

Report on the experiments performed at ESRF Beamtime ME 1221

Subject: “In situ X-ray diffraction analysis of the microstructure evolutions during heating of a nitrogen martensitic stainless steel”.

The material studied in the experiment is a martensitic stainless steel enriched in nitrogen. These alloys are promising for several industrial applications due to their high mechanical properties associated with fine precipitation of one or more family of precipitates. Moreover they present also excellent corrosion properties associated with the high chromium content remaining in the matrix. It is thus fundamental to gain a good understanding of the sequences of phase evolutions during the different steps of the process leading to the final amount of precipitates (2 to 7%) in order to optimise the final properties of the alloys.

After solution treatment in the austenite temperature range the alloy is cooled to room temperature and martensite is formed. Some preliminary experiments carried out at ESRF in 2004 [1] led to the phase evolution on heating and to the amount of precipitates remaining in the austenite before cooling. These results pointed out the sequence of phases evolution and namely the interaction between dissolution of precipitates and transformation of the matrix from ferrite to austenite.

The aim of the present experiment was to investigate the further evolutions of the quenched martensite with residual austenite during the heating and tempering of the martensite. An in situ analysis using high energy X ray diffraction was thus planned allowing a continuous characterization of the phases evolutions without introducing any bias as compared to ex situ characterization. The specimens were previously prepared at LSG2M (heating to 1050°C at a controlled heating rate, and cooling to room temperature). For each specimen we recorded the thermal treatment and the dilatometric response. For all tests, the initial microstructure was a mixture of metastable martensite, residual austenite ($\approx 25\text{wt}\%$), primary carbides ($\approx 2\text{-}3\text{wt}\%$) and nitrides ($0\text{-}0.05\text{wt}\%$). Specimens were heated using either a radiant furnace or a resistive one depending on the programmed heating rate. The temperatures were measured thanks to a K thermocouple spot welded on the specimen surface. The Debye Scherrer diffraction rings were recorded on either a Mar345 detector (low heating rates) or on a Frelon camera (CCD detector) (high heating rates). The phase amounts and the cell parameters were quantified using the procedure used in [1]. All planned experiments were performed.

In the present report we will present some of the most representative results.

- 1) The transformation from the body-centered tetragonal martensitic structure into the body-centered cubic ferritic structure occurred by a strong decrease of the lattice parameter $c_{\alpha'}$ and a low increase of the lattice parameter $a_{\alpha'}$. Considering the evolutions of the lattice parameter $c_{\alpha'}$ of the martensite, different precipitation stages were detected: 120-270°C, 270-380°C, 470-620°C and 620-730°C (Heating rate 12°C/min) (Figure 1). The third and fourth precipitation stages were associated with the increase of the mass fractions of the $M_{23}C_6$ and M_2X structures above 600°C. The precipitation kinetics of the M_2X structure at 600-675°C was much more rapid than the precipitation kinetics of the $M_{23}C_6$ structure.
- 2) During the heating up to 600°C, the fraction of retained austenite didn't vary, but some variations of the lattice parameter emphasized the changes in the mechanical state of the austenite: compression of the austenite followed by a relaxation of the internal stresses, consecutive to the first stage of tempering of the martensite, between 250°C and 440-480°C. (Figure 1). This original experimental result could not be pointed out by ex situ experiments.
- 3) The decomposition kinetics of the retained austenite was obtained during the holding at different temperatures. The formation kinetics of the $M_{23}C_6$ structure was linked to the

decomposition kinetics of the retained austenite (Figure 2). According to the activation energy calculations, the $\gamma_R \rightarrow \alpha + (\text{Fe,Cr,Mo})_{23}\text{C}_6$ transformation was controlled by the diffusion of chromium and molybdenum in the austenite.

4) According to thermodynamic calculations and measures of the lattice parameters, the secondary $(\text{Fe,Cr,Mo})_{23}\text{C}_6$ carbides are richer in Cr and Mo than the primary $(\text{Fe,Cr,Mo})_{23}\text{C}_6$ carbides. The a/c ratio of the lattice parameters of the hexagonal M_2X structure decreased during the holding at 600-675°C, proceeding from a chemical and/or mechanical accommodation of a non-equilibrium structure towards the equilibrium M_2X structure. It may correspond to an evolution from a $(\text{Cr,V})_2(\text{C,N})$ carbonitride toward the equilibrium $(\text{Cr,V})_2\text{N}$ nitride.

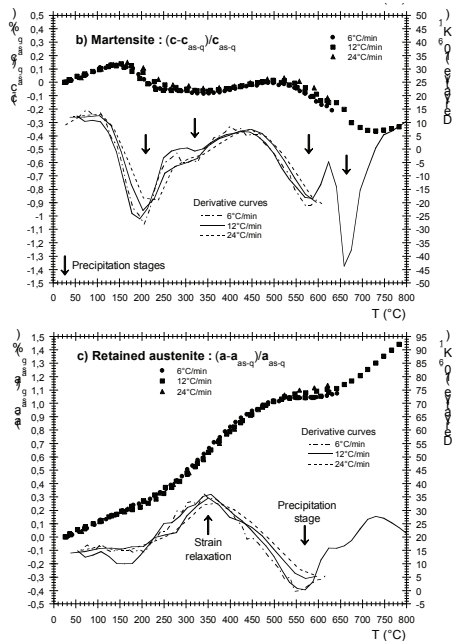


Figure 1: Evolution of the relative cell parameters c of martensite and a of austenite.

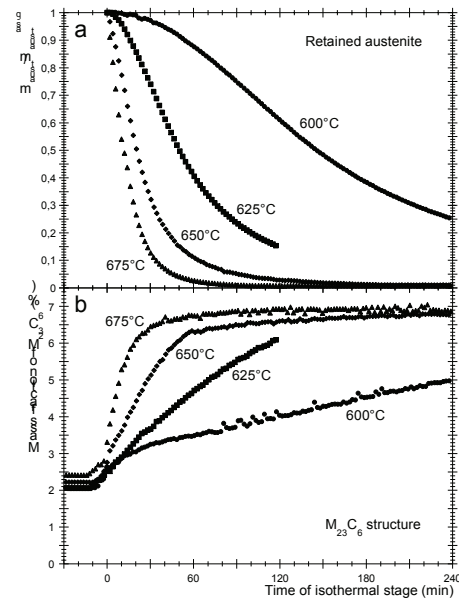


Figure 2: Simultaneous evolution of relative austenite mass fraction and carbide amounts

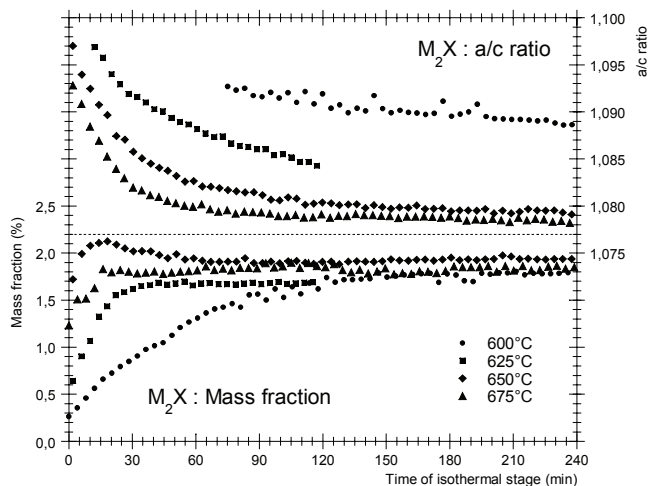


Figure 3: a/c ratio evolution of the lattice parameters of the M_2X structure (upper part) and M_2X mass fraction evolution (lower part) as a function of the time of isothermal stage, for the four studied temperatures.

Conclusions:

In situ quantitative characterizations of tempering of martensite were realized. The evolution of the phases' amounts as well as their cell parameters allowed establishing original links between the different evolutions. Moreover, the results show without any doubt the changes in the mechanical state of the austenite associated with the precipitation in the martensite, which is a new experimental result. Publication of these results is under way.