

CRYSTAL STRUCTURE AND LATTICE DYNAMICS OF HYDROGEN-LOADED AUSTENITIC STEEL

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We investigated the crystal structure and hydrogen vibrations in a hydrogen-loaded AISI 310 type austenitic steel (Fe-25Cr-20Ni) by neutron diffraction and inelastic neutron scattering. The samples with hydrogen content of H/Me = 0.43 and 0.93 were prepared in a hydrogen gas atmosphere at pressures up to 7.0 GPa. This doping procedure yields a more homogeneous hydrogen distribution within the sample than cathodic charging and allows clarifying the role of the concentration gradients and stresses on the phase transformation. Only fcc phase with increased lattice parameter was observed in both samples, however vibrational spectra show a modification of the broad peak at H/Me = 0.43 into two components, one at higher H content.

1. INTRODUCTION

After cathodic charging, ϵ_H -martensite is formed in the austenitic steels, which disappears after outgassing in the stable steels. In unstable austenitic steels during ageing of the hydrogenated samples, ϵ_H -phase vanishes while α' -martensite appears [1, 2]. It is common for the cathodic charging at low temperatures to produce strong gradients of the hydrogen concentration and consequent stresses near the surface. Therefore, phase transformations observed during the hydrogen loading could be connected as well with these stresses. The loading of the samples in the hydrogen gas atmosphere at high pressures and elevated temperatures yields a more homogeneous hydrogen distribution within the sample. However the data for the hydrogen-induced phase transformations obtained so far in such samples are contradictory. In Ref. 3, the x-ray diffraction (XRD) patterns of AISI 310 and 304 type steels charged with hydrogen at 70 MPa and 573 K show small $(10\bar{1}0)$ and $(10\bar{1}1)$ peaks of ϵ_H -phase. At the same time in Fe-18Cr-10Mn-16Ni steel loaded with hydrogen at a substantially higher pressure of 7 GPa and the same temperature, the reflections of ϵ_H -phase have not been observed in XRD patterns taken at 173 K [4]. While in Ref. 3, the hydrogen content was rather low (≈ 0.25 at.%), in Fe-18Cr-10Mn-16Ni steel, the hydrogen content was about 37.5 at.%, which is comparable with the hydrogen content achieved by electrolytic hydrogenation.

In the present study, we investigated the crystal structure and hydrogen vibrations in AISI 310 type austenitic steel by neutron diffraction (ND) and inelastic neutron scattering (INS). Samples were doped with hydrogen at elevated temperature in a hydrogen gas atmosphere at pressures up to 7 GPa. In steels of this composition, cathodic hydrogen charging leads to the formation of ϵ_H - and, probably, γ_H -phases [1-3]. So far, ND and INS studies were performed on austenitic steels of similar composition only at low hydrogen contents of 0.3 at.% [5].

2. EXPERIMENTAL

The samples were prepared from the commercially produced AISI 310 type austenitic stainless steel, received as cold-rolled foil 0.25 mm in thickness. Alloy composition supplied by the manufacturer is the following (in wt.%, Fe - balance): 24-26 Cr, 19-22 Ni, <0.5 Mn, <1 Si, <0.05 C. The samples were loaded with hydrogen by exposing 8 mm diameter discs of the alloy to a temperature of 620 K and a hydrogen

pressure of 2.3 or 7.0 GPa for 24 hours followed by cooling under pressure to 120 K. Then samples were placed in liquid nitrogen, where they were stored until the neutron scattering experiments.

The neutron diffraction experiments on Fe-25Cr-20Ni steel were performed with instrument E9 at the Hahn-Meitner-Institut, Berlin, using neutrons with a wavelength of 0.1307 nm. The sample charged at 2.3 GPa consisted of a stack of 6 discs. The sample charged at 7.0 GPa consisted of 3 discs. During hydrogen loading it was broken into pieces and was wrapped in an aluminium foil. To prevent the outgassing of hydrogen, the measurements have been carried out at 80 K. Samples were placed in a cylindrical container made of vanadium foil of 0.25 mm thickness. Discs were aligned to be parallel with the plane of experiment determined by wave vectors of incident and scattered neutrons. In order to get information about possible texture in the samples and to average effects of the texture, each measurement was divided into 18 individual scans with different sample orientations (between -90° and $+90^\circ$ with respect to the incident neutron beam).

The inelastic neutron scattering spectra of the same samples were measured at NIST Center for Neutron Research at the National Institute of Standards and Technology, Gaithersburg with the Filter Analyzer Neutron Spectrometer (FANS) in the Be-graphite-Be filter mode (cut-off filter energy of ≈ 1.8 meV). The energy-loss spectra were obtained for incident energies ranging from 50 to 200 meV with 48 detectors at scattering angles between 40 and 115 degrees and with a Cu (220) monochromator. The energy resolution was about 6.7 meV full width at half maximum at $\hbar\omega = 130$ meV ($\hbar\omega$ is the neutron energy loss). The measured spectra were normalised to the counts of a monitor mounted before the sample. Thus, both changes in the incident neutron flux and the energy dependence of the detector efficiency were taken into account and the measured spectrum is essentially a hydrogen-amplitude-weighted vibrational density of states. Data from the hydrogen-doped samples placed into a flat aluminium container were taken at 80 K. The spectrum of the hydrogen-free sample measured in the same container was used as background to obtain the scattering intensity from the dissolved hydrogen.

3. RESULTS AND DISCUSSION

3.1. Crystal structure

The diffraction spectra of the initial steel and steel charged at 2.3 GPa show reflections corresponding only to the fcc crystal lattice (Fig. 1). Spectra of the sample charged at 7.0 GPa shows also peaks originating from an aluminium foil. With increasing hydrogen content, an increase in the background, associated mainly with incoherent scattering from hydrogen, is clearly seen.

The ND data were analysed using the FULLPROF program for Rietveld refinement [6]. The calculated diffraction patterns and the results of the Rietveld refinement are shown in Fig. 1 and Table 1. Increasing hydrogen content is accompanied by a continuous shift of the reflections corresponding to lattice expansion without the occurrence of phase transformations. The analysis of the uncharged steel sample revealed that a weak texture is apparent with (111) as the predominant orientation.

Table 1: Results of the Rietveld refinement of the diffraction patterns of Fe-25Cr-20Ni austenitic steel doped with hydrogen at hydrogen gas pressure P_H .

H ₂ pressure, P_H , GPa	Unit cell parameter, Å	Hydrogen occupancy	R-factor
Initial state	3.5818(1)	-	5.6
2.3	3.6564(2)	0.43(4)	3.9
7.0	3.7771(3)	0.92(6)	2.8

Hydrogen is known to occupy the interstitial sites of metal lattices due to its small atomic radius. For the sample charged at 7.0 Gpa, the data analysis revealed that hydrogen occupies only the octahedral sites. The hydrogen occupancy was refined to be 92% ($\pm 6\%$). For the sample charged at 2.3 Gpa, hydrogen occupancy was found to be about 43% ($\pm 4\%$) assuming that hydrogen occupied only the octahedral sites. The experimental data could not be described for hydrogen occupying only the

tetrahedral sites. The ratios of the obtained values for the hydrogen occupancies of both samples are in good agreement with estimates based on the increase in the lattice parameter and the increase of the background levels as functions of the hydrogen content.

This sample appears to be ferromagnetic after hydrogen loading (pieces of the sample cling to steel tweezers). Narita, Altstetter and Birnbaum [3] observed the increase of magnetic permeability, which is a measure of the volume fraction of ferromagnetic phases, in 310 and 304 steels due to the formation of ferromagnetic α -phase and γ_H -hydride-like phase. However, our measurements do not show noticeable magnetic contribution to the intensities of the reflections from Rietveld analysis. Moreover, no other phases except the fcc austenitic phase were observed.

3.2. Vibrational energy spectra

Fig. 2 shows INS spectra taken at 80 K from the Fe-25Cr-20Ni stainless steel samples with hydrogen contents $H/Me=0.43$ and 0.93 . The broad peak at ≈ 120 meV in both samples results from the hydrogen vibrations. Additionally, the INS spectra exhibit extra scattering intensity in the energy range between 70 and 90 meV due to some H_2O ice accumulating on the sample during loading into the sample cryostat.

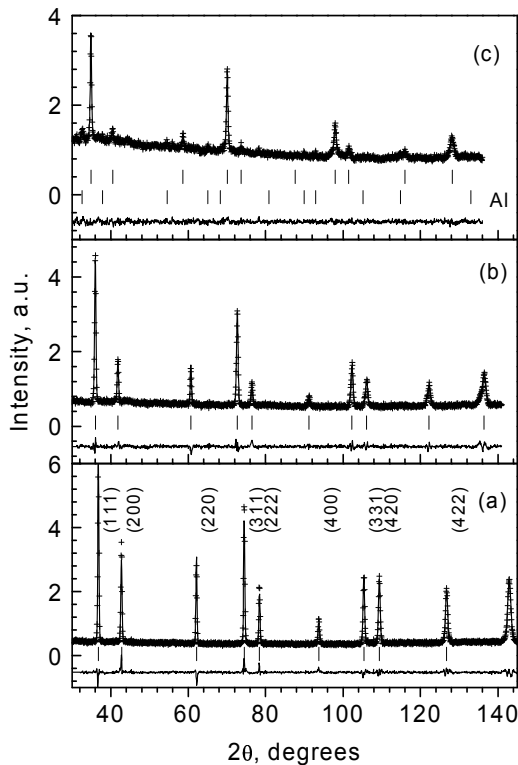


Fig. 1 Diffraction patterns of Fe-25Cr-20Ni alloys doped with hydrogen: (a) initial steel, (b) doped at 2.3 GPa and (c) doped at 7.0 GPa.

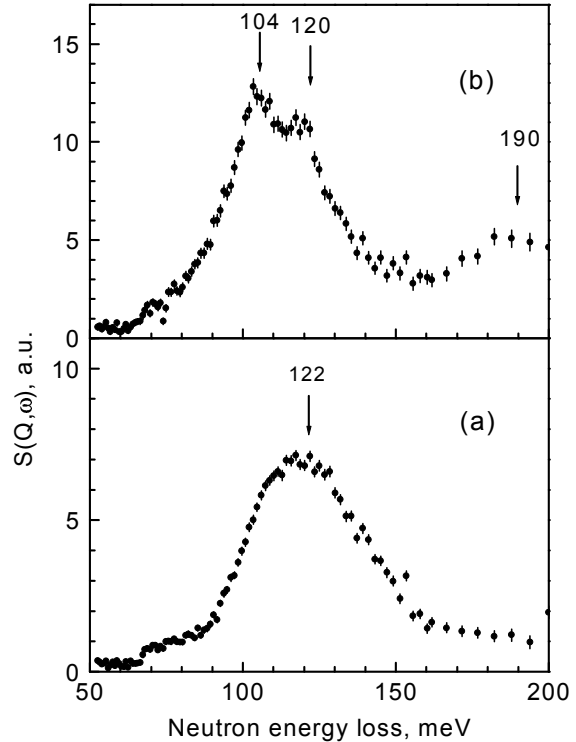


Fig. 2 The dynamical structure factor of Fe-25Cr-20Ni steel doped with hydrogen: (a) doped at 2.3 GPa and (b) doped at 7.0 GPa.

The energy of the hydrogen peak in the sample with $H/Me=0.43$ (≈ 122 meV) is higher than in the sample with $H/Me=0.93$ (≈ 113 meV), which reflects the decrease of the H-Me interaction with increasing lattice parameter (Table 1). The widths of the hydrogen peaks are comparable in the both samples (42 and 46 meV), but the peak structure is essentially different. At higher hydrogen content, the hydrogen peak has a two-component structure with two maxima at 104 and 120 meV. In addition, the increase in intensity observed near 190 meV is probably related to the second harmonics of the fundamental vibration of the hydrogen atoms with the mean energy of ≈ 113 meV. The splitting and

broadening of the hydrogen peak could be explained as the result of the dispersion of the optical phonon branches as was found in $\text{MnH}_{0.41}$, $\text{NiH}_{1.05}$ and $\text{PdH}_{0.99}$ fcc hydrides [7]. An alternative reason for the splitting of the hydrogen peak could be phase transformations, however it should be excluded because our ND data show only fcc phase in both samples within the accuracy of the experiment and analysis.

The hydrogen peak in the sample with $\text{H/Me}=0.43$ does not show pronounced structure and is very similar to the hydrogen spectra measured in the same Fe-25Cr-20Ni steel at much lower hydrogen content of 0.33 at.%. In this sample, the energy of the hydrogen peak at 80 K was found to be 132.5 ± 0.4 meV with a peak width of 32.0 ± 1.0 meV [5]. As mentioned above for the high concentrations, the widths can be related to dispersion from H-H interactions. This explanation fails in the case of the lowest concentration, so that the broadening and the smoothing of the hydrogen peak in this case must probably be connected with the Me-H force constant disorder in the present multi-component alloy.

Thus, exclusive of the structure of the hydrogen peak at hydrogen contents close to $\text{H/Me}=1$, there are no drastic differences in the position and width of the hydrogen peaks for the broad range of hydrogen concentrations. On going from $\text{H/Me}=0.93$ to 0.43 and then to $\text{H/Me}=0.003$, the spectra shift to higher energies with modest decreases in the peak width. These continuous shifts taken together with the presented diffraction data show that there is no evidence for a miscibility gap in the phase diagram. A large number of publications report on the appearance of other phases on hydrogenation using cathodic charging. This may suggest that the other phases are not due to the sole presence of the hydrogen but caused by elastic stresses that necessarily exist in the course of electrolytic hydrogen doping.

Conclusion

Samples of Fe-25Cr-20Ni steel hydrogenated in high-pressure cells have been investigated by neutron diffraction and inelastic neutron scattering. Increasing hydrogen contents causes a continuous expansion of the fcc lattice without the occurrence of phase transformation. Rietveld analysis shows that hydrogen occupies the octahedral interstitial sites. The occupancies in the samples doped at hydrogen gas pressures of 2.3 and 7.0 GPa were refined to be 43% and 92%.

The hydrogen vibrational energies in an fcc Fe-25Cr-20Ni stainless steel alloy with $\text{H/Me}=0.43$ and 0.92 were found to be 122 and 113 meV. The decrease of the hydrogen energies with increasing hydrogen content was without drastic differences in the width of the hydrogen peaks within the broad range of the hydrogen concentrations. In agreement with the diffraction data, this shows that hydrogen precipitation is unlikely.

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