Observation of Tritium Distribution in V-4Cr-4Ti alloy by Tritium Radioluminography *1

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Tritium distribution in V-4 mass%Cr-4 mass%Ti alloy has been observed by the tritium radioluminography, and the relation between the tritium distribution and the constituent elements of the alloy have been investigated. In the as-cast specimen, tritium concentration has been higher in the titanium enriched region, that is, the local tritium concentrations at the lower and higher titanium region are 156 and 202 mol ppb, respectively. The tritium distribution has shown a strong correlation with the titanium segregation in the interdendritic region. In the heat treated specimen, the tritium distribution has been rarely affected by the interdendritic titanium segregation. Tritium concentration at the central area and at the surrounding area in the specimen surface have been 209 and 147 mol ppb, respectively. It has been thought that this accumulation of tritium to the central area is caused by the Gorsky effect which generated due to the constraint condition of the stress field in the plate shaped specimen. In the heat treated specimen, the tritium distribution has been more strongly affected by the shape of the specimen than by the titanium segregation in it.

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1. Introduction

Tritium is the radioactive isotope of hydrogen, and emits only low energy β -rays. Thus, tritium has been used to observe hydrogen distribution in metals. Tritium radioluminography¹⁾ is a useful technique to visualize hydrogen distribution in materials quantitatively, based on the photo-stimulated luminescence of the imaging plate (IP).²⁻⁴⁾ In this method, tritium charged specimen is placed on the IP, and then the two-dimensional distribution and intensity of the β -rays emitted from tritium are detected. The quantitiveness of the radioluminography for the tritium distribution is excellent because the IP possesses an extremely high sensitivity and wide dynamic range of about five orders for the β -rays.⁵⁾ By the tritium radioluminography, it is possible to observe not only the two-dimensional hydrogen distribution but also the hydrogen concentration at the local area on the specimen surface.

In our previous work, we performed the quantitative observation of the hydrogen distribution in pure vanadium,^{6,7)} some vanadium alloys⁸⁻¹³⁾ and Ti-Cr alloy¹⁴⁾ by the tritium radioluminography, and showed the effect of the microstructure or constituent element on the tritium distribution in these materials. In the present work, tritium radioluminography is applied to V-4 mass%Cr-4 mass%Ti (mass% will be omitted hereafter) alloy which is one of the candidate for the first wall materials of the nuclear fusion reactor.¹⁵⁾ The relation between the tritium distribution and both the constituent elements and microstructure is investigated.

2. Experimental Procedure

V-4Cr-4Ti alloy was prepared by arc-melting vanadium (99.95%), chromium (99.9%) and titanium (99.9%) in high

purity argon atmosphere. The button-like ingot was cut to make plate specimens 1 mm in thickness. Some specimens were sealed in quartz tube after evacuating by a rotary pump and diffusion pump, and were heat treated at 1473 K for 24 h and then quenched into water. The plate specimens were polished using abrasive paper and mirror finished using alumina paste with 0.05 μ m particles.

Tritium addition into the specimens was performed by an electrochemical cathodic charging method at room temperature. The electrolyte was 0.1 kmol/m³ NaOH aqueous solution containing tritium of 1.9 PBq/m³. The current density and charging period were 200 A/m² and 2 h, respectively. The ratio of tritium atom N_T to protium atom N_H in the electrolyte was $N_T/N_H = 1.5 \times 10^{-5}$. Then the tritium added specimens were immersed into dilute acetic acid, washed with water, rinsed in ethyl alcohol and then dried. The alkaline electrolyte adsorbed on the specimen surface is eliminated by this treatment.

The tritium added specimen was placed on an IP, Fujix TR2040, for 24 h to expose it to the β -rays emitted from tritium in the specimen. In this treatment, a tritium-labelled microscale (Amersham RPA510) which is a plastic film containing eight levels of known amount of tritium was placed on the IP to translate the tritium radioactivity into the tritium concentration. The detail of the qualitative analysis of tritium concentration is described in the previous papers.^{1,7)} After the exposure, two-dimensional mapping of the intensity of β -rays recorded in the IP was measured by means of an IP-reader (Fujix FDL5000) and the tritium radioluminograph was obtained. The pixel size of the radioluminograph obtained by the IP-reader was 25 μ m $\times$ 25 μ m, meaning that the resolution of the radioluminograph is 25 μ m.

After the radioluminography, tritium in the specimen was exhausted by heating at 473 K for 1 h in vacuum and then the distribution of constituent elements and microstructures were examined. The distribution of the constituent elements

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of the specimen such as vanadium, chromium and titanium was observed by means of the wavelength dispersive X-ray spectrometer (WDX, JEOL JXA-8900). The crystal structure of the specimens before and after hydrogen charging was examined by means of a X-ray diffractometer using Cu-K α radiation.

3. Results and Discussion

Figure 1 shows X-ray diffraction profiles of the V-4Cr-4Ti specimen, (a) and (b) being as-cast and heat treated specimen, respectively, before and after hydrogen charging. It is confirmed that these specimens have BCC single phase before and after hydrogen charging. The 110 peak positions of both the as-cast specimen and heat treated specimen are slightly different for the hydrogen uncharged specimens, that is, the 110 peak position shifts to higher diffraction angle by the heat treatment. The calculated lattice spacings of both specimen shows that the (110) lattice spacings decrease 0.18% after the heat treatment. This shows that the lattice strain introduced during arc-melting is modified by the heat treatment.

For the hydrogen charged specimens, the peak positions of both the as-cast specimen and heat treated specimens shift to lower diffraction angle, indicating that the lattice expansion occurs due to the hydrogen dissolution. Figure 2 shows the change of the lattice spacings of both the as-cast specimen and heat treated specimens after hydrogen charging. The change of the lattice spacings in the heat treated specimen is larger

Fig. 1 X-ray diffraction profiles of (a) as-cast and (b) heat treated V-4Cr-4Ti specimens before and after hydrogen charging.

Fig. 2 Change of the lattice spacings in as-cast and heat treated V-4Cr-4Ti specimens by the hydrogen charging.

than that in the as-cast specimen. This shows that the amount of hydrogen dissolved into the heat treated specimen is larger than that in the as-cast specimen.

Figure 3(a) shows a tritium mapping image of the as-cast V-4Cr-4Ti specimen on tritium added surface obtained by the tritium radioluminography. Tritium is observed to be non-uniformly distributed. The relative concentration of the tritium is displayed graphically by a color scale bar in sixteen steps below Fig. 3(a), that is, the regions of higher, middle and lower hydrogen concentration in the radioluminograph is indicated by the colors of red, yellow and blue, respectively. Tritium concentration seems to vary depending on the microstructure in the specimen. Figure 3(b) to (d) show the mapping images of vanadium, chromium and titanium, respectively, obtained by WDX. Figure 3(e) to (h) show the enlarged pictures of the tritium, vanadium, chromium and titanium, respectively, in the area of square rounded portion in Fig. 3(a). In these mapping images, titanium is clearly observed to be segregated in the interdendritic region, while chromium has a weak tendency for segregation. It seems that both the vanadium and chromium are complementally distributed to the titanium distribution. By comparing the distribution of tritium and titanium, it is found that the tritium concentration at the microscopic region correlates closely with the titanium distribution. The local tritium concentrations at the lower titanium region ① and higher titanium region ② in Fig. 3(e) are 156 and 202 mol ppb, respectively. By considering that the heat of hydride formation is higher in titanium and lower in vanadium,¹⁶⁾ hydrogen is thought to be easily accumulated to the titanium rich region. And it seems that the lattice strain between the matrix and the titanium segregation caused by the difference of atomic radius between titanium and chromium also accumulate the hydrogen. Therefore, it is concluded that the tritium distribution is strongly affected by the titanium segregation in the interdendritic region.

Figure 4(a) shows a mapping image of the heat treated V-4Cr-4Ti specimen on the tritium added surface, and Fig. 4(b) to (d) show the mapping images of vanadium, chromium and titanium, respectively. Figure 4(e) to (h) show the enlarged pictures of the tritium, vanadium, chromium and titanium, respectively, in the area of square rounded portion in Fig. 4(a). In Fig. 4(a), tritium is observed to be accumulated to the central area in the specimen, and the tritium concentration is relatively low at the surrounding area. The tritium concentrations at the region ① and ② in Fig. 4(a) are 147 and 209 mol ppb, respectively. This higher tritium concentration in the central area is not attributed to the deformation of specimen but the accumulation of hydrogen to this area, because the difference of thickness between the central area and surrounding area after the tritium addition was less than 0.1 mm and the maximum range of β -rays emitted from tritium is about 3 mm in air. The accumulation of tritium to the central area was observed in the plate specimens of palladium⁹⁾ and V-50 mol%Ti alloy¹⁰⁾ in our previous paper. It is reported¹⁷⁾ that the thickness increases as the hydrogenation progress while the length and width decreases due to the influence of constraint condition of the stress field in the palladium plate specimen. If we assume that the specimen is plane strain state, the deformation by the hydrogen penetration to the thickness direction is easily generated in the cen-

Fig. 3 (a) Mapping image of tritium on the tritium added surface of as-cast V-4Cr-4Ti specimen obtained by tritium radioluminography, (b) to (d) the mapping images of vanadium, chromium and titanium, respectively, obtained by WDX. (e) to (h) the enlarged pictures of tritium, vanadium, chromium and titanium, respectively, in the area of square rounded portion in (a).

Fig. 4 (a) Mapping image of tritium on the tritium added surface of heat treated V-4Cr-4Ti specimen obtained by tritium radioluminography, (b) to (d) the mapping images of vanadium, chromium and titanium, respectively, obtained by WDX. (e) to (h) the enlarged pictures of tritium, vanadium, chromium and titanium, respectively, in the area of square rounded portion in (a).

tral area than in the surrounding area because of the constraint condition of the stress field in the plate shaped specimen. It is thought that this stress field results in the accumulation of hydrogen to the central area by the Gorsky effect¹⁸⁾ which moderates the stress in the plate shaped specimen.

At the microscopic area, Fig. 4(e), tritium seems to be randomly distributed, that is, tritium distribution is rarely affected by the microstructure in contrast to the as-cast specimen. In Fig. 4(h), titanium is observed to be segregated in the interdendritic region similar to the as-cast specimen in Fig. 3(h), and both the vanadium and chromium are also observed to be complementally distributed to the titanium distribution. Comparing the tritium and titanium distribution, it is found that the tritium distribution has a weak tendency to correlate with the titanium segregation in the interdendritic region. The interface between the titanium rich interdendritic region and titanium poor dendritic region becomes obscure compared with that in as-cast specimen. This loss of the sharpness of the interface is due to the diffusion of segregated titanium into the matrix by the heat treatment. This heat treatment also cause the modification of the lattice strain introduced during arc-melting, as mentioned in the result of X-ray diffraction experiment in Fig. 1. It is thought that the shaded interface of the dendritic structure and the decrease of the remaining strain causes the reduction of accumulation power of tritium in the heat treated specimen. Therefore, it is concluded that tritium distribution is more strongly affected by the shape of the specimen than by the titanium segregation in it.

4. Conclusions

The distribution of tritium and constituent elements in V–4Cr–4Ti alloy was observed by the tritium radioluminography and by the wavelength dispersive X-ray spectrometry, respectively, and the relation between the distribution of them was examined. In the as-cast specimen, the tritium distribution strongly correlates with the titanium segregation in the interdendritic region. While, in the heat treated specimen, tritium accumulates to the central area in the specimen, and tritium

distribution is rarely affected by the titanium segregation. The tritium distribution is strongly affected by the constraint condition of the stress field generated by the hydrogen penetration in the plate shaped specimen.

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