)), whereas after thermal treatment peaks at lower temperature are also present (Fig. 5(b)). It has been shown in Ref. [8] that treatments at low temperatures (100–200°C) also induce changes of the C–Cr distribution of MANET steel. If a homogeneous Cr content (11%) is assumed in the alloy, it is impossible to obtain an acceptable fitting of the IF spectrum in (b) using the theoretical model of Tomilin et al. [12]. The analysis shows instead that this Q^{-1} curve is consistent with the presence of zones with different Cr content.

The IF spectrum of as-quenched F82H mod. (Fig. 5(c)) differs from that of MANET (Fig. 5(a)) for the relative height of peaks due to C relaxation: the more intense peaks in Fig. 5(c) are those relative to associates with three and four Cr atoms, a minor component corresponds to peaks 1 and 2. Furthermore, a significant N contribution (the broad maximum centred at ~50°C) is present. Even if the total N content is higher in MANET than in F82H mod., this results indicates that the N content in solid solution, which is the only one to give rise to IF peaks, is higher in F82H mod. than in MANET. After tempering (Fig. 5(d)) the intensity of the broad maximum at 50°C, which is the overlapping of four N relaxation peaks [13], decreases due to nitride precipation. The relative intensities of C relaxation peaks 3 and 4 remain unchanged, whereas those of peaks 1 and 2 slightly increase. This result is remarkable because it indicates the substantial stability of C–Cr distribution in F82H mod. steel also after prolonged tempering at 700°C.

The present work shows that there is a correspondence between the stability of the initial C–Cr distribution and the structural-mechanical stability of martensitic steels with different Cr content. Previously [10], the same result was found in studying MANET steel quenched from the austenitic field with different cooling rates in the range 150–3600°C/min: higher cooling rates produce a stable distribution of C–Cr associates and the material is stable after prolonged treatments at 700°C. In the future the research will be extended to other Cr martensitic steels to verify whether these results have a general validity. However, so far, the stability of C–Cr associates in as-quenched steels appears to be one of the most important factors to avoid, or at least to minimize, Cr segregation, embrittlement and thus mechanical instability. The experiments performed by us concerned only unirradiated materials, but it is reasonable to suppose that C–Cr associates distribution can play an important role also on Cr segregation leading to α' phase formation during neutron irradiation.

5. Conclusions

The results of the present work can be so summarized:

1. The Cr martensitic steels MANET and F82H mod. subjected to the same treatments (austenitization, quenching and tempering at 700°C) exhibit a different structural and mechanical evolution. After prolonged tempering times, zones with different Cr content form in MANET giving rise to internal stresses, a mixed mode of fracture and mechanical instability. These phenomena do not take place in F82H mod.
2. After quenching MANET and F82H mod. present a different distribution of C–Cr associates. The distribution of F82H mod. remains nearly unchanged after 20 h of treatment at 700°C, whereas the MANET undergoes significant variations, even for treatments at lower temperatures (100–200°C).
3. From these and previous results it appears that the stability of the initial C–Cr distribution is decisive to have stable martensitic steels without segregation phenomena.

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