Effects of 10 MeV electron irradiation at high temperature of a Ni–Mo-based Hastelloy

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Abstract

A Hastelloy alloy was irradiated with 10 MeV electrons at 650 °C for 700 h to a total dose of 2 × 10⁻³ displacements per atom (dpa). The microstructure of irradiated and non-irradiated specimens of this alloy were investigated by transmission electron microscopy (TEM). The non-irradiated specimens were analyzed by 3-D atom probe tomography (APT) in a local-electrode atom-probe (LEAP™). TEM analysis before the irradiation detects small precipitates with a mean diameter of 22 nm, which are coherent with the FCC matrix. The number density of these precipitates is \( \sim 7 \times 10^{18} \text{m}^{-3} \). Electron diffraction patterns from these precipitates exhibit superlattice reflections corresponding to the L₁₂ ordered structure. The chemical composition of the precipitates, as measured by APT, is around 75 at% Ni with additions of Al, Ti and Mo. After electron irradiation, small precipitates with an irregular morphology are observed. The number density of these new precipitates about \( 10^{20} \text{m}^{-3} \) is greater than that of the L₁₂ ordered precipitates before irradiation. The L₁₂ superlattice reflections disappear completely, instead diffuse diffraction spots are observed at \( (140)_{\text{FCC}} \), which is attributed to compositional short-range order (SRO). The results are discussed with respect to the influence of the electron irradiation on the morphology and structure of the ordered precipitates.

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1. Introduction

Molten-salt reactors (MSR) are promising next generation nuclear reactors that will be able to not only produce electric power, but also allow for re-burning, deep burning, and nuclear transmuting of radioactive waste [1,2]. Ni–Mo-based Hastelloy alloys are structural materials used in this type of reactor, in which they are subjected to intense irradiation. The irradiation can cause a complete alteration of the microstructure and thereby deteriorate the corrosion resistance and mechanical properties of these alloys. Since atomic exchanges are responsible for the modification or activation of kinetic processes, high-energy particle irradiation, e.g. electron or proton irradiation, can be utilized to induce ballistic as well irradiation-enhanced thermally activated atomic jump processes. Controlled use of such irradiations can be employed to simulate and to analyze specific microstructural changes in detail.

In this short communication, the effects of 10 MeV electron irradiation on a Hastelloy alloy containing L₁₂-type ordered precipitates are reported. These precipitates are important microstructural elements for the desired mechanical properties as needed for the use as reactor materials. Transmission electron microscopy (TEM) and 3-D atom probe tomography (APT) are applied for the initial investigation of the microstructure followed by a TEM analysis after the irradiation.
2. Experimental

A Hastelloy alloy with the nominal composition Ni—11.7 Mo—6.2 Cr—1.5 Fe—0.8 Al—0.5 Ti—0.5 Mn—0.5 Nb—0.15 Si—0.05 Y (wt%) or Ni—7.3 Mo—7.2 Cr—1.6 Fe—1.8 Al—0.6 Ti—0.5 Mn—0.3 Nb—0.3 Si—0.03 Y (at%) was investigated in this study. The Hastelloy specimens were embedded in heterogeneous assemblies into molten fluorides. Details of the sample preparation can be found elsewhere [3]. The material was homogenized at 1100 °C for 1 h and aged at 675 °C for 50 h. Specimens with the dimensions 28 x 28 x 0.3 mm³ were prepared and irradiated with 10 MeV electrons at 650 °C for 700 h at the electron irradiation test facility (EITF) at NSC-KIPT Kharkov at a current density of 1.25 A m⁻² [4]. The total fluence was 2 x 10²³ electron m⁻², which corresponds to a total dose of 2 x 10¹⁰ displacements per atom (dpa) for the investigated irradiation depth.

Before and after irradiation, the microstructure was characterized by high-resolution TEM in a Philips CM30 microscope operating at 300 kV. Thin foils suitable for TEM investigations were prepared by electrochemically jet polishing using a HNO₃–CH₃OH electrolyte. For microchemical analysis, a 3-D LEAP3000 (Imago Scientific Instruments) and 3DAP tomograph (TAP, Cameca) were employed. The specimens for APT and for 3DAP tomography were first cut into rods of 0.2 x 0.2 x 10 mm³. Sharp tips were then obtained by electrolytically polishing in a solution of HNO₃ in methanol at 7 V DC at room temperature. APT and 3DAP tomography analyses were performed at a temperature of ca. 60 K, with a pulse-to-DC-voltage ratio (pulse fraction) of 0.2, and with a pulse repetition frequency of 200 and 1 kHz, respectively.

3. Results and discussion

The influence of a high energetic particle irradiation on the microstructure of such a complicated alloy can only be investigated after a very careful analysis of the initial microstructure before irradiation. For this reason, TEM was used for the investigation of atomic order changes, TEM/EDX for composition determination, and APT for detailed compositional structural characterization. A typical unirradiated microstructure of the Hastelloy alloy after homogenizing at 1100 °C for 1 h and aging at 675 °C for 50h is illustrated by the TEM bright field micrographs displayed in Fig. 1. Fig. 1a shows an image from a region containing grain boundaries. The grain boundaries are decorated by up to 1 μm large precipitates, indicated in Fig. 1a by arrows, with varying compositions of the main elements Ni, Ti, Mo and Y; e.g. Mo₁₉Ni₂₆Ti₄₄, Mo₃₁Ni₁₅Cr₁₀ and Mo₁₆Ni₁₉Y₃₁ as measured by EDX analysis in the TEM. Typical precipitate morphologies within the grain interior are shown in the TEM bright-field image displayed in Fig. 1b. Small precipitates with bright contrast and a mean diameter of 22 nm are homogeneously distributed throughout in the matrix without any obvious correlation with extended microstructural elements such as defect clusters, dislocations, or grain boundaries. The corresponding selected-area electron-diffraction (SAED) pattern of a matrix region containing these small precipitates is shown in the inset of Fig. 1b. The [0 0 1] zone-axis electron diffraction pattern exhibits superlattice reflections, which are generated by the small precipitates embedded in the matrix. The superlattice reflections correspond to the ordered L₁₂ structure. The precipitates therefor are identified as the γ’-phase, which is coherent with the FCC γ-matrix. The number density of the precipitates is about 7 x 10¹⁸ m⁻³. The chemical concentration of the γ’-precipitates is measured by APT tomography with nanometer spatial resolution. Fig. 2a displays a 3-D reconstruction of the analyzed volume with just the Al atoms shown for clarity. The rectangular parallelepiped has the dimensions 63 x 62 x 268 nm³ and contains ~2 x 10⁷ atoms. Two phases appear in the investigated volume: the matrix phase depleted in Al and an Al-rich precipitate phase. It is concluded from their dimensions, circular projection, and dispersion that these precipitates are identical to the L₁₂-type precipitates observed in the TEM image displayed in Fig. 1b. The precipitate number

![Fig. 1. TEM images of a Hastelloy alloy homogenized at 1100 °C for 1 h and aged at 675 °C for 50 h. (a) BF TEM image, large Ni–Ti–Mo–Y precipitates are seen at grain boundaries; (b) DF TEM image of homogeneously distributed small precipitates, which formed in the interior of the grains. The [0 0 1] zone-axis electron-diffraction pattern (inset) exhibits L₁₂-type superlattice reflections.](image-url)
densities measured by APT and TEM are nearly the same. The compositions of the matrix and the precipitates are determined from concentration profiles. In order to reduce the statistical error, the proxigram method [5] is used to obtain the proxigram concentration profiles shown in Fig. 2b, measuring concentration vs. distance from an isoconcentration surface. A concentration threshold of 9 at% Al was chosen for the isoconcentration surface used for the proxigram. This value is the mean value of the Al concentration in the matrix (2.6 at%) and the $\gamma$-precipitates (15.4 at%). The concentration profiles in Fig. 2b demonstrate that the matrix/precipitate ($\gamma$/g) heterophase interface has a chemical width of about 2 nm for Cr, Ti and Al (Fig. 2b), whereas the interface is sharper for Ni (about 1 nm). Additionally, a significant Ni-enrichment is observed at the matrix side of the $\gamma$/g interface (arrow in Fig. 2b). Chromium and Mo partition to the $\gamma$-phase, whereas Al and Ti are strongly enriched in the $\gamma'$ phase. Niobium does not partition between $\gamma$-matrix and $\gamma'$-precipitate phases.

The average composition of the Al-enriched $\gamma'$-precipitates is derived from six precipitates from two different measurements. The $\gamma$-matrix concentration is derived from three data sets measured by 3DAP tomography and APT. The results are presented in Table 1, together with the nominal composition of the Hastelloy alloy. As is seen from Table 1, the measured compositions of the $\gamma$-matrix and $\gamma'$-precipitates are not consistent with the nominal composition of Hastelloy. The Cr and Al concentrations are too large and the Ni concentration is too low. A possible reason for the discrepancies may be the preferential field evaporation of Ni. It is noted that two independent (3DAP and APT) atom-probe tomographs were utilized to measure the concentration of the $\gamma$-matrix

![Fig. 2. (a) Three-dimensional reconstruction of Al-atom positions in a volume $63 \times 62 \times 268$ nm$^3$, obtained by APT using a LEAP$^\text{TM}$ tomograph, of the Hastelloy alloy after homogenizing at 1100 °C for 1 h and aging at 675 °C for 50 h. Several Al-rich L1$_2$-type precipitates appear as circular regions with a high density of Al atoms. (b) Concentration profiles of the main components obtained by the proxigram method [5], using an isoconcentration surface of 9 at% Al.](image)

Table 1
Nominal overall composition of the Hastelloy alloy, of the $\gamma$-matrix and of the L1$_2$-ordered Al-rich $\gamma'$-precipitates (in at%)

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Mo</th>
<th>Cr</th>
<th>Al</th>
<th>Ti</th>
<th>Mn</th>
<th>Si</th>
<th>Nb</th>
<th>Fe</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nom. Compos.</td>
<td>80.2</td>
<td>7.3</td>
<td>7.2</td>
<td>1.8</td>
<td>0.6</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
<td>1.6</td>
<td>0.03</td>
</tr>
<tr>
<td>$\gamma$-Matrix</td>
<td>74.7±0.01</td>
<td>8.4±0.01</td>
<td>10.27±0.01</td>
<td>2.58±0.005</td>
<td>0.72±0.002</td>
<td>0.71±0.002</td>
<td>0.49±0.002</td>
<td>0.18±0.001</td>
<td>1.88±0.004</td>
<td>ND</td>
</tr>
<tr>
<td>$\gamma'$-Precipitate</td>
<td>72.15±0.05</td>
<td>3.9±0.2</td>
<td>1.8±0.01</td>
<td>15.39±0.04</td>
<td>4.03±0.02</td>
<td>0.74±0.01</td>
<td>0.8±0.01</td>
<td>0.18±0.004</td>
<td>0.88±0.01</td>
<td>ND</td>
</tr>
<tr>
<td>Partitioning ratio</td>
<td>1.03</td>
<td>2.15</td>
<td>5.7</td>
<td>0.17</td>
<td>0.18</td>
<td>0.96</td>
<td>0.61</td>
<td>1</td>
<td>2.14</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The quoted uncertainties are the one-sigma standard deviations derived from counting statistics. ND, element not detected.
A transformation of the initial precipitates from L12-type new precipitates by irradiation-enhanced diffusion [8]. LRO by ballistic transport only or to form separate found in Ni3Mo or in Ni4Mo precipitates after irradiation for the Hastelloy alloy after 10 MeV electron irradiation.

The microstructural changes of the alloy after irradiation with 10 MeV electrons at 650 °C for 700 h are as follows: The large precipitates at the grain boundaries remain unchanged after electron irradiation. The small γ'-precipitates with the spherical morphology and L12-ordered long-range order (LRO) are no longer detected. Instead, small precipitates with an irregular morphology are observed. Fig. 3 shows a TEM bright-field image of the irradiated Hastelloy. The number density of these new precipitates (about 10^20 m^-3) is greater than that of the L12-ordered γ'-precipitates found before irradiation.

Most interesting is the fact that the L12 superlattice reflections disappear completely. Instead, diffuse diffraction spots are often attributed to a short-range ordered (SRO) state, since they have been observed in the as-quenched structure and in electron-irradiated Ni–Mo alloys [6,7]. This result suggests an irradiation-induced order transformation of the original L12-ordered γ'-precipitates. The total dose of 2 × 10^-3 dpa is, however, too small to either destroy the LRO by ballistic transport only or to form separate new precipitates by irradiation-enhanced diffusion [8].

A transformation of the initial precipitates from L12-type LRO to (1\frac{1}{2}0)_{FCC} SRO requires a change of the atomic compositional order inside the γ'-precipitates. Such a transformation has been observed in Ni–Mo alloys, where SRO with (1\frac{1}{2}0)_{FCC} superstructure reflections has been found in Ni3Mo or in Ni4Mo precipitates after irradiation [9,10]. The Mo concentration in the investigated Hastelloy alloy, 7.3 at%, is, however, too small to assume the formation of Ni3Mo precipitates. As was shown by the APT analyses, the L12-order in the γ'-precipitates is based on a concentration of about 75 at% Ni, with Al, Ti and Mo additions, considerably enriched in Al, but depleted in Mo, in comparison to the γ-matrix composition. Small changes in composition induced by the electron irradiation, however, may destabilize the L12 order, and thus cause a change of the ordered state. From thermal-aging experiments it is well known that the LRO state of similar precipitates in Ni3Mo-based alloys is very sensitive to the addition of ternary elements, such as Al, Ta, V, or W [11]. Aging in the temperature range between 600 and 800 °C can lead to different LRO states, depending on the ternary element added. In this investigation, a different compositional order appears under electron irradiation as has been found for many binary alloys [8]. At present, we cannot extract the details of the atomic changes involved; however, APT measurements are in progress to determine the local atomic composition in the irradiation-induced transformed precipitates. An interpretation of the present results will be helped by an analysis of the dose dependence of the order-destruction kinetics, which requires measurements of the order and morphology of the precipitates at several sample depths.

4. Summary

A Ni–Mo-based Hastelloy alloy, utilized as a structural material for the accelerator-driven molten-salt reactor, was investigated before and after 10 MeV electron irradiation. The initial specimens were investigated by means of TEM and APT/3DAP. After homogenization and aging of Hastelloy specimens, large Ni-based precipitates at grain boundaries and small intragranular precipitates were detected. The small intragranular precipitates are enriched in Al with an L12-type ordered structure, having an average diameter of about 22 nm and a number density of \( \sim 7 \times 10^{18} \text{m}^{-3} \). After electron irradiation, the L12 superlattice reflections disappear completely, and, instead, diffuse diffraction spots are observed at the (1\frac{1}{2}0)_{FCC} positions, which have been attributed in binary alloys to an SRO state. The transformation is interpreted to be caused by irradiation-induced small local chemical changes that destabilize the L12 LRO that leads to SRO under electron irradiation.

Acknowledgments

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Fig. 3. TEM bright-field image and selected-area electron-diffraction pattern along a [001] zone axis exhibiting diffuse SRO diffraction spots for the Hastelloy alloy after 10 MeV electron irradiation.
References


