

Paramagnetic to ordered magnetic phase transition of He⁺ ions irradiated stainless steel studied by XMCD: A new perspective for early stage detection of defects in solids

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Abstract. X-ray absorption and magnetic circular dichroism measurements have been carried out on stainless steel 316 samples, both before and after He⁺-ion irradiation. It was found that Fe and Cr were both oxidised in the surface layer due to exposure to ambient with the Cr oxidation layer running deeper into the sample. Irradiation with He⁺ ions apparently lead to a change in the chemical composition of the Fe oxide layer, from a more FeO-like to a more Fe₂O₃-like with the presence of some metallic Fe. Most importantly the irradiation process induced a paramagnetic to an ordered magnetic phase transition as revealed by the measurements done in magnetic remanent state. After irradiation no He bubbles were observed in the cross-sectional scanning electron microscopy images.

1. Introduction

The literature about radiation damage of iron based alloys is wide and several excellent reviews [1, 2] and books [3, 4] have extensively treated the topic from a theoretical and experimental point of view. Steels able to resist the extraordinarily hostile environment characterized by high temperatures, high pressures and high neutron fluxes are of paramount importance for the nuclear industry especially for the development of new advanced nuclear reactors and fusion reactors able to satiate the necessities of an energy hungry world. Suitable candidate materials for such applications for high pressure vessels need to be screened. The research in advanced materials has produced a number of new austenitic stainless steels containing for example M(Ti)C or phosphide precipitates able to trap He avoiding the typical swelling and loss of plasticity caused by the microscopic He bubbles produced under neutron irradiation. Also 9Cr martensitic steels with a bcc crystal structure are resistant to damage induced by radiation with the bcc structure clearly more resistant to dislocation with respect to the fcc structure of austenitic steels [2].

In this contest, however, much must be done to investigate the initial phases of defect production. The creation of point defects and the dislocation of the atoms inside the crystal structure are the reasons for the catastrophic changes at a macroscopic level. The investigation of the magnetic properties and in particular the paramagnetic to ferromagnetic transition, frustrated spin glass and anti-ferromagnetic properties in this class of materials is of high interest in order to understand the basic effect of, and definitively to meet the challenges of developing advanced materials resistant to irradiation. In this framework we investigated the possibility to use X-ray magnetic circular dichroism

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(XMCD) to study the magnetic properties of stainless steel 316 before and after irradiation with He⁺ ions.

In this work preliminary results of XMCD measurements combined with scanning electron microscope (SEM) images are presented. Microscopic and spectroscopic techniques together with molecular dynamics simulations give important information about defect creation and the paramagnetic-ordered magnetic phase transitions at an early stage. The atomic specificity and surface sensitivity of synchrotron based spectroscopic techniques give a new perspective in understanding the transformation of irradiated alloys at an atomistic level. The results show the different behavior under irradiation of the individual components of an alloy.

2. Experimental

A few pieces of (1 x 1 cm²) of Stainless Steel 316 (Avesta Polaris) were cut from a larger untreated sheet. The nominal composition of the steel is Cr 17.25 %, Ni 10.1 %, Mo 2.1 %, Mn 2 %, Si 1%, C 0.04 %, N 0.04 %, P 0.03 %, S 0.03 % and Fe is in remanence. The pieces were first polished with 1 micron diamond finish and further polished with 0.04 micron colloidal silica and subsequently cleaned in an ultrasonic bath in ethanol and acetone. The resulting samples are mirror clean and did not undergo any further treatment. One sample has been kept as a reference, while a second sample has been irradiated using a He⁺ plasma (300 W RF), in the MP³ chamber of the Materials Engineering Institute, at ANSTO. During sample preparation the gas pressure was kept at 3×10^{-3} mbar with an estimated dose rate of 0.025×10^{14} ions cm⁻²/s. The total estimated dose was 5×10^{15} He⁺ ions cm⁻². The XMCD measurements were done on beamline 4-ID-C at the Advanced Photon Source, Argonne National Laboratory, USA. Further complementary absorption spectra (XAS) were recorded at the soft x-ray beam line at the Australian Synchrotron in Melbourne.

The 4-ID-C beam line is dedicated to the studies of magnetic properties in the soft-X-ray regime providing left and right circular polarized light. The samples were measured in the high magnetic field end station where large static magnetic fields up to 7T can be applied. The measurements were done by recording the drain current, i. e. the total electron yield (TEY) normalized to the incident photon current as measured from the beam line gold meshes (I₀).

XAS spectra were measured at the Australian Synchrotron using linear polarized light without a magnetic field applied. The signal recorded was the TEY normalized to I₀ from a gold grid located in a separate chamber positioned after the refocusing mirror.

The SEM images were recorded with a Zeiss Supra 55VP field emission instrument operated in high vacuum mode at an accelerating voltage of 20kV. The image is a back scattered electron image at a magnification of 20000x. The sample preparation for the cross-section images involved mounting in a conductive epoxy resin and polished to a 1-micron diamond finish and then further polished to 0.04 micron with colloidal silica. To avoid contamination the samples have been first measured at the synchrotron and then prepared for the SEM.

3. Results and Discussion

The X-ray magnetic circular dichroism (XMCD) measurements have been carried out with an applied continuous magnetic field of 5 T parallel to the incoming beam. The beamline setup allows changing the direction of the polarized light from right to left at each energy point of the energy scan. The dichroic signal has been calculated by subtracting the positive and negative circular polarized light at each point. The result is a very smooth and noise free signal. Measurements were performed using the reverse magnetic field for control purposes. The base pressure in the magnet chamber during the experiment was in the low 10^{-10} mbar, while the temperature of the sample has been kept constant at 155 K. The measurements were done while keeping the sample at 30 degrees to the incoming beam, the energy resolution is of about 0.1 eV.

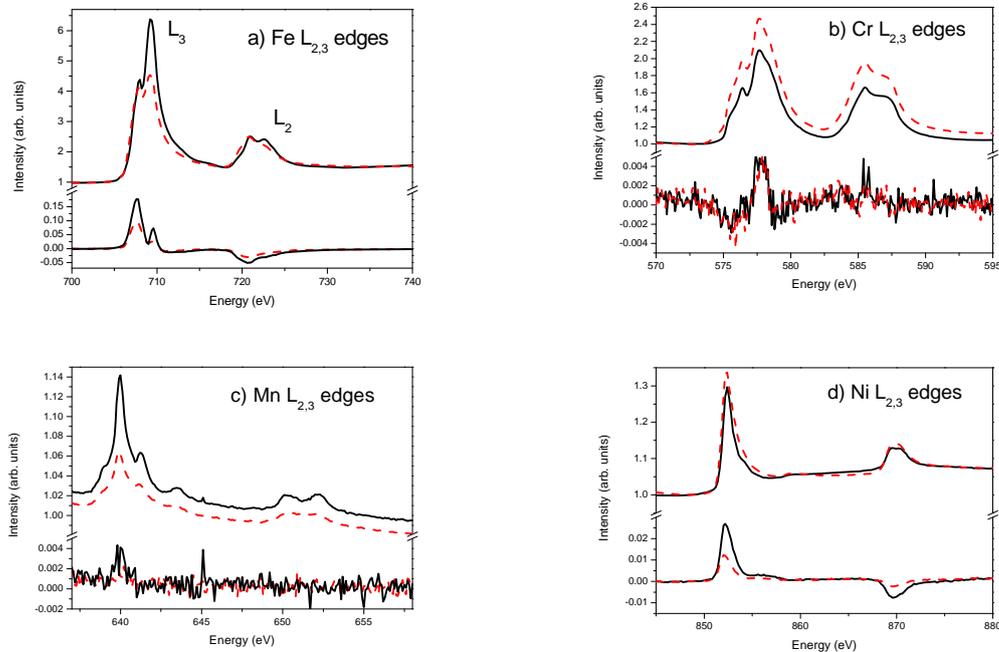


Figure 1. Absorption (top lines) and XMCD (lower lines) spectra of a) Fe, b) Cr, c) Mn and d) Ni. The red dashed curves -non-irradiated samples, black line -irradiated using 5×10^{15} He⁺ ions cm⁻²

In principle, the XMCD signal through the application of the well known sum rules [5, 6] allows the determination of the orbital and spin moment per atom of the heavy 3d metals, Fe, Co, Ni. However, such a feat, obtainable only by this experimental technique, is possible if the samples are oxide free. Only for this narrow experimental case are the assumptions (single electron approximation, edge separation, etc.) of the sum rules valid. The sum rules are not longer valid if traces of oxides with consequent orbital hybridization are present. However, for the purpose of this paper, a comparative study of an irradiated and non irradiated specimen with no damage visible under microscopic investigation is only presented: the calculation of absolute values for the orbital and spin moments is therefore not important. The purpose of this experiment was simply to verify that magnetic dichroism is able to detect differences in slightly irradiated samples and to verify if differences exist between the different metallic components of a multi atomic species system.

The measurements were acquired at the L_{2,3} edges of Cr (570 eV to 600 eV), Mn (630 eV to 660 eV), Fe (700 eV to 740 eV) and Ni (840 eV to 890 eV). Absorption spectroscopy at these edges probes the empty 3d states promoting the excitation of electrons from 2p_{1/2} (L₂) and 2p_{3/2} (L₃) orbitals to the 3d states therefore effectively probing these empty states. The technique in this energy range and in the TEY mode is surface sensitive with a penetration depth of about only 10 nm. The relatively low irradiation energy (20 kV) has been chosen keeping in mind this penetration depth aiming for surface damages.

Figure 1 shows the absorption spectra (upper curves) with the XMCD signal (lower curves) for Fe (figure 1a), Cr (figure 1b), Mn (figure 1c) and Ni (figure 1d). A splitting of both edges in the Fe spectrum can be observed, indicating that the Fe on the surface is oxidised. The presence of oxide has been confirmed by the absorption measurements made on the same sample at the Australian Synchrotron and shown in figure 2a. After irradiation the ratio between the first and second peak at the L₃ edge changes dramatically (see figure 1a), which could indicate that after irradiation the oxide composition is more Fe₂O₃ like, with a prominent first peak and a much higher second peak [7]. While a composition where FeO seems to be predominant where the splitting of the L₃ edge has two peaks of

almost equal intensity [8]. On the other hand the XMCD signal, shown in the lower part of figure 1a, increases after irradiation for both components with a predominance of the signal coming from the first peak suggesting the presence of metallic Fe in the irradiated sample while the non-irradiated sample has a predominance of FeO.

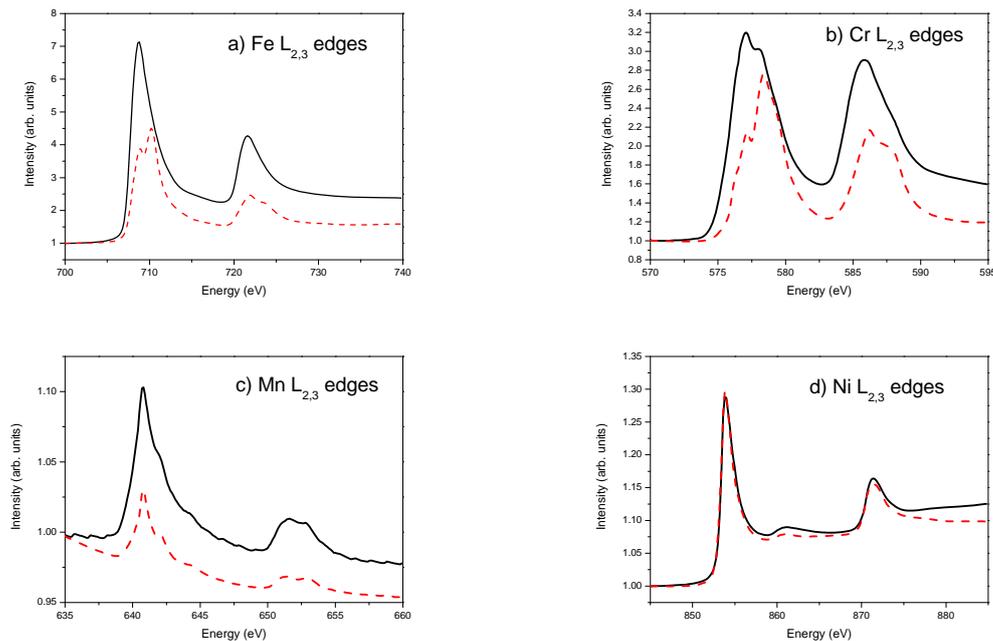


Figure 2. XAS spectra of the non irradiated sample before and after removing the surface layer with a SiC file in-situ. a) Fe, b) Cr, c) Mn and d) Ni. Black line - clean surface. Red dashed line - oxidized surface

Comparing the XMCD signals in figure 1 it can be observed that for the irradiated sample the XMCD signal increases considerably for Fe (figure 1a) and especially Ni (figure 1d). On the other hand the Mn edge (figure 1c) doesn't bare a magnetic moment before irradiation, but the irradiated sample shows clearly a growing magnetic moment in the same direction as for Ni and Fe. At the Cr edge (figure 1b) the situation is different. The edge shows a complex splitting which is a clear indication of an oxidised surface. The white line shape is consistent with the expected Cr_2O_3 - a protective layer for the stainless steel. The XMCD signal in this case remains exactly the same for the irradiated and non-irradiated samples. The shape of the white line as well as the XMCD signal remains the same, perfectly unaffected by the effect of He^+ ion etching of the surface.

All XMCD spectra shown in figure 1 have the same sign, it can be immediately concluded that the magnetic moments of all the steel metallic components are oriented in the same direction with the XMCD signal always positive at the L_3 edge followed by an inversion at the L_2 edge.

The magnetic measurements were all performed on a surface exposed to normal ambient conditions and evidently oxidized. To clarify this point a few microns of the surface layer were removed in-situ with a silicon-carbide (SiC) instrument (base pressure 2×10^{-10} mbar) in the end station of the soft x-ray beam line at the Australian Synchrotron. After removing the sample surface edge splitting disappears and a clear Fe metallic signal can be recorded. The results are shown in figure 2a. The white line of Fe (figure 2a) clearly changes from fully oxidised to metallic, while Cr (figure 2b) even

after scratching retains a certain degree of oxidization, suggesting that the oxide layer of Cr runs deep in the surface by more than a few microns. The shape of the white line of Mn and Ni (figure 2c and 2d) remains the same, suggesting that in stainless steel 316 almost no oxidation occurs for these two components at the surface even if for the Ni a slightly broader L_2 -edge and a very small energy shift at L_3 can be observed for the non scratched sample (see figures 1d and 2d).

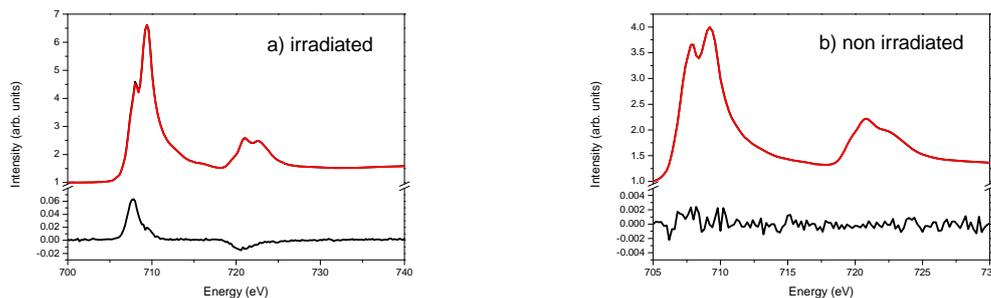


Figure 3. Absorption and XMCD at the Fe $L_{2,3}$ edges measured in remanence for: a) irradiated stainless steel 316, b) non-irradiated stainless steel 316.

The most significant result is concerned with the measurements performed in remanence. After measuring the sample with the 5T applied field the magnetic field was removed and again the XMCD signal measured. While the irradiated sample shows a signal about half the signal intensity recorded under 5T magnetic field, as can be seen in figure 3a, the non irradiated sample doesn't have any residual magnetic moment (figure 3b). Therefore, we can conclude that under irradiation the Fe component made a transition from a paramagnetic to a magnetic ordered phase. It is also interesting to note that the magnetic signal is only coming from the first peak, probably related to Fe_2O_3 or to a large fraction of non oxidised Fe atoms, while the second XMCD peak can be seen just as a small shoulder. The Ni edge also shows a transition from paramagnetic to magnetically ordered state however the signal in this case is less than 1/3 of the original. This fact could suggest that the Ni magnetic moment is induced by the magnetic order shown by Fe. Further experimental and theoretical investigation will be necessary to clarify this point. Mn and Cr are not magnetically ordered and the XMCD signal disappears after removing the applied magnetic field.

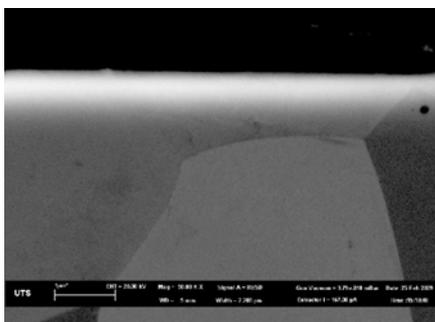


Figure 4. SEM picture of the cross-section of the irradiated 316 stainless steel, no He bubbles or defects are visible with the 1 micron resolution. The single grains of different orientation are clearly visible.

In general the irradiation of a steel surface opens cavities, He is not soluble in the steel and bubbles of He have been consistently observed after neutron irradiation coming from (n, p) and (n, α) reactions. While little or no difference at all can be observed in the SEM images of the surface of the irradiated and non irradiated samples, it is very interesting that the sample section showing the surface of the irradiated sample doesn't show any He bubbles or near surface damages in the 1 micron range as is evident in figure 4. In this figure a rounded edge can be observed, which is an effect of polishing.

The observed magnetic ordering could be easily ascribed to the creation of vacancies at the Fe sites with the presence of a ferromagnetic Fe₂O₃ γ -phase or more in general to the presence of Fe with an unfilled 3d electron shell. This shell in general is known to have a character in between a collective, non-magnetic and localized, magnetic shell. The magnetism of the Fe atoms in this case could be related to the electronic localization. The presence of point defects created by the irradiation favors localized electrons and further increases the magnetic moment of the neighbor atoms. Although the XMCD signal is proportional to the total magnetic moment in an oxidized system it is not possible to calculate the spin and orbital moments absolutely. However, it should be possible to estimate the number of point defects created by irradiation. This could be done considering the proportionality between the area of the XMCD signal and the total magnetic moment. Starting from the hypothesis that no point defects exist for the non-irradiated samples, as can be demonstrated by not having a XMCD signal in remanence, the signal observed in the remanent measurements is then directly proportional to the number of defects created by the irradiation. In this way it should be possible to experimentally establish the number of point defects created under certain irradiation conditions. The theoretical development is beyond the scope of this paper and this point will be further explored in future publications.

4. Conclusion

Stainless steel 316 samples were irradiated by He⁺ ions at a dose of 5×10^{15} ions cm⁻². Both the irradiated and non-irradiated samples were studied using X-ray absorption spectroscopy, X-ray magnetic circular dichroism measurements and scanning electron microscopy. The measurements revealed that He⁺ ion irradiation induced a paramagnetic to a magnetic ordered phase transition in the stainless steel sample. The study also suggests that it is possible to deduce the number of defects, induced by ion irradiation, from the XMCD results.

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