TEM investigation of the tempering behaviour of the maraging PH 17.4 Mo stainless steel

C. SERVANT
Laboratoire de Métallurgie Structurale, Bât 413, UA CNRS 1107, Université Paris-Sud Centre d’Orsay, 91405 Orsay Cedex, France

EL H. GHERBI, G. CIZERON
Laboratoire de Structure des Matériaux Métalliques, Bât 465, Université Paris-Sud Centre d’Orsay, 91405 Orsay Cedex, France

The PH 17–4 Mo steel (Z6 CND 17.04.02), used in the steam generator of nuclear reactors, was investigated in order to determine the structural evolution occurring during tempering carried out under various conditions of duration and temperature. The formation and growth of different types of carbides such as Mo2C, M23C6 and M7C3 and of Fe2Mo intermetallic compound were studied and also of reversed austenite. A small secondary hardening peak was observed for tempering close to 400°C which is related to the Mo2C carbide precipitation; beyond this temperature, softening occurs.

1. Introduction
During the last twenty years, due to the important requirements of the nuclear and aeronautical industries, the ferritic, austenitic, martensitic and austenomartensitic stainless steels (with a tempering capacity) have undergone great development. It has been proved that among these different steels, the martensitic ones lead to the best compromise of the mechanical properties up to relatively high temperatures (1–5). Furthermore, by annealing in the austenitic range these materials acquire a sufficient ductility to be machined; and besides, by tempering at moderate temperatures, nucleation and growth of very small precipitates occur in the martensite leading to an increase of the material hardness.

This paper describes various phenomena which occur during the tempering of a PH 17.4 Mo (Z 06 CND 17.04.02) stainless steel used in the steam generators of some nuclear reactors. It may be mentioned that in an earlier work [6], carried out on the same steel, we especially described and analysed the structural evolutions occurring during different thermal treatments performed between 20 and 1400°C, using various heating and cooling rates.

2. Experimental procedure

2.1. Material
The chemical composition of the PH 17.4 Mo steel under consideration in the present paper is given in Tables I and II, respectively, for major and minor additions.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt %)</td>
<td>0.051</td>
<td>15.95</td>
<td>4.65</td>
<td>1.24</td>
</tr>
</tbody>
</table>

The steel, manufactured by Acieries Aubert et Duval (41 rue de Villiers, Neuilly-sur-Seine, BP120-92202, France), was provided as a bar of 80 mm diameter and 140 mm length. It was first solution-treated at 1020°C, then oil-quenched and aged at 580°C. In the following, this state will be referred to as the “as-received” state. As will be shown below, the duration of the industrial tempering carried out at 580°C has been deduced while comparing the microstructures of the as-received state with those of samples tempered at different temperatures (Tt) and for various times (tt). Some samples in the as-received state were reheated at 1100°C for 30 min under argon atmosphere, then water-quenched. This state is further referred to the “as-quenched” state. It has been shown by optical microscopy that the steel in this state consists of lath martensite and δ-ferrite with a volume fraction of about 18%.

2.2. Experimental methods
The structural evolutions of the steel studied in its different states were followed by

(i) differential dilatometric analysis, performed with a DPH 55 type dilatometer, under primary vacuum, with heating (Th) and cooling (Tc) rates equal to 300(°C) h⁻¹. The samples were 5 mm × 5 mm × 20 mm parallelepipeds;

(ii) thermomagnetic analysis carried out under primary vacuum in a Type II Adamel-Chevenard (ISA, Division Adamel et Lhomargy, Ivry-sur-Seine, France) apparatus, the heating and cooling rates being also both equal to 300(°C) h⁻¹. The samples used were cylinders of 2 mm diameter and 10 mm length;

(iii) X-ray diffraction, performed with a Siemens apparatus using copper radiation filtered with a thin foil of pure iron; the set-up was equipped with a
TABLE II Composition of PH 17.4 Mo steel for minor additions

<table>
<thead>
<tr>
<th>Elements</th>
<th>Composition (wt %)</th>
<th>Elements</th>
<th>Composition (wt %)</th>
<th>Elements</th>
<th>Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.001</td>
<td>Nb</td>
<td>0.010</td>
<td>N</td>
<td>&lt; 0.020</td>
</tr>
<tr>
<td>P</td>
<td>0.028</td>
<td>W</td>
<td>0.020</td>
<td>As</td>
<td>&lt; 0.010</td>
</tr>
<tr>
<td>Si</td>
<td>0.370</td>
<td>V</td>
<td>0.035</td>
<td>Sn</td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>Mn</td>
<td>0.785</td>
<td>Cu</td>
<td>0.070</td>
<td>Sb</td>
<td>&lt; 0.002</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td></td>
<td></td>
<td>Pb</td>
<td>&lt; 0.003</td>
</tr>
</tbody>
</table>

crystal of graphite used as a back monochromator;

(iv) hardness measurements under a 300 N force carried out on a Malicet and Blin (Société Malicot et Blin SKF, Ivry-sur-Seine, France) apparatus;

(v) electron microscopy and microdiffraction, in a Jeol 100C at 100 kV. Thin foils were obtained using a Struers device (dual jet electropolishing technique) at 60 V with a current density of 0.2 A cm\(^{-2}\), in a bath kept at -8 °C, and containing 725 cm\(^3\) methyl alcohol, 175 cm\(^3\) ethylene glycol monobutylic ether and 100 cm\(^3\) perchloric acid.

3. Experimental results

3.1. Dilatometric and thermomagnetic analysis

The differential dilatometric curve recorded with \( i/h = 300 \text{ (°C) h}^{-1} \) (Fig. 1) shows the dimensional variations developed in the as-quenched sample. Indeed, it can be noticed that the curve exhibits a slight curvature between 100 and 250°C corresponding to a transient increase of the mean expansion coefficient of the sample. This can be related to the diminution of the residual stresses formed during the prior martensitic transformation. Then from the \( A_{cd} \) point (which is equal to 620 °C for \( i/h = 300 \text{ (°C) h}^{-1} \)) a strong contraction reveals the austenitic transformation until the \( A_{or} \) point (equal to 965°C for this particular \( i/h \)). During the cooling, we only observe the martensitic transformation starting at the \( M_s \) point, at 150°C; this transformation appears by a strong expansion. The \( M_f \) point is slightly higher than 20°C. The use of the \( A_{c} \), \( A_{cm} \), \( M_s \) and \( M_f \) points instead of the \( A_{c}, A_{cm}, M_s \), and \( M_f \) temperature can be justified by the fact that pearlite transformation does not occur in the case of PH 17.4 Mo steel.

The thermomagnetic curve recorded by using the same heating rate is shown in Fig. 2. It only exhibits before the \( A_{eq} \) point an increase of the magnetic intensity mainly beyond 350°C; this behaviour corresponds to a change in the size of the Weiss domains [6, 7] rather than to a change in composition of the martensitic matrix. Therefore the comparison of the thermomagnetometric curve shown in Fig. 2 and those recorded on steels having a different composition of PH 17.4 Mo steel [8] shows that PH 17.4 Mo steel does not contain enough carbon to lead to the formation of \( \epsilon \) or \( \text{Fe}_3\text{C} \) carbides in the martensite. Indeed, no noticeable contraction corresponding to such precipitates was observed for temperatures lower than 300°C on the dilatometric curve shown in Fig. 1. The decrease of the magnetic intensity observed in two successive stages beyond the \( A_{eq} \) point has been related to various phenomena and has been widely analysed in a previous paper [6]. We can briefly summarize it as follows.

Before the \( A_{eq} \) point, precipitation phenomena occurring in the martensitic matrix (discussed in the next section) lead to a heterogeneity in this phase as far as the addition element content is concerned: i.e. \( M_f \) zones are respectively enriched (\( M_{E} \)) or depleted (\( M_{D} \)) in these elements, particularly (Ni + Mo). Beyond the \( A_{eq} \) point, these two sets of martensites transform into austenite in two successive stages according to a decomposition mechanism which is similar to the one occurring in the case of a metastable phase diagram for which diffusion processes take place, according to the relations

1st stage: \( M_{E} \rightarrow \gamma_{DE} + M_{DE}, \gamma_{DE} \)

2nd stage \( M_{D} \rightarrow \gamma_{DDE} + M_{DDE}, \gamma_{DDE} \)

The first decrease of the magnetic intensity observed in Fig. 2 from the \( A_{eq} \) point is reversible and has been