Tempering of a martensitic stainless steel: Investigation by in situ synchrotron X-ray diffraction

Adeline Bénéteau [a,b], Elisabeth Aeby-Gautier [b], Guillaume Geandier [b], Patrick Weisbecker [c], Abdelkrim Redjaïmia [b], Benoît Appolaire [d,*]

[a] *Snecma, 171, bd de Valmy – BP31, 92702 Colombes, France*
[b] *IJL, CNRS-Université de Lorraine, Parc de Saurupt, 54011 Nancy, France*
[c] *LCTS, CNRS-Université de Bordeaux 1, 3 allée de la Boétie, 33600 Pessac, France*
[d] *LEM, CNRS-ONERA, 29 av. de la Division Leclerc, 92322 Châtillon, France*

Abstract

Tempering of a martensitic stainless steel is investigated by means of in situ X-ray diffraction using high-energy synchrotron radiation. The simultaneous evolutions of the fractions of martensite/ferrite, retained austenite, $M_{23}C_6$ and M_2X (X = N,C) precipitates are determined during a continuous heating, and show that precipitation of M_2X can be observed directly only above 650 °C, concomitantly to the transformation of austenite into ferrite. However, a careful cross-analysis of the evolution of the lattice parameters of all phases shows the precipitation of metastable carbides/nitrides at low temperatures, followed by some stress relaxation. Between 500 and 650 °C, the lattice parameters of M_2X feature changes associated with the evolution of their composition, as supported by the analysis of additional isothermal agings, and consistently with the literature. Finally, the complex variations of the lattice parameters of austenite are analyzed thanks to a simple micromechanical model, supporting the previous conclusions and highlighting the subtle interplay between precipitation and stress relaxation.
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1. Introduction

Upon heating an as-quenched martensitic stainless steel, martensite and retained austenite transform into ferrite, both with rejection of alloying elements as well as with the formation of precipitates. In the case of Fe–C–N steels alloyed with Cr, Mo and V, carbon and nitrogen compete in a complex way, both in their redistribution during low temperature aging and in the formation of precipitates at higher tempering temperatures [1].

Tempering processes in martensitic stainless steels have commonly been studied by ex situ methods, such as hardness measurements, Mössbauer spectroscopy and transmission electron microscopy, the last technique often involving carbon extraction replicas. Conventional X-ray diffraction has been used to obtain the fraction of retained austenite at room temperature as well as the lattice parameters. Thanks to an improved resolution of the weak reflections, synchrotron X-ray diffraction can be used at room temperature to better quantify precipitates, as was done in Refs. [2,3] for α''-$Fe_{16}N_2$ nitrides and ε/η carbides in Fe–N, Fe–C and Fe–C–N martensites submitted to long-term agings at temperatures below 130 °C. The kinetics of martensite aging, usually measured by dilatometry, can also be

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* Corresponding author.

E-mail addresses: elisabeth.gautier@univ-lorraine.fr (E. Aeby-Gautier), benoit.appolaire@onera.fr (B. Appolaire).

monitored by time-resolved high-energy X-ray diffraction (HEXRD), with Rietveld analysis of all the diffractograms. It is worth stressing that, in addition to the identification of phases and the evolution of their fractions, the evolution of their mean lattice parameters can be obtained and fruitfully used in the analysis of the transformations. Recently, this approach has been proved to be relevant for investigating phase transformations during heat treatment in Al alloys [4], Ti alloys [5–8] and steels [9], in particular by bringing insight into the transformation pathways and giving some clues about the mechanisms involved [10].

In the present work, we follow this approach to investigate the phase evolutions in a martensitic stainless steel during heating from the as-quenched state. In particular, we aim to determine the precipitation sequence of carbides/nitrides associated with martensite aging and decomposition of retained austenite, involving changes in chemical composition and stress state. Particular emphasis is put on the subtle interplay between the aging process and stress relaxation, which has not hitherto been quantified. For this purpose, the paper is organized as follows. First, the steel investigated and the experimental techniques and procedures are described in Section 2. Next, the results obtained by HEXRD and supplemented by transmission electron microscopy (TEM) observations are presented in Section 3. Finally, in Section 4 a consistent picture is given of the observed changes and transformations, addressing in particular the issue of the precipitation pathway by a cross-analysis of the different experimental signatures.

2. Material and experimental procedure

2.1. Material

A high nitrogen martensitic stainless steel, provided by Aubert & Duval, was manufactured using an electrical furnace processing followed by electroslag consumable electrode remelting. Nitrogen was added by gaseous stirring and/or addition of nitrided ferroalloys [11]. Longitudinal rods of 4 mm diameter and 30 mm length were cut from a 65 mm diameter bar, 10 mm from the surface. The nominal composition of the steel is reported in Table 1. The samples in the annealed state (ferritic structure) were submitted to a 1050 °C solutioning treatment for 45 min, followed by air-quenching to room temperature.

The as-quenched matrix, analyzed by X-ray diffraction, is composed of martensite, retained austenite and the remaining primary precipitates that did not dissolved completely during the solution treatment, as shown in Ref. [9]. The mass fraction of retained austenite quantified by

Rietveld analysis is within 26.5–29.5%, depending on the sample. The mass fractions of the undissolved primary $(Fe,Cr,Mo)_{23}C_6$ face-centered cubic (fcc) carbides and $(Cr,V)_2N$ hexagonal nitrides are 2 and 0.5%, respectively. Their average size is within 150–400 nm.

2.2. Experimental procedure: in situ synchrotron X-ray diffraction

The experiments were carried out at the European synchrotron Radiation Facility (ESRF, Grenoble, France) on the ID15B beamline. The experimental device is shown in Fig. 1. A beam of about 89 keV is selected from the white beam thanks to an Si monochromator. The beam size is limited by two perpendicular slits. Diffraction diagrams with 100 and 400 μm slits were compared and gave both satisfactory diffractograms. Consequently, the 400 μm slits were chosen to reduce the acquisition time. The sample is located within the tubular furnace, fitted with two holes in the beam path. The temperature is measured with a thermocouple spot welded on the sample surface. Hence, the temperature variations were continuously controlled. The transmitted diffraction cones are intercepted by a mar345 (mar research, Hamburg) image plate detector located at about 1 m away from the sample. All the settings were performed with a reference sample of Al powder (cubic, $a = 0.40494$ nm). The accurate position of the transmitted central beam and the accurate wavelength ($\lambda = 0.01397$ nm) were determined thanks to the Al powder rings. The abscissa scale is converted from pixels to 2θ using the position of the Al peaks.

Due to the small average grain size compared to the 400×400 μm^2 beam size, the Debye–Scherrer rings were continuous all along the circumference without needing to rotate the sample. Only minor variations of the intensity along the rings were observed, caused by a slight grain texture. The Debye–Scherrer rings were integrated along the circumference to obtain the diagrams of the diffracted intensity as a function of the diffraction angle 2θ. The 2θ range extends from 0.83 to 8.35°, corresponding to d_{hkl} ranging from 0.096 to 0.964 nm. One diffraction diagram

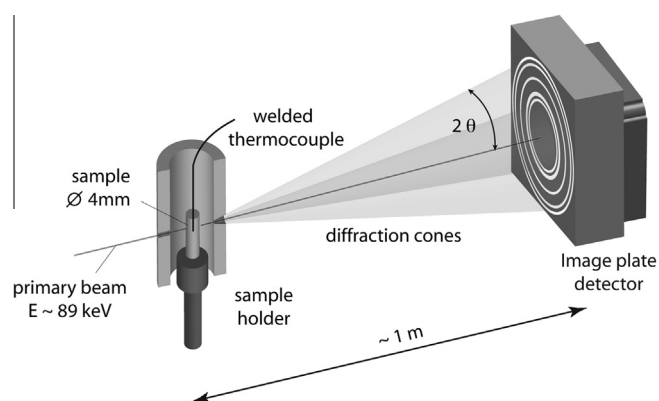Fig. 1. In situ synchrotron X-ray diffraction experimental device.

Table 1
Nominal composition (mass%) of the steel.

Fe	Cr	Mo	V	C	N	Si	Mn	Ni
Bal.	15.57	1.7	0.28	0.4	0.2	0.15	0.4	0.3