IRRADIATION-INDUCED HARDENING OF MARTENSITIC STEELS CANDIDATES FOR FUTURE GENERATION NUCLEAR REACTORS

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Martensitic steels with 7-12 wt% Cr are candidates for the internal structures of future generation nuclear reactors or spallation sources, because of their remarkable mechanical properties and resistance to swelling; but they suffer from radiation hardening and embrittlement below 400°C, even at moderate doses. In order to promote their use, it is necessary to understand the evolution of their microstructure and its relationship with the degradation of mechanical properties during irradiation.

The unmixing of the b.c.c. Fe-Cr solid solution below 600°C into two isomorphous phases, Fe-rich (α phase) and Cr-rich (α' phase), observed in thermally-aged alloys with Cr content between 10 and 90 at.%, is an important feature of the binary Fe-Cr equilibrium phase diagram (see Fig. 1). The phase separation occurs at the nanometer scale and induces hardening of the solid solution. α' has also been observed in martensitic/ferritic steels by Transmission Electron Microscopy (TEM) after thermal ageing or neutron irradiation at 400-550°C for Cr content above 13 wt%, but up to now not at lower temperatures (300°C), even after long irradiation (up to 40 displacements per atom (dpa)).

In fact, Small-Angle Neutron Scattering (SANS) is much more powerful than TEM or X-ray scattering to study the α-α' phase separation, because of the large difference between the neutron coherent scattering lengths of Fe and Cr. Also, the A ratio of the magnetic and nuclear SANS contrasts between matrix and particles gives information on the chemical composition of the particles.

In the present study [1], nine martensitic steels with various chemical compositions have been investigated: four Reduced Activation (RA) materials from AEA-Culham, UK (LA4Ta, LA12LC, LA12TaLC and LA13Ta), a low Cr content RA material supplied by JAERI, Japan (F82H), and four "conventional" commercial steels (EM10, HT9, T91 and MANET II). The materials were irradiated in the OSIRIS (CEA, Saclay) or in the HFR (NRG, Petten) reactors at temperatures of 250, 325 and/or 400°C, for doses of 0.7, 2.4 and/or 2.9 dpa.

The neutron scattering experiments were performed at room temperature at the LLB on the PAXY small-angle instrument, under a saturating magnetic field (= 2 Tesla) perpendicular to the incident neutron beam direction.

The main results of this work are summarized below.

1) In the unirradiated state, all materials show a strong SANS signal due to the $M_{23}C_6$ carbides formed during initial thermal treatment; this $M_{23}C_6$ population does not evolve under irradiation. After irradiation, most samples display a supplementary SANS signal, mainly observed at large q; this shows that a new nanometer-sized precipitation has formed. As example, the increase in SANS signal between the LA4Ta steel (Fe-11Cr-0.7W) sample irradiated 0.7 dpa at 325°C and the as-received sample shows a broad maximum around $q \sim 1.1$ nm^{-1}. This indicates a spatial periodicity in composition, with a characteristic length $2\pi/q \sim 5$-6 nm, similar to that observed in the thermally aged Fe-Cr solid solution. Moreover, the A value of the irradiation-induced SANS signal ($A = 1.9 \pm 0.2$) is in agreement with α-α' phase separation of the ferritic matrix. Detailed work on the thermally aged Fe-Cr binary alloy suggests that for the considered Cr concentrations (< 20%), a model of isolated Cr-enriched α' precipitates surrounded by a spherical exclusion volume depleted in Cr is adequate [2].

2) The volume fraction of precipitated α' phase increases with the irradiation dose (e.g. from 0.8% at 0.7 dpa to 3.4% at 2.9 dpa for LA4Ta at 325°C) and as the irradiation temperature is lowered (e.g. from 0.1% at 400°C to 0.6% at 250°C for LA12LC at 2.4 dpa). Up to 2.9 dpa, these parameters have only a weak influence on the average size of α' precipitates (radius ≈ 1.3 nm).

3) On Fig. 2 is indicated, for each steel irradiated for 0.8 dpa at 325°C, the volume fraction of α' phase obtained from SANS analyses, versus the Cr content in solid solution in the ferrite matrix (deduced from THERMOCALC type calculations). Except in the EM10 alloy, this precipitated α' volume fraction increases monotonously with the Cr content in the matrix. The Cr threshold concentration in the ferrite for α-α' unmixing under irradiation, deduced from the SANS results (7.2 at.%Cr at 325°C and 8.3 at.%Cr at 400°C) are found to agree with the

THERMOCALC predictions for the Fe-Cr system (see Fig. 1).

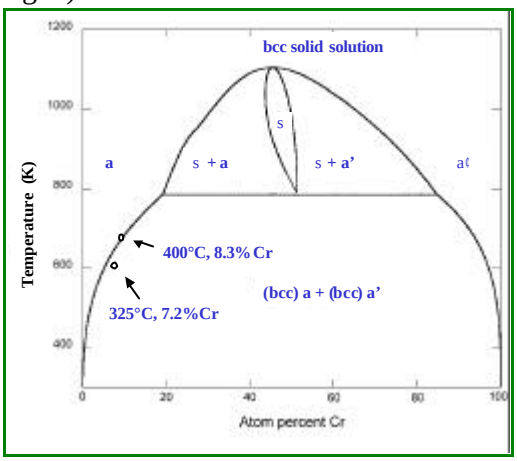

Figure 1. Fe-Cr binary phase diagram calculated from high temperature thermochemical data. Experimental points for the threshold of α' precipitation in irradiated steels deduced from the present SANS study are reported.

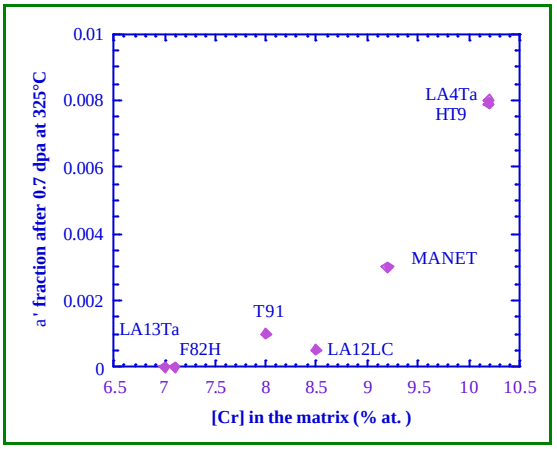

Figure 2. α' volume fraction deduced from SANS data after neutron irradiation of 0.7 dpa at 325°C as a function of the Cr amount in the ferrite matrix.

4) The above results show that the precipitation kinetics under irradiation are much faster than during thermal ageing. For the studied materials (Cr content < 20 wt%), the α' phase forms by nucleation and growth process. Two mechanisms can be involved: either (i) an *irradiation-accelerated* mechanism, where the point defect supersaturation allows the achievement of equilibrium much faster than in out-of-pile conditions at the same temperature; or (ii) an *irradiation-induced* mechanism, where the coupling between migrating point defects and solute atoms (Cr) can induce a non-equilibrium state. Experimental evidence exists for a weak binding between vacancies and Cr atoms in the Fe-Cr solid solution; however, our observation that the Cr threshold concentrations in the ferrite for α' precipitation under irradiation are not significantly different from the out-of-pile values obtained from modelisations of the equilibrium Fe-Cr phase diagram (see Fig. 1) suggests that the unmixing is dominated by a simple irradiation-accelerated mechanism.

5) For the materials with the lowest Cr content (F82H and LA13Ta), the SANS signal is unchanged by the irradiation at 325°C up to 0.7 dpa. In the case of F82H (Fe-7.5Cr-2W), a weak increase of the scattered intensity is observed after 3.4 dpa at 325°C.

The A ratio value does not correspond to α' precipitation, but is in agreement with vacancy clusters (A = 1.4). These could be small cavities or dislocation loops which have been observed by TEM in the form of "black dots" [3]. Their number densities deduced from TEM and SANS data (≈ 3×10^{23} m^{-3}) are in better agreement if the defect form factor is assumed to be cavity-like.

5) All the materials studied in the present work show a large increase ($\Delta\sigma_{irr}$) of yield stress after irradiation, ranging from 50 to 275 MPa. No simple correlation appears between $\Delta\sigma_{irr}$ and the chemical composition or microstructural parameters. The contribution of α' precipitates to the hardening of the martensitic steels has been estimated from a study on thermally-aged Fe-20%Cr alloys [4], where it is mainly due to dislocation-shearing of isolated precipitates obtained by nucleation-growth mechanism. This contribution to $\Delta\sigma_{irr}$ ranges from 10-20 to 100 MPa; this is always smaller than the measured increase of yield stress, but represents a significant part of it in the case of the Cr-rich materials: for example, ≈ 60-65 MPa compared to measured $\Delta\sigma_{irr}$ values of 100 MPa for LA4Ta and 260 MPa for HT9 irradiated 0.7 dpa at 325°C. However, the main hardening contribution seems to be due to radiation-induced point defects clusters, as the largest yield stress increase at 325°C was found in the F82H irradiated 2.9 dpa, where we observed a vacancy cluster (but no α') contribution to the SANS.

References

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