TRANSMISSION ELECTRON MICROSCOPY CHARACTERIZATION OF RADIATION-INDUCED PRECIPITATES WITH HIGH ENERGY IONS IN STABILIZED AUSTENITIC STEELS

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Abstract

In the present work techniques such as Bright Field (BF), Stereomicroscopy, Convergent Beam Electron Diffraction (CBED) and X-ray Energy Dispersive Spectrometry (EDS) were used in order to characterize microstructurally radiation-induced precipitates (RIP) with Ni++ ions irradiation in 1.4970 (Ti stabilized) and 1.4981 (Nb stabilized) austenitic stainless steels at 600 and 650 °C, respectively. The 3.66 MeV Ni++ ions were originally generated in a Tandetron linear accelerator so that the irradiation doses of 360 and 1800 dpa were produced in each steel. Transmission Electron Microscopy (TEM) samples were electrochemically thinned by using the Controlled Depth Preparation technique. For both irradiation doses, a higher number density of RIP was found in the 1.4981 than in the 1.4970. It was also found that most of the RIP correspond with the G cubic phase, fact that was confirmed when computer simulations of dynamical CBED patterns were performed. Most of the RIP shapes are plate-like and its growing crystallographic direction develops mainly along the [011]. Crystallographic and morphological alignment was also found between RIP and matrix (γ phase).

Key words: Radiation-Induced Precipitation (RIP), Convergent Beam Electron Diffraction (CBED), Controlled Depth Preparation, displacement per atom (dpa), Stereomicroscopy.

Resumen

En este trabajo se utilizaron las técnicas de Campo Claro (BF), Esteromicroscopía, Difracción Electrónica de Haz Convergente (CBED) y Espectроскопия de Dispersión de Energía de Rayos X (EDS) para caracterizar microestructuralmente los precipitados inducidos por la irradiación (RIP) con iones Ni++ en los aceros austeníticos 1.4970 (estabilizado con Ti) y 1.4981 (estabilizado con Nb) a 600 y 650 °C, respectivamente. Los iones Ni++ de 3.66 MeV se generaron en un acelerador lineal Tandetron para producir las dosis de irradiación de 360 y 1800 dpa en cada acero. Las muestras estudiadas por Microscopía Electrónica de Transmisión (TEM) fueron preparadas usando la técnica electroquímica de Preparación a Profundidad Controlada. Para ambas dosis de irradiación, hubo una mayor densidad numérica de precipitados en el acero 1.4981 que en el 1.4970. La mayoría de los RIP corresponden a la fase cúbica G, lo cual fue confirmado realizando simulaciones por computadora de patrones de CBED para el caso dinámico. La forma de la mayoría de los RIP es del tipo placa y la dirección principal de crecimiento es a lo largo de la dirección cristalográfica [011]. Se encontró alineamiento morfológico y cristalográfico de RIP con la matriz (fase γ).

Palabras Clave: Precipitación inducida por la irradiación (RIP), Difracción electrónica de haz convergente (CBED), Preparación a profundidad controlada, desplazamiento por átomo (dpa), Esteromicroscopía.

1. Introduction

Since the last two decades a great effort has been done to create materials that can be used as fusion and fission nuclear reactors walls. Two candidates are the 1.4970 and 1.4981 stabilized stainless austenitic steels (see table 1).

<table>
<thead>
<tr>
<th>Steel</th>
<th>Elemental composition (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>1.4970</td>
<td>65.9</td>
</tr>
<tr>
<td>1.4981</td>
<td>63.1</td>
</tr>
</tbody>
</table>
Nowadays, the phenomena of Radiation-Induced Precipitation and Segregation, RIP and RIS, respectively, have been studied mainly when materials are irradiated with protons, neutrons, electrons or ions. RIS allows knowing how the chemical composition is changed, while RIP allows knowing how the crystal structure is changed, including the creation of defects.

Recently, enough research has been done on the chemical composition changes close to grain boundaries of Fe-Cr-Ni austenitic alloys [1-3]. Furthermore, there exists RIS studies in austenitic steels taking into account only the effect of: orientation between grains [2], type of incident particle [4], chemical composition of the alloy [5], temperature variation of the alloy [6] and irradiation dose [7]; however, few works have been done about the crystal structure determination of this kind of precipitates, especially using Convergent Beam Electron Diffraction techniques [8]. A few Selected Area Electron Diffraction (SAD) studies of RIP in steels similar to ours have been reported [9-11], but very few work has been done using CBED [12] and nobody has reported before an experimental and theoretical CBED study of radiation-induced precipitates in steels similar to ours.

Because of the smallness of the precipitation volume fraction in our steels, it was not possible to get X-ray diffraction studies but CBED, which is a more suitable characterization technique for studying the crystal structure of second phases. It was the purpose of this paper to study the microstructure of RIP created under extremely high irradiation doses.

2. Experimental conditions

2.1. Steels preparation for its irradiation.

Specimens of 1×1×0.01 cm³ were cut and mechanically polished using 6, 4 and 2 μm diamond paste, successively. Then, in order to eliminate the possible dislocations, the specimens were annealed in a quartz muffle at 1100 °C for one hour in a vacuum of 10-7 mbar.

2.2. Steels irradiation.

Specimens were irradiated in a GIC Tandetron linear accelerator [13], with 3.66 MeV Ni++ ions, at two different doses, 360 and 1800 dpa. During the irradiation, the 1.4970 and 1.4981 specimens were subjected to 600 and 650 °C, respectively.

2.3. Samples preparation for their observation by TEM.

A Disc Punch was used to cut disks of 3 mm diameter. In order to know the depth of maximum damage in the irradiated specimens, calculations of the generated vacancies profile (see figure 1) were done by using the TRIM (TRansport of Ions in Matter) software [14]. In this way, the irradiated specimen side was electrochemically thinned down to 0.9 μm depth using the Controlled Depth Preparation technique [15]. Finally, covering the thinned side, the disks were electrochemically back-thinned until perforation. In this way, the border of the hole should have an adequate thickness to performance TEM studies.

2.4. Samples observation by TEM.

The samples were studied in a Philips EM-430 (with LaB₆ filament) transmission electron microscope operated at 300 kV. Because of the smallness of the radiation-induced precipitates, these were studied by CBED using a 20 nm diameter electron beam. The samples were observed by using a cooling-holder at −170 °C, which helped to avoid contamination on the sample. The chemical composition study in the precipitates was carried out by Energy Dispersive X-ray Spectrometry (EDS), using a 3 nm diameter electron beam, obtained in a Philips CM20 transmission electron microscope with field emission filament.

3. Experimental results

By Bright Field images, it was observed that in the irradiated steels secondary phases appeared, i.e., precipitates with different shape and size (see figure 2). Because the true morphology of the RIP can not be appreciated on a two-dimensional micrograph, the three-dimensional shape of the radiation-induced precipitates was studied by Stereomicroscopy, and it was found that almost all of them have a plate shape; a few of them are capsule-like. For the same irradiation dose, it was determined that there was a
higher number density of precipitates in the 1.4981 steel than in the 1.4970 as can be compared in the table 2. In the table 3 are indicated the average sizes of the longer part of the precipitates, and it can be appreciated that as the irradiation dose was increased the size of the precipitates increased. In the matrix of all samples were observed dislocations.

Table 2. Number density of precipitates.

<table>
<thead>
<tr>
<th>Dose (dpa)</th>
<th>Number density of precipitates $\times 10^{21}$ (prec./m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.4970 steel</td>
</tr>
<tr>
<td>360</td>
<td>1.5</td>
</tr>
<tr>
<td>1800</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 3. Size of the longer part of precipitates.

<table>
<thead>
<tr>
<th>Dose (dpa)</th>
<th>Size of precipitates (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.4970 steel</td>
</tr>
<tr>
<td>360</td>
<td>80</td>
</tr>
<tr>
<td>1800</td>
<td>183</td>
</tr>
</tbody>
</table>

All precipitates were rich in Ni and Si (see figure 3), however, it must be mentioned that the range of percentages of these elements changed, depending on the shape, i.e., different kind of precipitates; anyway, in the case of 1.4970 steel at 1800 dpa, Ni was not higher than 70 % and Si was less than 30%; while in 1.4981 steel the Ni was not higher than 50 % and Si was less than 25 %.

In both steels and for the two irradiation doses, it was determined, by electron diffraction techniques, that the radiation-induced precipitates correspond to an FCC Bravais lattice, and most of them correspond to G phase. In order to interpret the intensity variation on experimental CBED patterns, computer simulations of dynamical CBED patterns were done using the EMS (Electron Microscopy Simulations) software [16]. In figure 4, experimental and theoretical CBED patterns are compared. As comparing model, we have taken the unit cell of Nb$_6$Ni$_{16}$Si$_7$ with a 11.25 Å lattice parameter reported by Lee [10] and the atom positions (see table 4) obtained indirectly from Villars [18]. Others scarce crystalline phases found in the 1.4970 steel at 360 dpa, were $\gamma'$-phase (see figure 5), CrC and $\eta$ (see figure 6), and, at 1800 dpa, $\text{M}_6\text{C}_2$.  

\[ \text{M}_6\text{C}_2 \]
Fig. 3. Typical EDS spectrum which shows that Ni and Si are the main elements in the radiation-induced precipitates for both types of steels. The chemical composition, revealed by this spectrum, is approximately \( \text{Ni}_{28}\text{Si}_{28}\text{Fe,Cr,Ti,Mo,Mn} \).

Fig. 4. (a) Experimental and (b) theoretical CBED patterns corresponding to G phase (\( \text{Nb}_{6}\text{Ni}_{16}\text{Si}_{16} \)) at [111] zone axis. A thickness of 10 nm and 50 beams were considered for the dynamical simulation (b).

Table 4. Atom positions for the \( \text{Nb}_{6}\text{Ni}_{16}\text{Si}_{16} \) phase.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.378</td>
<td>0.378</td>
<td>0.378</td>
</tr>
<tr>
<td>Ni</td>
<td>0.178</td>
<td>0.178</td>
<td>0.178</td>
</tr>
<tr>
<td>Si</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td>Si</td>
<td>0</td>
<td>( \frac{1}{4} )</td>
<td>( \frac{1}{4} )</td>
</tr>
<tr>
<td>Nb</td>
<td>0.203</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 5. SAED pattern showing weak reflections due to \( \gamma \) phase (primitive cubic lattice) aligned with strong reflections due to \( \gamma \) phase (matrix) FCC. Zone axis: [-112].

Fig. 6. CBED pattern close to \( \eta \) phase structure. This pattern corresponds to a plate-like precipitate in the 1.4970 steel irradiated at 360 dpa. Zone axis: [-223].

Partial coherence of radiation-induced precipitates in the matrix was observed only in the 1.4981 samples. Crystallographic and morphological alignment evidence between precipitates and matrix was found at the [011] precipitate direction, which was also the preferred growing direction (see figure 7).

4. Discussion

By TEM observations it was appreciated a great number of defects in the irradiated steels, mainly dislocations, dislocations loops and partial dislocations. The creation
Fig. 7. (a) SAED pattern taken from the 1.4981 steel irradiated at 360 dpa. Zone axis: [-122]. The weak reflections come from G phase radiation-induced precipitates. The crystallographic relationship is [022]_G : [022]_y'. (b) Dark field image using the 022 weak reflection.

of this kind of defects is fundamental in the formation of radiation-induced precipitates because it is well known that such defects serve as nucleation sites for elements which diffuse and segregate during irradiation.

Thus, dislocation loops as defect sinks, enhance the formation of precipitates because of the selective segregation of elements into them. In this sense, because of the dislocation loops were observed in all samples, it would be expected that new precipitates be formed if the irradiation continued, however, the observation of dislocation loops or faulted primary precipitates in the 1.4970 steel irradiated at 1800 dpa suggests us that either precipitates are in the early stages of growing or they are becoming dissolved into the matrix.

For both irradiation doses, it was determined that there was a higher number density of precipitates in the 1.4981 steel than in the 1.4970. We attribute this fact to a higher quantity of Ni, Si, Mo and stabilizing element in the initial composition of the 1.4981 steel. The elemental composition changes slightly from one precipitate to another. However, every studied radiation-induced precipitate proves to be rich in Ni and Si. It is well know that Ni and Si as subdimensioned elements in stainless steels [25], migrate together with vacancies and sink into dislocation loops or grain boundaries [5], facts that explain well the Ni-Si enrichment in all analyzed precipitates. Also, in all studied radiation-induced precipitates was found the stabilizing element: Ti in 1.4970 steel precipitates and Nb in the ones corresponding to the 1.4981. This might not be favorable for matrix Cr-stabilizing, because Ti and Nb are in the studied steels to form carbides. According to our experimental results it is suggested that the 1.4981 steel could be more hardened than the 1.4970 steel because of the higher number density of precipitates in the former. Differences in number density, morphology, size and crystal phases of radiation-induced precipitates in both types of steels as an effect of the different initial alloying elements has been reported by Lee [26].

For both irradiated stainless steels, it was observed crystallographic and morphological alignment between radiation-induced precipitates and matrix. It was determined that the direction at which precipitates present a major growing is the [011]. This result indicates that the [011] direction is, energetically, the most favorable for the growing and alignment of precipitates. The [011] growing direction of the precipitates indicates that diffusion is taking place along compact planes type (011) in the cubic unit cell of precipitates.

In order to know the atom positions of G phase, we found out in Villars' book [18] that the Nb₆Ni₁₆Si₇ structure is equivalent to that one of the Mn₂₃Th₆, so by searching the atom positions of Mn₂₃Th₆ in Daams' book [17] and taking into account the relative stoichiometric proportions, the atom positions of Nb₆Ni₁₆Si₇ were established. It was possible to get a good match between experimental and theoretical CBED patterns using this model; however, in some cases this matching was not possible. We suspect that chemical composition variations among phases, and locally in each precipitate, could have a very big influence on the observed intensity variation at CBED patterns. Composition variation was confirmed by EDS analyses. More precise and systematic measures in this direction are required to feedback the CBED simulations. More precise and systematic measures in this direction are required to feedback the CBED simulations. It is clear that Nb₆Ni₁₆Si₇ is related to 1.4981 steel and Ti₆Ni₁₆Si₇ would be related to the 1.4970 steel. Although this structure is ternary we think that other elements such as Cr, Mn, Mo and Fe from matrix, might occupy substitution positions in the G phase unit cell.

It has been pointed out that the lattice parameter of the G phase is different from that of the matrix. Such as it was previously indicated, before the irradiation the steels suffered a thermal treatment for eliminating possible defects.
phase is \( a = 11.25 \, \text{Å} \) [10], however, for the \( \eta \) phase different \( a \) values have been reported: 10.7 [9], 10.8 [10], 10.85 [19], 10.95 [20] and 11.08 Å [21], which is not easily distinguished by conventional electron diffraction techniques. For solving this problem, it is known that the HOLZ (Higher Order Laue Zones) lines position at the central disk of a CBED pattern is one of the most precise methods for determining the crystal lattice parameters [22], however, because higher reciprocal lattice layers were weakly excited, the observation of HOLZ lines in our CBED patterns was not possible. Considering the former case, to distinguish between both phases, first we compared the values of the interplanar distances for low zone axis. This gives a good criterion to determine which one of the reported values for both phases is closer to the experimentally determined one. Because the \( \eta \) phase has a \text{Fd}3\text{m} space group, it is supposed that certain reflections should have been absent, however, when this was not the case it was not possible to assure that the reflections corresponded to \text{Fm}3\text{m} space group (G phase) because they might be present due to double diffraction effects. In this case, we got CBED patterns at \([011]\) zone axes and tilted them around the \([001]\) direction, i.e. around the axis that contains the 200 reflection. Thus, as the sample was being tilted, the \([111]\) reflections should have been weaker and the 200 reflection would have disappeared, if the \( \eta \) phase was present;* if the 200 reflection remains excited, this will come from the G phase. This last is true if the electron diffraction maps given by Edington [23] or Spence [24] are used; however, according to our computer simulations of dynamical CBED patterns, this is not always true, changing the disk-disk relative intensity also when the sample thickness and number of beams taken for calculations, are changed.

5. Conclusions

In the 1.4970 stainless steel irradiated at 360 dpa, the RIP were identified as \( \gamma' \), CrC, \( \eta \) and G phases, and at 1800 dpa, as \( \text{M}_{23}\text{C}_6 \) and G phases. In the 1.4981 steel was only determined the G phase for both irradiation doses. In general, in all cases the most plentiful radiation-induced precipitates were identified as the G phase.

Scarce \( \eta \) phase was found as plate-like radiation-induced precipitates, whereas the G phase was found both in plate-like and capsule-like precipitates.

As the irradiation dose was increased in each steel, from 360 to 1800 dpa, it was found that the number density of precipitates decreased: 40% in the 1.4981 steel and 30% in the 1.4970. For 360 dpa, there was a number density of precipitates 4.3 higher in the 1.4981 steel than in the 1.4970.

The chemical composition is lightly different from precipitate to precipitate, however all of them are rich in Ni and Si, and correspond to an FCC Bravais lattice. Acceptable agreement was observed for experimental and simulated CBED patterns, however, for some patterns was not possible to get a good match between their intensities. In such cases, differences in precipitate composition could be affecting the disk-disk relative intensity on CBED patterns and it has to be taken into account for each particular simulation.

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* A similar procedure can be done if the diffraction pattern is obtained at \([013]\) zone axis.