AGEING UNDER THERMAL TREATMENT OR NEUTRON IRRADIATION OF LOW ACTIVATION MARTENSITIC STEELS

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Low Activation Martensitic (LAM) steels are candidates for internal structures of fusion reactors. The concept of Low Activation steels was introduced in nuclear industry for new materials that offer benefits on maintenance operations and waste management. For martensitic/ferritic steels, the main alloying elements such as molybdenum, niobium and nickel present in commercial steels are substituted by elements such as tungsten, vanadium, manganese and tantalum. These elements have a similar influence on the processing and the structure, but exhibit a lower radiological impact. The assessment of potential reduced activation martensitic steels requires a good understanding of the microstructural features in correlation with the mechanical behaviour. Consequently, much effort is underway to study the microstructural evolutions in these materials occurring under thermal ageing or neutron irradiation, and the effects of the substitution of W to Mo and Ta to Nb.

The microstructural investigations are focused on the following phenomena :
- precipitation of various carbides or nitrides : in particular of $M_2(C,N)$ particles responsible of a "secondary" hardening phenomenon (defined in §1),
- formation of the Laves phases $Fe_2(Mo,W)$ under long thermal ageing around 500°C,
- decomposition by a spinodal mechanism of the ferritic phase resulting in an ultra fine-scale interconnected network of Fe-rich α and Cr enriched α' phases or in very small α' particles around 400°C.

All these microstructural evolutions (which are at the origin of hardening phenomena and embrittlement) were studied in different martensitic steels with a chromium content between 7 and 12 at.%, using Small Angle Neutron Scattering (SANS). Indeed SANS allows, in this kind of materials, to characterise very small precipitates at early ageing time when they are not detected by Transmission Electron Microscopy. This is in particular the case for α-α' decomposition, which introduces very weak contrast for X-rays or electron scattering. Furthermore, the ferritic matrix being ferromagnetic, the A(q) ratio of the magnetic and nuclear contrasts between the matrix and particles gives information about their chemical composition [1].

1. Study of the secondary hardening phenomenon

In quenched (after 1h at 1050°C) and subsequently annealed at 450-550°C materials which simulate the thermally affected zone near a weld, one observes, at relatively short annealing time, an increase of the hardness which is called secondary hardening [2]. It is related to the first steps of Cr-rich M_2X (X= C or N) precipitation; the latter is detected by Transmission Electron Microscopy (TEM), but only after almost 100 annealing hours when the size of the particles is close to 10 - 20 nm. In order to describe the precipitation at the early stage of thermal ageing treatment, SANS experiments were performed on a conventional alloy “T0” (Fe-9%Cr-1%Mo) and on a LAM material “F82H” (Fe-7.5%Cr-2%W), previously aged for various durations at 500°C.
For the T0 alloy, an increase of the SANS intensity is observed at all annealing times. The mean diameter and number density N_p of the M_2X particles deduced from SANS are shown on figure 1. At short ageing time (<5h), the particles size remains small (1 to 2 nm) whereas N_p increases (“nucleation” stage). Around 5h ageing time, N_p and the hardness reach simultaneously their maximum value, corresponding to optimal pinning of the dislocations by the small precipitates. At long ageing time, N_p and the hardness decrease sharply whereas the average precipitate diameter increases by one order of magnitude (“coalescence” stage).

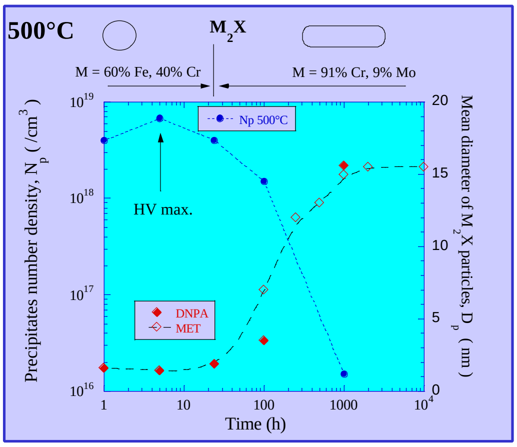

Figure 1 : Evolution with ageing time at 500°C of the mean size and the number density of the M_2X precipitates measured by TEM and SANS in the T0 alloy.

The form factor of the precipitates, obtained from the fit of the SANS curves, is spherical for the shorter time (t<100 h) and afterwards rod shaped ellipsoidal with a ratio between the big and the small axis of about 3. For large precipitates, the aspect ratio and the mean size measured after 1000 h, are in good agreement with TEM observations.

The A(q) ratio was found to decrease strongly with ageing time (i.e. from 6.6 to 2.4); this could be explained only by a progressive enrichment in Cr and by assuming that the interstitial element X is essentially carbon and not nitrogen. At long ageing time, the A ratio is in agreement with the presence of 9% Mo in the carbides measured by TEM.

For the low Cr content LAM alloy F82H, the maximum volume fraction of the carbides is noticeably smaller than for T0 (0.7% instead of 1.5%); this can explain the very weak increase of the hardness observed in the F82H alloy (figure 2). Besides, the chemical composition of the carbides at long ageing times, consistent with the A value, is 80%Cr-20%V (at. %) : contrary to the case of Mo in the T0 alloy, W does not enter in the composition of the M_2C carbides.

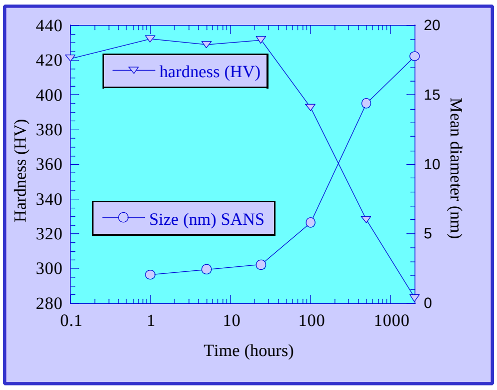

Figure 2 : Evolution with ageing time at 500°C of the hardness and of the mean size of the M_2X precipitates measured by SANS in the Low Activation F82H alloy.

2. Ageing under long thermal treatment or neutron irradiation

In austenitized (quenched from high temperature) and subsequently tempered (annealed 1 h at 750°C) materials, long thermal ageing performed at temperatures between 250 and 550°C up to 22000 h, can induce an important Ductile-to-Brittle Transition Temperature (DBTT) shift directly related to the formation of new phases[3]. SANS measurements realised on several types of alloys (conventional and LAM) have shown different behaviours depending on the chemical composition. In particular, SANS was able to detect the formation of very small precipitates (nm size), not observed by TEM. For example, the formation of α' precipitates was observed by SANS in conventional and LAM alloys containing initial Cr content above 9% under thermal ageing at 400°C.

Some of these alloys were studied after fast neutron irradiation up to a dose of 0.8 d.p.a. (displacement per atom) at 325°C. In a Low Activation ("La4Ta") alloy containing 11.2%Cr, neutron irradiation induces an increase of the scattered intensity (figure 3) which can be attributed to the α-α' spinodal decomposition not observed under thermal ageing at this temperature. **In this case, the neutron irradiation induces accelerated phase separation**.

The "F82H" alloy presents no evolution under thermal ageing whatever the temperature as well as under irradiation up to 0.8 dpa. These behaviours are in qualitative agreement with the mechanical properties of the materials.

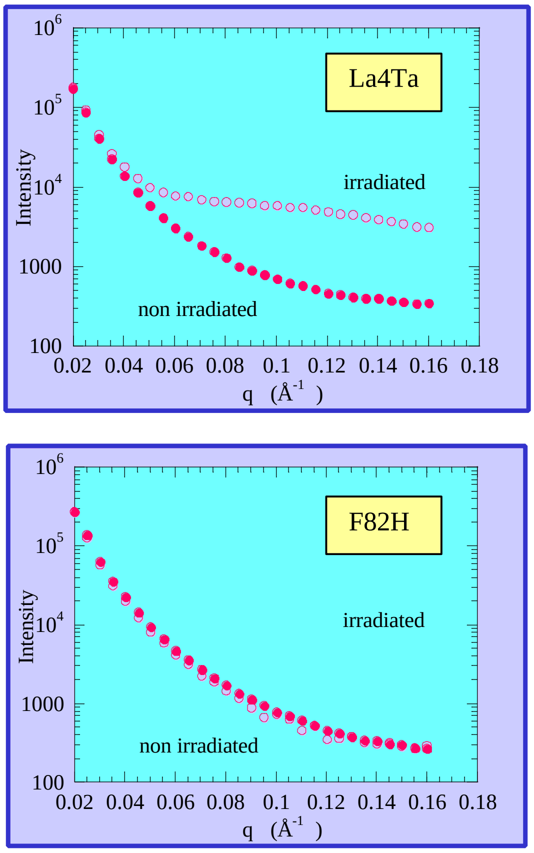

Figure 3 : SANS intensity scattered by two low activation alloys (F82H and La4Ta) before and after neutron irradiation.

In summary, the combined use of SANS and TEM allows to obtain a detailed description of precipitation. This study has put in evidence the role of the initial chemical composition on the alloys behaviour under thermal treatment or neutron irradiation. SANS measurements allowed a direct correlation of the microstructure evolution with the secondary hardening phenomenon.

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