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Influence of heat treatment on tritium distribution in V–4Cr–4Ti alloy

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Abstract

Tritium was loaded into cold-rolled and recrystallized specimens of a V–4Cr–4Ti alloy (NIFS-HEAT-2) at 673 K by a gas absorption method, and macroscopic distributions of tritium concentration in the specimens were examined by means of imaging plates. In the cold-rolled specimen, the distribution of tritium concentration was not uniform; bands of tritium-accumulated regions were observed along the rolling direction. Such bands of tritium-accumulated regions remained clearly visible even in the specimen recrytallized at 1173 K for 2 h. A more uniform concentration distribution, however, was observed for the specimen annealed at 1273 K for 2 h. The correlation between microstructure and tritium distribution is discussed.

1. Introduction

Vanadium alloys containing Cr and Ti have been recognized as attractive candidate structural materials for blankets of fusion reactors because of their low induced radioactivity by neutron irradiation and favorable mechanical properties [1,2]. The diffusivity and solubility of hydrogen isotopes in this type of alloy, however, are high in comparison with other candidate materials, and hence the behavior of tritium and other hydrogen isotopes has to be well understood to avoid excessive tritium inventory and hydrogen embrittlement. The accumulation of He produced by (n, α) reactions and β-decay of tritium has to be kept below/at acceptable level.

It is known that Ti acts as a trapping site for hydrogen isotopes in V alloys [3,4]. Recently, Ohnuki et al. [5] have found that defects such as dislocations, vacancies and voids also trap hydrogen isotopes effectively up to 773 K, and such interactions between hydrogen isotopes and defects lead to hardening of the V alloys. They also reported that the extent of hardening in a V–4Cr–4Ti alloy was larger than that in pure V; alloying elements intensified the hardening [5]. In these studies, the concentration distribution of trapping sites is implicitly assumed to be uniform at least on a macroscopic scale, but this has not been confirmed.

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Non-uniform distributions of trapping sites should result in some scatter in mechanical properties through non-uniform distributions of hydrogen isotopes and He. Different mechanical properties can be obtained at the same value of average hydrogen/tritium concentration, depending on the distribution of trapping sites. Therefore, it is important to understand the concentration distribution of trapping sites in the alloys and the influence of heat treatment on it.

According to Nagasaka et al. [6] and Heo et al. [7] who examined the microstructures of a V–4Cr–4Ti alloy (NIFS-HEAT-2), elongated grains with band structures of precipitates consisting of Ti, C, N, and O were developed along the rolling direction during cold rolling. Recrystallization, accompanied with the decrease in hardness, started at about 1000 K, and the hardness was at a minimum value at 1173 K. Even after recrystallization annealing at 1173 K, the grains were not fully isotropic (0.55 aspect ratio) [7]. Annealing at higher temperatures resulted in the development of isotropic grains and increased hardness owing to the decomposition of precipitates with the increase in impurity concentration in the matrix [7].

In the present study, three types of specimens of a V–4Cr–4Ti alloy (NIFS-HEAT-2) having different microstructures were prepared based on the observations of Nagasaka et al. [6] and Heo et al. [7] by (a) cold rolling, (b) recrystallization annealing at 1173 K for 2 h, and (c) recrystallization annealing at 1273 K for 2 h. Tritium was loaded into these specimens at 673 K by a gas absorption method, and its concentration distributions were observed at room temperature by a technique of imaging plate. A non-uniform distribution of tritium was clearly observed for the specimens in the as-rolled condition and annealed at 1173 K for 2 h.

2. Experimental

Three types of specimens of V–4Cr–4Ti alloy were prepared from a cold-rolled sheet of NIFS-HEAT-2 (0.5 mm in thickness, 99.5% in reduction of thickness). One of the specimens was examined in the as-rolled condition. The two other specimens were prepared by annealing at 1173 K for 2 h or at 1273 K for 2 h. The microstructures of these specimens can be summarized as (a) elongated grains accompanied with bands of the precipitates, (b) a recrystallized structure with the minimum hardness, and (c) fully recrystallized structure accompanied with dissolution of a portion of the precipitates. A specimen of pure V was also prepared by cold rolling for comparison; the reduction in thickness was 99.5%.

These specimens were polished with abrasive papers and mirror-finished using alumina paste with 0.06 μm particles. Tritium was loaded into the specimen by a gas absorption method with a vacuum apparatus which was similar one used in the previous study [8]. First, the specimen was set into a reaction chamber made of quartz glass, and the chamber was evacuated below 10^{-6} Pa. Then the specimen was heated in vacuum at 723 K for 4 h to remove an oxide layer from the specimen surface and hydrogen dissolved in the specimen as impurity. After reducing the specimen temperature to 673 K, the chamber was isolated from the pumping system by closing valves, and tritium gas diluted with deuterium ($T/D = 5.6 \times 10^{-3}$) was introduced into the chamber. The tritium gas was absorbed by the specimen almost completely under the present conditions. The total concentration of hydrogen isotopes in the specimen was controlled at 100 mol ppm by adjusting the initial pressure of tritium gas between 1.73 and 13.8 Pa according to specimen size; the concentration of tritium was 0.56 mol ppm. After the tritium absorption, the specimen was kept at 673 K for 30 min to obtain a uniform distribution of tritium through the specimen thickness. According to data on the diffusion coefficient of tritium in a V–4Cr–4Ti alloy reported by Hashizume et al. [9], the diffusion length of tritium during this treatment adequately exceeded the specimen thickness. Then the specimen was slowly cooled down to room temperature.

The specimen containing tritium was placed on an imaging plate (IP), Fujix TR2025, for 24 h at room temperature to expose the IP to β-rays emitted from tritium in the specimen. The practical range of β-rays in the alloy at the mean energy (5.69 keV) was determined to be 180 nm by the equation recommended by Gledhill [10]. After the exposure, two-dimensional mapping of β-ray intensity recorded in the IP was measured by means of an imaging analyzer (Fujix FDL5000). In this analyzer, a He–Ne laser beam was scanned on the surface of the IP, and the two-dimensional mapping of the intensity of photo-stimulated luminescence (PSL), which is proportional to the intensity of β-rays [11], was obtained. Such a two-dimensional mapping of PSL intensity is hereafter described as a radioluminograph. The pixel size of the radioluminograph, i.e. spatial resolution, was 25 μm × 25 μm.

3. Results

Fig. 1(a) shows a typical example of the radioluminographs for the V–4Cr–4Ti alloy specimen in the as-rolled condition. A change in color from blue to red indicates an increase in the tritium concentration. It is clearly shown that the tritium concentration distribution is not uniform. In particular, bands of tritium-accumulated regions are observed along the rolling direction. As the spatial resolution of radioluminography is 25 μm × 25 μm, it is insufficient to distinguish trapping sites individually. Hence, the bands of tritium-accumulated regions correspond to areas where trapping sites are concentrated. The line profile of PSL intensity at the position indicated in this figure is shown in Fig. 2. Tritium concentrations in band-like regions are about twice as high as that in the matrix is. By taking account of the above-mentioned spatial resolution of radioluminography, the real tritium concentration in trapping sites is believed to be higher.

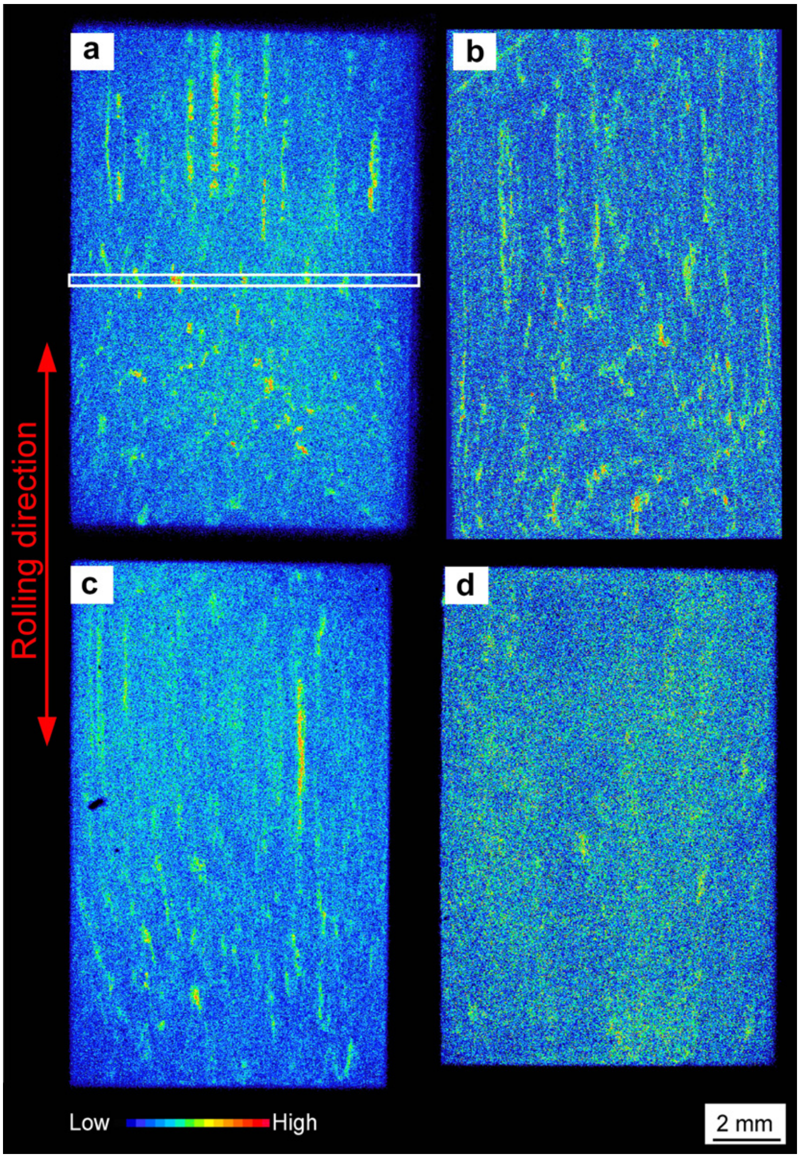

Fig. 1. Radioluminographs of V–4Cr–4Ti alloy specimens (a) in as-rolled condition, (b) annealed at 1173 K for 2 h, (c) and (d) annealed at 1273 K for 2 h.

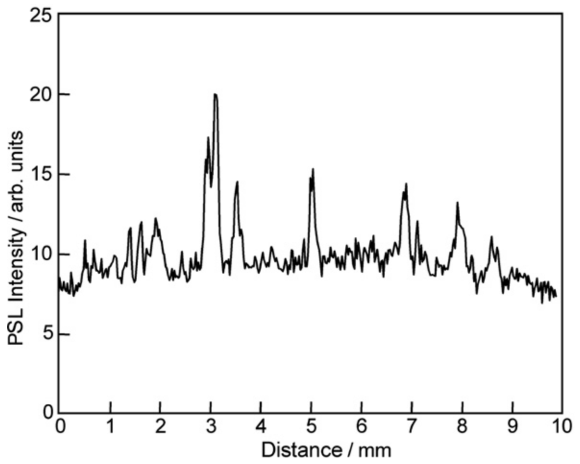

Fig. 2. Line profile of PSL intensity at the position indicated in Fig. 1(a).

The radioluminograph of the specimen annealed at 1173 K for 2 h is shown in Fig. 1(b). The bands of tritium-accumulated regions are also present in this specimen. No significant difference is observed between Fig. 1(a) and (b), although the microstructures of the specimens were quite different from each other as reported by Heo et al. [8]: recrystallization already took place at 1173 K.

Two examples of the radioluminographs of V–4Cr–4Ti alloy specimen annealed at 1273 K for 2 h are shown in Fig. 1(c) and (d). The density of the bands of tritium-accumulated regions is slightly different from specimen to specimen in this annealing condition as shown in these figures. However, the difference in tritium concentration between the band-like regions and the matrix is small in comparison with other types of the specimens shown in Fig. 1(a) and (b). In addition, the density of the bands of tritium-accumulated regions is also lower, that is the concentration distribution of tritium is more uniform in the specimen annealed at 1273 K.

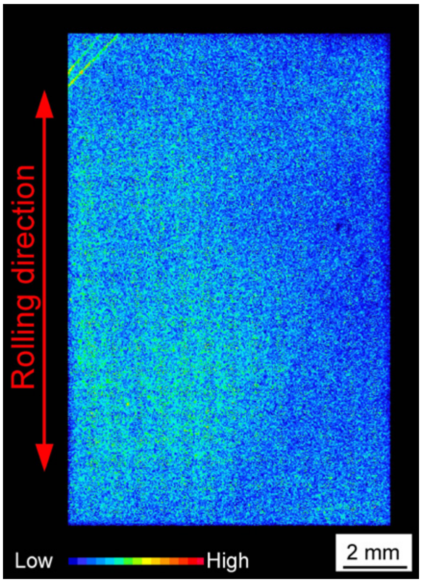

Fig. 3. Radioluminograph of pure V specimen in as-rolled condition.

The radioluminograph of the pure V specimen in the as-rolled condition is shown in Fig. 3. The concentration distribution of tritium appears to be almost uniform in this specimen in contrast to the V–4Cr–4Ti alloy specimen shown in Fig. 1(a). Such uniform distribution of tritium does not necessarily mean that there were no trapping sites in this specimen. It is plausible that the trapping sites such as dislocations were introduced uniformly in the case of pure V.

4. Discussion

The non-uniform distribution of tritium observed for the V–4Cr–4Ti alloy specimens (Fig. 1(a) and (b)) is not due to the precipitation of V hydride (tritide) phase, because the total concentration of hydrogen isotopes (100 mol ppm) in the present specimens were lower than the terminal solubility in V [12] by orders of magnitude. As described in the previous section, the concentration distribution of tritium in the pure V specimen was almost uniform in the as-rolled condition. Hence, the non-uniform tritium distribution observed in the V–4Cr–4Ti alloy specimens can be ascribed to the effects of alloying elements. Since Ti atoms act as hydrogen trapping sites in V alloys [3,4], the macroscopic distribution of Ti dissolved in the matrix of the as-rolled specimen was examined by means of electron probe micro-analysis at a magnification too low for the precipitates to be distinguished. This examination, however, showed that Ti had a uniform concentration distribution. Hence, it was concluded that Ti dissolved in the matrix did not contribute to the formation of the bands of tritium-accumulated regions shown in Fig. 1(a) and (b).

It is known that the precipitates form band structures along the rolling direction during the rolling of V–4Cr–4Ti alloy as mentioned above [6,7]. In addition, the annealing temperature of 1273 K at which a more uniform tritium distribution was obtained corresponds to the temperature at which the decomposition of precipitates started [7]. Hence, it is appropriate to consider that precipitates play an important role in the formation of the bands of tritium-accumulated regions along the rolling direction. The sizes of the precipitates, however, are much smaller than the spatial resolution of radioluminography, and hence the underlying mechanisms of tritium accumulation are still not well understood. On the other hand, a technique of tritium autoradiography combined with transmission or scanning electron microscopy [13] provides spatial resolution comparable to the sizes of precipitates in the present alloy, although autoradiography is not superior to radioluminography in quantitative analysis. Further investigations by combining these two techniques are necessary to clarify the underlying mechanisms of the formation of the bands of tritium-accumulated regions.

Ohnuki et al. [5] examined the mechanical property of a V–4Cr–4Ti alloy specimen annealed at 1173 K after cathodic charging of hydrogen and observed significant hardening. The extent of hardening was considerably higher for the V–4Cr–4Ti alloy specimen than for a pure V specimen [5]. A correlation between such intensified hardening and the non-uniform tritium distribution (Fig. 1 (b)), however, is not clear at the present, because the concentration of hydrogen in their specimen was not described in their paper [5]. The influence of hydrogen isotopes on the mechanical properties should be sensitively dependent on the concentration. A non-uniform distribution of hydrogen isotopes, however, does not necessarily degrade the mechanical property of a host material: e.g. Sugisaki et al. [14] have examined the influence of macroscopic hydrogen distribution on the impact strength of Zircaloy-2 and found that the impact strength of the specimen with a non-uniform hydrogen distribution was higher than that of the specimen with a uniform distribution. They ascribed this observation to the increase in the volume fraction of ductile regions with low hydrogen concentrations [14]. A similar effect, in principle, can appear also for V alloys. In any case, further investigations are required to understand the influence of non-uniform tritium distributions on mechanical properties.

5. Conclusions

(1) The concentration distribution of tritium in the V–4Cr–4Ti alloy specimen in the as-rolled condition was not uniform; bands of tritium-accumulated regions were observed along the rolling direction.
(2) The influence of heat treatment at 1173 K on tritium distribution was small, while a more uniform distribution was observed after annealing at 1273 K.
(3) In the case of pure V, a uniform distribution of tritium was observed in the as-rolled condition.
(4) The precipitates consisting of Ti, C, N and O appear to play an important role in the formation of the bands of tritium-accumulated regions in V–4Cr–4Ti specimens.

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References

[1] T. Muroga, T. Nagasaka, K. Abe, V.M. Chernov, H. Matsui, D.L. Smith, Z.-Y. Xu, S.J. Zinkle, J. Nucl. Mater. 307–311 (2002) 547.
[2] R.J. Kurtz, K. Abe, V.M. Chernov, D.T. Hoelzer, H. Matsui, T. Muroga, G.R. Odette, J. Nucl. Mater. 329–333 (2004) 47.
[3] S. Tanaka, H. Kimura, Trans. Japan Inst. Metals 20 (1979) 647.
[4] D.J. Pine, R.M. Cotts, Phys. Rev. B 28 (1983) 641.
[5] S. Ohnuki, T. Yasuda, T. Suda, S. Watanabe, B.M. Oliver, J. Nucl. Mater. 329–333 (2004) 481.
[6] T. Nagasaka, N.J. Heo, T. Muroga, M. Imamura, Fusion Eng. Des. 61&62 (2002) 757.
[7] N.J. Heo, T. Nagasaka, T. Muroga, J. Nucl. Mater. 325 (2004) 53.
[8] R. Hayakawa, Y. Hatano, A. Pisarev, K. Watanabe, Phys. Scripta T108 (2004) 38.
[9] K. Hashizume, J. Masuda, T. Otsuka, T. Tanabe, Y. Hatano, Y. Nakamura, T. Nagasaka, T. Muroga, J. Nucl. Mater., these Proceedings, doi:10.1016/j.jnucmat.2007.03.239.
[10] J.A. Gledhill, J. Phys. A: Math. Nucl. Gen. 6 (1973) 1420.
[11] H. Saitoh, T. Hishi, T. Misawa, T. Ohnishi, Y. Noya, T. Matsuzaki, T. Watanabe, J. Nucl. Mater. 258–263 (1998) 1404.
[12] R. Lässer, J. Nucl. Mater. 155–157 (1988) 766.
[13] G.R. Caskey Jr., in: N.F. Fiore, B.J. Berkowitz (Eds.), Advanced Techniques for Characterizing Hydrogen in Metals, Metallurgical Society of AIME, Warrendale, Pennsylvania, 1982, p. 61.
[14] M. Sugisaki, K. Hashizume, Y. Hatano, IAEA-TECDOC-1316, 2002, p. 63.