Neutron scattering structure studies of materials loaded by high neutron fluence

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Abstract
A dedicated shielding box enabling safe manipulation with highly radioactive specimens was developed in NPI Řež as an auxiliary equipment of neutron diffraction stress/strain scanners. The box was designed to provide the following functions – an easy specimen installation in the hot cells, a remote control of specimen positioning, input and output beam shutters and collimators. Employing this facility, the stress mapping experiments on radioactive components can be realized by means of the current stress/strain scanners. Similarly, the method of small-angle neutron scattering has been advantageously used for studies of evolution of microstructure changes of strongly irradiated steels, however, on a larger scale in comparison with the dimension of the crystal lattice. Several related experimental results are presented.

Introduction

Material properties as e.g. ductility, strength, elasticity, brittleness could be strongly influenced by a radiation damage at a high neutron fluence with a considerable effect on the functional fatigue and operational life of components under irradiation and thermo-mechanical loading. From the safety point of view, very critical items are reactor construction steels and especially the weld joints on the reactor core components. Just the knowledge of evolution of microstructure changes and the residual stress level in the dependence on time and neutron fluence plays a key role for assessment of the component integrity and for an estimation of the operation live. Studies of structure defects as well as the residual stresses in as produced and used components are thus of a great importance. In this way neutron scattering provides unique possibilities of nondestructive testing of such microstructure changes resulting in structure defects and/or residual stresses. The nondestructive neutron scattering methods for scanning of the internal stresses in polycrystalline materials as well as small-angle neutron scattering for studies of inhomogeneities in surrounding homogeneous bulk material have become widely used and the employment of these techniques for material characterization is then very attractive [1]. As the measured effects are relatively small, a special sample environment should be used to avoid unacceptable detector signal coming directly from the radiating samples.

Residual stresses are stresses that are "locked-in" within a material, and can exist without any external load. They are caused by incompatible internal permanent strains. However, they can be generated or modified at every stage in the component life cycle, from original material production to final disposal or can be formed in a material during repairs. Welding is e.g. one of the most significant causes of residual stresses and typically produces large tensile stresses whose maximum value is approximately equal to the yield strength of the materials being joined and balanced by lower compressive residual stresses elsewhere in the component. Therefore, residual stresses or their development brought about by an applied external force are difficult to predict in engineering materials and can have a strong influence on their basic mechanical properties. Residual stresses may reduce the performance parameters or cause failure of manufactured products. The large penetration depth and selective absorption of neutrons make them a powerful tool in nondestructive testing of materials in a rather large depth under the surface. Moreover, neutron diffraction is phase sensitive. Neutron diffraction studies can thus significantly help one to improve the manufacturing quality of engineering components, to optimize their design criteria in applications and to predict their operational life.

A special task represents the determination of residual stresses in highly radioactive samples, which were exposed to neutron fluence for a long time. For this purpose a special
compact shielding box, where the radiated sample is situated, was constructed in NPI Řež. This dedicated facility enables us an easy specimen installation in the hot cells and a remote control of specimen positioning and beam shutters. Employing this shielding box, the strain/stress mapping experiments on radioactive components can be then realized by means of the current stress/strain scanner.

Small-angle neutron scattering (SANS) also belongs to nondestructive experimental techniques widely used for structure investigations of condensed matter. This technique has also its unique advantages. Particularly, SANS enables to distinguish inhomogeneities from a homogeneous matrix consisting of very close elements in the periodic table. Moreover, rather bulky samples (0.1-1 cm$^3$) can be studied due to the low attenuation of neutrons in most materials. SANS scattering is concerned with the measurement of elastic scattering cross-sections in a range of momentum transfer values $Q$ between $10^{-5}$-$10^{-1}$ Å$^{-1}$. The scattering into this momentum space range provides information on size, shape and concentration of inhomogeneities in studied materials within the space size from about 30 Å to 30 μm. However, it is practically impossible to cover this broad Q-range by the only one type of a SANS instrument. While the most common collimator facilities are used in SANS experiments with $Q_{max}>2x10^3$ Å$^{-1}$, double-crystal (DC) nondispersive settings have been proved to be more efficient when higher Q-resolution is required.

**Residual strain/stress measurement by neutron diffraction**

The stresses displace atoms from their original positions in a crystalline material, which in fact result in changes of the interatomic distances, which vary, from those in a stress-free case. The stresses are not measured directly by diffraction techniques, but one measures residual strains, which are then converted to stresses using appropriate moduli. Neutron diffraction along with X-ray diffraction, where angular positions of diffraction maxima are directly bound with the values of lattice constants through the Bragg equation, offers a unique non-destructive technique for investigation of stress fields. Thus, the elastic strains are derived from the change in the lattice spacing of the crystalline material. By translating the specimen through a neutron beam, stresses at different locations can be determined. In fact, neutron diffraction is the only non-destructive and highly accurate method which can facilitate 3-D mapping of residual stress in bulk components.

A crystalline material when placed in a neutron beam of the wavelength $\lambda$, which is comparable with the lattice spacing, gives a diffraction pattern with position for a plane $(hkl)$ defined by the Bragg relation

$$2d_{hkl} \sin \theta_{hkl} = \lambda,$$  \hspace{1cm} (1)

where $d_{hkl}$ is the interplanar spacing (lattice spacing), $\lambda$ the neutron wave-length and $\theta_{hkl}$ is the half of the angle between the incident and the scattered beams (see Fig.1). As for a fixed $\lambda$, the Bragg angle $\theta_{hkl}$ is sensitive only to the change of the lattice spacing $d_{hkl}$, the strain (the strain component) is measured in the direction of the scattering vector, $Q = k_f - k_i$, which bisects the angle between incident and diffracted beams and is perpendicular to the diffracting planes (as shown in Fig. 1). Lattice spacing can be determined from the measured angular position of the diffracted peak (Bragg reflection) by illuminating the specimen with a monochromatic collimated beam of neutrons. If the specimen contains no strain, the lattice spacing is called the strain free (stress free) value for the material and is

![Fig. 1. Schematic illustration of Bragg scattering geometry.](image-url)
denoted by \( d_{0,\text{hkl}} \). In a stressed specimen, lattice spacing is altered and a shift in angular position of the corresponding Bragg peak reflects the elastic strains according to

\[
\varepsilon_{\text{hkl}} = \frac{d_{\text{hkl}} - d_{0,\text{hkl}}}{d_{0,\text{hkl}}} = \frac{\Delta d_{\text{hkl}}}{d_{0,\text{hkl}}} = \frac{\sin \theta_{0,\text{hkl}}}{\sin \theta_{\text{hkl}}} - 1. \tag{2}
\]

Stress \((\sigma_{ij})\) and strain \((\varepsilon_{ij})\) are tensors quantities related to one another by the elastic stiffness tensor \(C_{ij}\), and the elastic compliance tensor \(S_{ij}\):

\[
\sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl}, \quad \text{and} \quad \varepsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl}, \tag{3}
\]

where \(\sigma_{ij}\) and \(\varepsilon_{ij}\) have 9 components, 6 of which are independent, and \(C_{ij}\) and \(S_{ij}\) have 81 components, 36 of them can be independent [2,3]. Essentially, most engineering calculations are based on isotropic continuum mechanics. In this case, \(C_{ij}\) can be written in terms of just two independent elastic components, such as Young’s modulus, \(E\), and Poisson’s ratio, \(\nu\). Consequently, the relationship between stress and strain can be expressed by using the generalized Hooke’s law

\[
\sigma_{ij} = \frac{E}{1 + \nu} \left[ \varepsilon_{ij} + \frac{\nu}{(1 - 2\nu)} (\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}) \right], \tag{4}
\]

where \(i, j = 1,2,3\) indicate the components of main directions.

The neutron strain scanner evaluates the variations of lattice spacing within a sample with a spatial resolution of the order of few millimetres given by the dimensions of the gauge volume. The diameter of the polycrystalline grains should be about two orders of magnitude smaller than the dimensions of the chosen gauge volume, which is geometrically defined by the used optical components (slits, collimators) and scattering angle. The best geometrical choice corresponds to \(2\theta = 90^\circ\). Consequently, if possible the best choice is an intense Bragg peak at \(2\theta\) in the vicinity of \(90^\circ\). Beam parameters of the dedicated diffractometer should be adjusted such that the angular position of the sample reflections could be measured with a precision of 0.01\%. For macrostrain/macrostresses scanning the FWHM of the diffraction profile at a scattering angle of \(90^\circ\) is usually \(< 1.5 \times 10^{-2}\) rad. If the resolution of the instrument is higher (FWHM \(\leq 2 \times 10^{-3}\) rad), even mirostrains/stresses in the plastic deformation region can be investigated on the basis of the peak profile analysis, when the plastic deformation results in a change of the width and the form of the diffraction peak profile. If the strain/stress diffractometer is equipped with a tension/compression rig and a heating system for samples, then, the response of the lattice of the sample under thermo-mechanical load in elastic as well as plastic deformation region can be investigated in situ.
New facility for neutron diffraction studies of residual stresses in highly radioactive materials in NPI Řež [4]

This dedicated facility enables us an easy specimen installation in the hot cells and a remote control of specimen positioning and beam shutters and collimators. Employing this shielding box, the stress mapping experiments on radioactive components can be then realized by means of the current stress/strain diffractometers. In the case of diffraction measurements of residual strains in austenitic stainless steels, the most convenient reflection seems to be 311 reflection due to the linear response of the dependence \( \sigma, \epsilon_{311} \) even beyond the yield point. The schematic sketch of the dedicated shielding box is shown in Fig. 1. The led container body is designed with the effective shielding layer of 16 cm. This shielding capacity would be sufficient to work with irradiated austenitic specimens up to maximum activity of \( 4 \times 10^{12} \) Bq. The internal space of the container is equipped with a linear stage and a specimen holder. Three independent beam shutters and collimators controlled by stepping motors are used for the incident and diffracted neutron beams in transmission and reflection geometry, respectively. The rotating steel collimators provide a circular channel of the diameter of 1 cm. The input and output beam were formed by Cd-masks of a size of \( 3 \times 3 \) mm\(^2\). The strain determined in such a diffraction experiment is then averaged over the gauge volume of \( 3 \times 3 \times 3 \) mm\(^3\). The irradiated specimen in a transport container was delivered into the hot cell of the LVR-15 reactor. Here, the specimen was installed into the experimental container which was afterwards transported directly to the reactor hall and installed at the corresponding spot of the neutron diffraction facility.

### Tab.1 Chemical composition of used steel (wt.%)  

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.031</td>
<td>0.57</td>
<td>1.27</td>
<td>0.016</td>
<td>0.012</td>
<td>17.10</td>
<td>9.30</td>
<td>0.52</td>
<td>0.040</td>
</tr>
</tbody>
</table>

The tested CT specimens were manufactured from the steel A347 weld joint sample. The material sample had been cut from the H4 circumferential weld joint of the BWR NPP core shroud. The CT specimens of notch length of 20 mm were machined to have the crack plane in heat-affected zone of the weld joint (Fig.2). At first, the CT specimen was irradiated in experimental reactor LWR-15 to \( 6.2 \times 10^{20} \) n/cm\(^2\), then tested inside the in-pile reactor water-loop BWR-2. It was supplied the normal BWR water environment of 150–200 ppb oxygen content and conductivity.
bellow 0.3 µS/cm for totally 2200 hours and the hydrogen BWR water environment for 230 hours in the loop. At the same time the specimen was loaded, first using cyclic and then constant load regime. The crack growth rate was measured using potential drop technique. After the tests the specimen was final fractured by fatigue at room temperature in air. The half of the CT specimen containing the base metal was further used for the neutron diffraction experiment. The total specimen activity was determined as 11 GBq.

This neutron diffraction experiment was mainly focused on the feasibility study of the new experimental container. The only one scan of the residual strains near the fracture surface (y = - 6mm) was realized in the radioactive CT specimen. The location of measuring points is shown in Fig. 2. The component of the strain tensor perpendicular to the fracture surface was only examined. For comparison, the reference non active CT specimen treated in the same way except the irradiation in reactor was examined as well. The results of diffraction mapping of residual strains are displayed in Fig. 3a,b. Despite of rather deep scan (6 mm under the fracture surface) both scans show similar peak of tensile residual strains of the same amplitude of $\varepsilon \sim 3 \times 10^{-4}$ located in the vicinity of the crack tip. The localization of the strain maximum is slightly different in both examined specimens, but it can be caused by irregular propagation of the crack tip. Taking into account the corresponding elastic modulus of about 200 GPa, the stress level is roughly estimated as 60 MPa. In the present experiment, a relatively good precision and sensitivity of about $\sim 6 \times 10^{-5}$ in strain determination was achieved. Finally, it can be stated that the application of this technique in evaluation of residual stress level in reactor components in dependence on their operation time and neutron fluence can be very important for assessment of the component integrity and for a support of the operation prolongation.

**Characterization of radiation-induced precipitates in reactor pressure vessel steels by SANS [5]**

Embrittlement of steels exposed to high doses of neutron irradiation essentially reduces the lifetime of reactor pressure vessels (RPV). The degradation of mechanical properties due to the irradiation is closely related to the creation of ultra-fine precipitates resulting from radiation-enhanced diffusion processes in damaged crystal lattice. There are significant differences in the nature of the *radiation-induced precipitates (RIP)* depending on the composition of RPV steels. Measurements by atom probe field ion microscopy (APFIM) and atom probe tomography (APT) show that copper-rich precipitates appear in steels with high levels of Cu after relatively low fluence [6,7]. On the other hand, rather diffuse aggregates of other solute atoms are formed if copper content is low like in the VVER-type RPV steels. These aggregates contain high amount (> 80 at.%) of iron, while the content

![Graph](image-url)
of solute atoms (typically Mn, Si, P and Ni) depends on the matrix composition. In both cases, the radiation-induced features have similar mean radius of about 1 nm and lead to similar embrittlement effects manifested as increase in yield strength, hardness or ductile-to-brittle transition temperature. While APT provides valuable data on composition and inner structure of the precipitates, their mean size or volume fraction can be measured efficiently by SANS. Although the information content of SANS data is too low to describe the complex microstructure of steels in detail, this method has substantial advantage of yielding integral characteristics of the precipitates like volume fraction, mean size or size distribution averaged over macroscopic sample volumes. These statistically representative parameters can be thus directly related to the mechanical parameters characterizing embrittlement. Moreover, magnetic interaction of neutrons with heterogeneities in ferromagnetic matrix permits to determine the ratio of total and nuclear scattering cross-sections (so called $A$-ratio) as an additional parameter, which helps to assess chemical compositions of the precipitates. In this study, we have employed the SANS method to characterize RIP in VVER type steels with varying Cu, Ni and P contents and the western-type steel A533B. From magnetic component of SANS, volume fractions and size distributions of the precipitates assuming their non-ferromagnetic character can be evaluated. Observed differences in radiation sensitivity (i.e. the dependence of RIP volume fraction on fluence) are discussed with the help of measured $A$-ratios and known chemical composition of the steels. The investigated materials included the base metals of the Cr-Mo-V and Cr-Ni-Mo-V steels (used in VVER 440 and 1000 reactors), the Cr-Ni-Mo-V steel alloyed additionally with Cu and P and the IAEA reference steel A533-B. Steel compositions are listed in Tab. 1. More details on composition, sample treatment and results of TEM analysis can be found in.

**Tab. 2. Composition of materials in wt%.

<table>
<thead>
<tr>
<th>steel</th>
<th>sample</th>
<th>V</th>
<th>Cu</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Kh2MFA</td>
<td>A0, A13</td>
<td>0.17</td>
<td>0.46</td>
<td>0.014</td>
<td>2.90</td>
<td>0.07</td>
<td>0.66</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>15Kh2NMFA</td>
<td>D0-D2</td>
<td>0.26</td>
<td>0.59</td>
<td>0.005</td>
<td>2.22</td>
<td>1.27</td>
<td>0.63</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>15Kh2NMFA+Cu</td>
<td>E0, E1</td>
<td>0.17</td>
<td>0.48</td>
<td>0.012</td>
<td>2.06</td>
<td>1.28</td>
<td>0.56</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>15Kh2NMFA+P</td>
<td>F0, F1</td>
<td>0.20</td>
<td>0.34</td>
<td>0.021</td>
<td>2.14</td>
<td>1.27</td>
<td>0.58</td>
<td>0.10</td>
<td></td>
</tr>
</tbody>
</table>

Specimens A0 ... F0 are original non-irradiated materials used for reference. The other samples were irradiated at the light-water research reactor LVR-15 in Řež at temperatures 275 - 300°C. The fluxes and fluence for neutron energies $E < 0.5$ MeV are given in Table 3.

**Tab. 3. Irradiation parameters.

<table>
<thead>
<tr>
<th>specimen</th>
<th>A13</th>
<th>C1</th>
<th>D1</th>
<th>D2</th>
<th>E1</th>
<th>F1</th>
</tr>
</thead>
<tbody>
<tr>
<td>flux [$10^{16}$ m$^{-2}$ s$^{-1}$]</td>
<td>57</td>
<td>57</td>
<td>29.5</td>
<td>34</td>
<td>26</td>
<td>26</td>
</tr>
</tbody>
</table>
fluence $[10^{24} \text{ m}^2]$

<table>
<thead>
<tr>
<th>Material</th>
<th>$A$</th>
<th>$A_{R}$</th>
<th>$A_{I}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>0.6</td>
<td>0.29</td>
<td>0.97</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.15</td>
<td>0.18</td>
<td>0.85</td>
</tr>
</tbody>
</table>

The SANS measurements were carried out at the pin hole SANS instrument in HMI Berlin for two detector distances of 1.1 m and 4 m and mean neutron wavelength of 0.6 nm, resulting in the total accessible range of scattering vector magnitudes (0.2-3) nm$^{-1}$. The specimen magnetization was saturated by horizontal magnetic field of 1.1 T. The size distributions for reference and irradiated samples are shown in Fig. 6. In all cases, RIP can be recognized as the peak at $R \sim 1.5$ nm. This peak is much higher for the materials containing copper (C, E) than for the low-Cu steels. Except for sample D1, the peak position remains roughly the same and the differences in peak integral should therefore correspond to differences in number density of RIP. However, changes in magnetic scattering contrast can also play role. Fig. 7a showing integrated volume fractions of RIP documents the differences in radiation sensitivity of precipitation between different steels. Values of $A$-ratio, $A \equiv 1 + (\Delta \rho M/\Delta \rho N)^2$ fitted for the two populations of precipitates are shown in Fig. 7b. While $\Delta \rho M$ is the same for all non-magnetic precipitates, $\Delta \rho N$ depends on their chemical composition. Differences in $A$-ratios therefore indicate varying chemical composition of the precipitates. Although the $A$-ratio alone is not sufficient for determination of chemical composition, it can help in considering possible role of different solute atoms in formation of RIP. Nuclei with scattering lengths much lower than Fe like V, Mn, Cr or vacancies increase the contrast for nuclear scattering and lead thus to low values of $A$-ratio. On the contrary, nuclei with scattering lengths close to iron like Ni or Cu raise the $A$-ratios.

On the basis of the obtained results we can state that non-irradiated materials are characterized in our results by the population of precipitates in the range of radii between 2 and 20 nm. Obviously, there are also larger precipitates in the steels, but they are not resolved in the $Q$-range of our measurements and contribute only by the Porod background. In the given size-range, vanadium-carbides are known to exist in VVER type steels. Indeed, the low $A$-ratio observed in sample A is close to the value $A = 2.4$ resulting from the composition of VC particles measured by APFIM in [8] and to other SANS results [9]. For the other steels, $A$-ratios are higher and indicate the presence of precipitates with different composition. Possible candidates from those actually observed in RPV steels in this size range are VN and Mo2C precipitates [10]. In the A533 steel (C), the vanadium-carbides cannot form and the average $A$-ratio is thus even higher.

As to the irradiated materials, we have observed much higher volume fractions of RIP in high-Cu steels (C, E) than in the low-Cu ones (A, D, F), though they were irradiated to similar fluence (see Fig. 7a). This is not surprising, as copper is known to contribute to the formation of RIP with the highest enrichment factor. However, the $A$-ratios were much lower than we could expect for Cu precipitates ($A$
Probable explanation is in high level of Mn ( > 30 at.%) and/or magnetisation of these precipitates. Such high Mn content was actually observed by APT in steels with high Cu and Mn levels [11]. The volume fractions were evaluated under assumption that the precipitates are nonmagnetic. While there is persistent controversy concerning the magnetic properties of Cu-rich precipitates [6, 11], this assumption is almost certainly incorrect for RIP in low Cu-steels (samples A,D,F) with high (> 80 at.%) concentration of iron [8]. Consequently, the measured volume fractions can appear lower due to the lower than assumed magnetic contrast. As a possible scenario, let us consider a solute aggregate with composition measured in [8], Fe + 12 at.% Si + 13 at.% Mn and assume 5 % of vacancies in the feature. This composition yields $A = 2.3$ equal to those measured for samples A, D and F provided that the average magnetic moment per Fe atom in the aggregate is by factor 0.7 lower than in the ferrite matrix. True volume fractions would then be higher by factor 4.1 compared to those in Fig. 7.

References

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