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The influence of interstitial impurities on temperature ranges of deuterium retention in austenitic stainless steel 18Cr10NiTi

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ABSTRACT

The influence of nitrogen, oxygen and helium on the temperature range of deuterium retention in 18Cr10NiTi stainless steel (of AISI304L type) has been investigated. It is demonstrated that the introduction of oxygen, nitrogen or helium into 18Cr10NiTi steel extends the upper limit in the high-temperature range of deuterium retention. It has been found that for 18Cr10NiTi stainless steel, pre-irradiated with helium ions, the increase in the temperature range of deuterium retention occurs in steps: on attainment of helium concentration of ~0.5 at.% He the temperature range increases by ~100 K, and on attainment of helium concentration of ~2.5 at.% He the temperature range increases by ~350 K. The introduction of oxygen into 18Cr10NiTi stainless steel results in the increase of the temperature range of deuterium retention in the direction of rise in temperature. In the deuterium thermodesorption spectrum, this manifests itself by the occurrence of an additional low-amplitude peak with the maximum temperature $T_m \sim 560$ K. The introduction of nitric impurity into 18Cr10NiTi stainless steel results in the extension of the temperature range of deuterium retention towards higher temperatures.

1. Introduction

As a constructional material for vessel internals of fission-type reactors WWER-1000, preference has been given to stainless steel 18Cr10NiTi, where the accumulation of hydrogen was neglected owing to its evolution at temperatures lower than the working temperature of the reactor operated at ordinary conditions. Garner et al. [1] have found the hydrogen retention in SS316 stainless steel exposed to reactor environment at temperatures exceeding the working temperatures. There is evidently no unambiguous explanation that can be offered now for this rather complicated and multilateral phenomenon. An enhanced bond of hydrogen dissolved in 18Cr10NiTi steel may be due to its interaction with transmutation elements (including helium), interstitial and substitutional impurities, vacancies and their complexes, dislocations and their pile-ups, grain and subgrain boundaries, phase constituents, etc. The present paper is concerned with the thermodesorption spectrometry studies into the influence of nitrogen, oxygen and helium on the temperature ranges of deuterium retention in 18Cr10NiTi austenitic stainless steel.

2. Experimental

The 18Cr10NiTi austenitic stainless steel samples, $10 \times 5 \times 0.15$ mm^3 in size, were fixed on the substrates (made of the same steel, ~0.3 mm in thickness), which simultaneously served as ohmic heaters. Prior to irradiation, the targets were subjected to a short-time (1 min) annealing at a temperature of ~1350 K in vacuum $\sim 2 \times 10^{-5}$ Pa in order to degas the specimen and to remove impurities from its surface.

The interstitial impurities were introduced into the 18Cr10NiTi steel specimens by implanting 28 keV N_2^+ or O_2^+ ions at a temperature of ~300 K to doses ranging from 3.5×10^{16} N/cm^2 to 1.8×10^{17} N/cm^2 and from 1.1×10^{17} to 2.3×10^{17} O/cm^2. Helium implantation into 18Cr10NiTi steel specimens at a temperature of ~300 K was carried out by successive bombardment with ions of two different energies. This provided a uniform saturation with helium in a depth range of 110–220 nm, first by exposure to the ion beam with $E \sim 70$ keV to doses between 5×10^{15} and 1×10^{17} at. He/cm^2, and then by exposure to the beam with $E \sim 30$ keV to a dose being 0.7 of the original value. The helium concentrations in the layer for the mentioned dose range were calculated to vary from 0.5 to 10 at.%. The energy values were chosen with due regard for helium depth profiles computed by the use of the program TRIM [2] for nickel.

As the impurity ion concentration reached the assigned value, the specimen was cooled down to a temperature of ~140 K, and

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then deuterium was introduced by ion implantation, the exposure dose being the same for all the specimens, namely, 1.0 or 1.5×10^{16} D/cm^2. The given diagnostic deuterium implantation dose corresponds to the phase of deuterium solid solution in the 18Cr10NiTi stainless steel and, therefore, exerts no influence on the metal structure. Deuterium was implanted with the use of the D_2^+ ion beam having an energy of 14 keV and a current density of ~5 μA/cm^2. After irradiation, the specimens were heated up to a temperature of ~1700 K at an average rate of ~5 K/s. In the course of heating, the deuterium retention under dynamic conditions was recorded by the mass-spectrometer set for the masses 4 D_2^+. The temperature variations during heating were measured by means of a chromel–alumel thermocouple fixed to the specimen.

3. Results and discussion

It has been demonstrated in [3] that a preliminary implantation of helium into 18Cr10NiTi steel leads to the formation of traps capable of retaining hydrogen in the temperature range between 500 and 900 K. In this case, the implanted hydrogen first fills the highest-temperature trap of all available ones, and only after its occupation, it fills the trap having the temperature higher than the remaining traps. So, with an increasing dose of implanted hydrogen there occurs a successive occupation of progressively lower-temperature traps, this leading to the development of hydrogen thermodesorption spectrum in the direction of temperature drop. Obviously, having chosen a low deuterium implantation dose from the thermodesorption spectrum as a test dose, it is possible to estimate the upper limit in the temperature range of deuterium retention in 18Cr10NiTi steel, and this was just done in the present work.

Fig. 1 shows the thermodesorption spectra of deuterium implanted in 18Cr10NiTi steel to a dose of 1×10^{16} D/cm^2. It can be seen from the figure that the upper limit of deuterium retention is dependent on the dose (concentration) of implanted helium. At the same time, as certain helium concentrations are attained with an increasing implantation dose, the rise in the temperature range of deuterium retention occurs in steps, by degrees of 100–350 K. In the helium concentration range under study two such steps are observed: one – in the 0.5–2.4 at.% He range (the temperature range of deuterium testing dose retention is extended from 470–620 K, and, respectively, the maximum temperature of the highest peak is $T_m \sim 530$ K), and the other step is observed in the 2.5–6 at.% He range (the temperature range of deuterium testing dose retention is extended from 500 to 900 K, and the maximum temperature of the highest peak is $T_m \sim 760$ K).

Fig. 2 gives the most typical curves of implanted deuterium retention from 18Cr10NiTi stainless steel samples, which have been preimplanted with nitrogen ions. With an increase in the nitrogen interstitial impurity content the temperature range of deuterium retention in 18Cr10NiTi steel is extended up in temperature. Curve 1 corresponds to deuterium retention from the sample not irradiated with N_2^+ ions, i.e., gives an idea of deuterium retention and release from steel samples in the absence of the nitrogen interstitial impurity. In this case, the spectrum exhibits one peak of gas release with the maximum temperature $T_m \sim 410$ K. Deuterium retention begins at a temperature of ~330 K and is completed at ~600 K.

The introduction of nitrogen interstitial impurity at a level of 3.5×10^{16} N/cm^2 results in the peak spreading and the extension of gas release range up in temperature (curves 2 and 3). A further increase in the nitrogen dose up to ~6.5×10^{16} N/cm^2 and ~1.1×10^{17} N/cm^2 has manifested itself in the change of the deuterium thermodesorption spectrum appearance, i.e., the spectrum now represents a complicated structure with poorly resolved, at least, two peaks. According to the investigations on the N–Ni system [4,5] in this dose range a formation and growth of nickel nitride take place. There is a good reason to believe that such kind of the spectrum (curves 4 and 5) may be due to the formation and growth of nitride components in 18Cr10NiTi stainless steel. The thermodesorption spectrum of implanted helium from the steel pre-irradiated with nitrogen ions to a dose of ~1.8×10^{17} N/cm^2 (curve 6) is qualitatively different from the previous spectra. It shows two well resolved peaks and an extended region of deuterium (substrate) retention between them. It can be assumed that the peaks observed in the deuterium thermodesorption spectrum are attributed to: (i) deuterium release from 18Cr10NiTi steel without any nitrogen interstitial impurity (peak with the maximum temperature $T_m \sim 410$ K); (ii) deuterium release from the

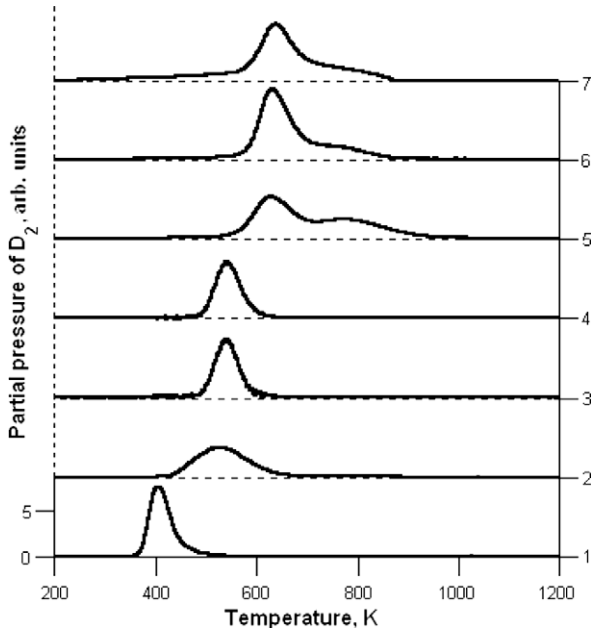

Fig. 1. Thermodesorption spectra of deuterium implanted into 18Cr10NiTi steel to a dose of 1×10^{16} D/cm^2 versus preimplanted helium concentration. 1 – 0; 2 – 1; 3 – 1.7; 4 – 2.4; 5 – 2.53; 6 – 4.5; 7 – 6 at.% He.

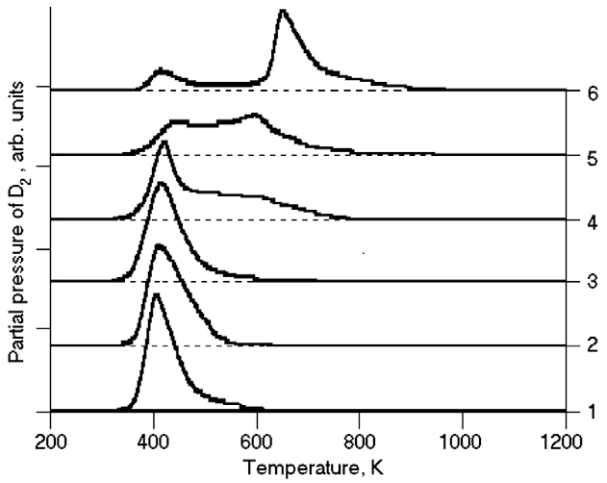

Fig. 2. Thermodesorption spectra of deuterium implanted into 18Cr10NiTi steel to a dose of ~1.5×10^{16} D/cm^2 versus preimplanted nitrogen concentration. 1 – 0; 2 – 3.5×10^{16} N/cm^2 (~10 at.% N); 3 – 5×10^{16} N/cm^2; 4 – 6.5×10^{16} N/cm^2; 5 – 1.1×10^{17} N/cm^2 (~30 at.% N); 6 – 1.8×10^{17} N/cm^2.

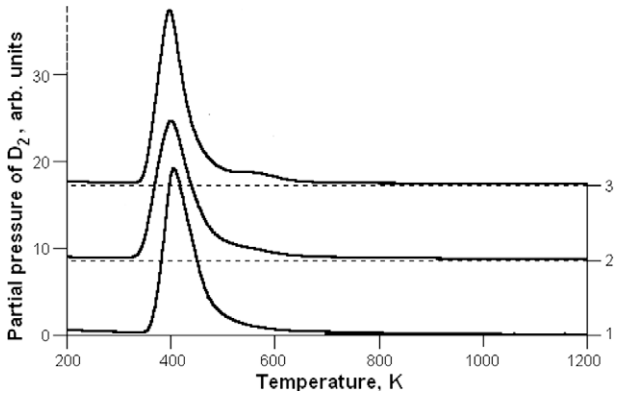

Fig. 3. Thermodesorption spectra of deuterium implanted in 18Cr10NiTi steel at $T_{irr} \sim 140$ K to a dose of $\sim 1.5 \times 10^{16}$ D/cm^2 for the samples pre-irradiated to different doses of oxygen ions at $T_{irr} \sim 300$ K: 1 – 0; 2 – 1.1×10^{17} O/cm^2; 3 – 2.3×10^{17} O/cm^2 (~70 at.%).

steady structures of nitrides formed (peak with the maximum temperature $T_m \sim 650$ K).

Fig. 3 shows the spectra of deuterium release from 18Cr10NiTi steel preimplanted with O_2^+ ions to two doses (curves 2 and 3). Curve 1 corresponds to the release of implanted deuterium from the sample unirradiated with O_2^+ ions. In the absence of the oxygen interstitial impurity, the deuterium thermodesorption spectrum exhibits only one well-resolved peak with the maximum temperature $T_m \sim 410$ K. The gas release begins at a temperature of ~330 K, and is substantially completed at ~650 K. A preliminary O_2^+ ion irradiation of the samples to a dose of $\sim 1.1 \times 10^{17}$ O/cm^2 leads to a change of the deuterium thermodesorption spectrum that manifests itself in an insignificant intensity increase of the high-temperature part of the gas release curve (curve 2). In this case, the maximum temperature of the peak and the temperature range of gas release remain practically unchanged. With a rise in the exposure dose up to $\sim 2.3 \times 10^{17}$ O/cm^2, the deuterium release spectrum has exhibited an additional inexplicitly resolved low-amplitude peak with the maximum temperature $T_m \sim 560$ K.

It should be noted that an occurrence of an additional deuterium thermodesorption peak, as well as, a further increase in the O_2^+ ion irradiation dose have not led to an increase in the temperature range of gas release. The deuterium release from 18Cr10NiTi steel in the additional peak evidences on the formation of a new structure, differing from the initial one, with a higher binding energy, that, in the case of oxygen introduction, may be explained by formation of oxides, and, consequently the conclusion about a low solubility of hydrogen in oxides can be drawn.

4. Conclusions

The undertaken studies have revealed a general regularity that shows up in the extension of the temperature range of implanted deuterium release up in temperature, irrespective of the nature of interstitial impurity pre-introduced into the 18Cr10NiTi austenitic stainless steel. The degree of this extension depends on both the type and concentration of the interstitial impurity.

The maximum increase of the upper limit in the temperature range of deuterium retention in 18Cr10NiTi stainless steel is observed in the presence of a helium interstitial component.

It has been found that for 18Cr10NiTi stainless steel pre-irradiated with helium ions the increase in the temperature range of deuterium retention occurs in steps, i.e., as the helium concentration attains ~0.5 at.% He, the temperature range increases by ~100 K, and as the helium concentration attains ~2.5 at.% He, the temperature range is extended by ~350 K more. The stepwise character of the increase in the temperature range of deuterium retention with pre-introduced helium dose increasing is the best probative evidence on the formation of helium complexes with a different content of atoms.

The nitrogen interstitial impurity concentrations, that may be accumulated in the 18Cr10NiTi stainless steel components in the course of reactor service, vary between ~0.01 and 0.02 wt%. The investigation results reported here encourage us to state that the nitrogen impurity of these values exerts practically no effect on the increase of temperature ranges of hydrogen retention in structural materials of in-vessel components of fission-type reactors WWER-1000 (18Cr10NiTi steel).

Generally, as the nitrogen interstitial impurity concentration in 18Cr10NiTi steel increases, the temperature range of deuterium retention extends towards the higher temperatures. It has been established [4,5] that attainable maximum nitrogen concentration in nickel is ~30 at.%. A further increase of the nitrogen content occurs not with concentration increasing but due to the implantation profile extension. Standard use of nickel as a model material allows us to confirm that in experiments the obtained maximum concentration of nitrogen in the implantation profile was attained.

The oxygen introduction into 18Cr10NiTi steel results in the extension of the temperature range of deuterium emission towards higher temperatures, this being reflected by the appearance of an additional peak with the maximum temperature $T_m \sim 560$ K in the deuterium thermodesorption spectrum.

The present results show that the use of the thermodesorption spectrometry is promising not only for measurements of the content of hydrogen isotopes accumulated in the material, but, first of all, for the diagnostics of structural changes in structural materials.

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