

Application of Tritium Radioluminography to the Detection of Hydrogen Diffusion in Ti-Cr Alloy

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Tritium radioluminography has been applied to determine the hydrogen (H) diffusion coefficients in $\text{Ti}_{50}\text{Cr}_{50}$ and $\text{Ti}_{40}\text{Cr}_{60}$ alloys, both with two-phase structures of a body-centered cubic (bcc) phase and a Laves phase. Using radioluminography, H distributions in those phases have been observed, and H penetration profiles have been measured. The tritium diffusion coefficients in the $\text{Ti}_{50}\text{Cr}_{50}$ and $\text{Ti}_{40}\text{Cr}_{60}$ alloys have been successfully determined by analyzing the tritium penetration profiles to be $3.3 \pm 0.3 \times 10^{-12}$ and $1.4 \pm 0.1 \times 10^{-12} \text{ m}^2/\text{s}$, respectively. These values suggest that the H diffusion in the Laves phase is slower than that in the bcc phase. It is also suggested that H diffuses by short-circuiting diffusion through the interface between the bcc phase and the Laves phase.

1. Introduction

Tritium radioluminography^[1] is a useful technique with which to visualize hydrogen (H) distribution in materials. In this method, an imaging plate (IP) is used as a detector for tritium due to its higher sensitivity and wide dynamic range for radiation rays.^[2,3] In a previous work, the authors performed a quantitative observation of H distribution in pure vanadium (V)^[1,4], V-based alloys,^[5-8] and Ti-Cr alloys^[9,10] by tritium radioluminography, and showed the effect of microstructure or constituent elements on the tritium distribution in these materials. In one of those experiments, radioluminography was made on a section of a V-5 mass%Fe alloy normal to the hydrogenated surface and observed the concentration profile of the equilibrium distribution of H. This result suggests that in any alloy in which H diffusion is less than that of the V-5mass%Fe alloy, it should be possible to obtain a gradually decreased H concentration profile and therefore to obtain the H diffusion coefficient.

In a Ti-Cr system, the hydrogenation property was investigated for the TiCr_2 Laves phase with a C14-type or C15-type structure^[11,12] and for a Ti-Cr solid solution alloy with a body-centered cubic (bcc) structure.^[13,14] The authors examined a relationship between the H distribution and the microstructure in the alloys by tritium radioluminography.^[9] In this experiment, H diffusion seems to be slow in comparison with the V alloys. Thus, in the present

work, the intention is to use tritium radioluminography to obtain an H diffusion coefficient in two-phase Ti-Cr binary alloys with a bcc phase and a Laves phase.

2. Experimental Procedure

$\text{Ti}_{50}\text{Cr}_{50}$ and $\text{Ti}_{40}\text{Cr}_{60}$ alloys in nominal composition were prepared by arc-melting titanium (99.9%) and chromium (99.9%) under a high-purity argon atmosphere, and were cut to make rectangular block specimens $5 \times 5 \times 10$ mm in size. The addition of H (protium and tritium) into the specimen was performed by an electrochemical cathodic charging method at room temperature. The electrolyte was a 0.1 kmol/m^3 NaOH aqueous solution containing tritium of 1.9 PBq/m^3 . The current density and charging period were 400 A/m^2 and 4 h, respectively. Before the addition of H, the specimens were covered with epoxy resin except for the H-added surface. The H-added specimens were kept at room temperature for 24 h and were cut in the long transverse direction, which is the H diffusion direction, to observe a cross-sectional distribution of tritium. Then the specimens were put on an IP (Fujix TR2040, Fuji Photo Film Co., Ltd); and the radioactivity of the tritium recorded in the IP was measured by means of an IP reader (Fujix FDL5000, Fuji Photo Film Co., Ltd) as the intensity of photo-stimulated luminescence (PSL). The detail of the quantitative analysis of the surface tritium concentration was described elsewhere.^[4] The PSL intensity was repeatedly measured every 24 h to examine the time dependence of the cross-sectional distribution of tritium. After the radioluminography, the tritium concentration profile along the diffusion direction was measured, and the tritium diffusion coefficient was determined.

3. Results and Discussion

Figure 1(a) and (b) show x-ray diffraction profiles of the $\text{Ti}_{50}\text{Cr}_{50}$ and $\text{Ti}_{40}\text{Cr}_{60}$ specimens, respectively. Both speci-

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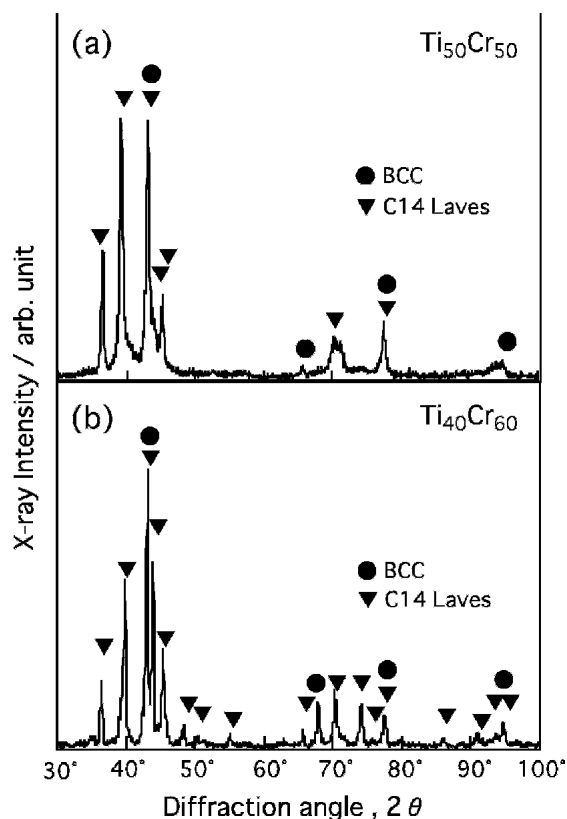


Fig. 1 X-ray diffraction profiles of as-cast specimens: (a) $\text{Ti}_{50}\text{Cr}_{50}$ specimen; (b) $\text{Ti}_{40}\text{Cr}_{60}$ specimen

mens consist of a bcc phase and a C-14-type Laves phase. The ratio of the amount of the Laves phase to the amount of the bcc phase in the $\text{Ti}_{40}\text{Cr}_{60}$ specimen is higher than that in the $\text{Ti}_{50}\text{Cr}_{50}$ specimen.

Figure 2(a) shows a tritium radioluminograph of the $\text{Ti}_{50}\text{Cr}_{50}$ specimen made at room temperature three days after the H addition, in which the cross-sectional tritium distribution is observed. In Fig. 2(a), the white contrast signifies a higher H concentration, as indicated by the scale bar. The H concentration is higher on the left-hand side (H added surface) and gradually decreases on the right-hand side of the specimen. This shows that the tritium penetrates into the interior of the specimen. Figure 2(b) shows a cross-sectional tritium distribution in the $\text{Ti}_{50}\text{Cr}_{50}$ specimen 9 days after the H addition, indicating that H has penetrated more deeply into the specimen. Figure 2(c) shows concentration profiles of tritium in the specimens 3 and 9 days after the H addition. The concentration profiles show Gaussian-like curves. However, the concentration profiles deviate slightly downward from the Gaussian curve near the H-added surface of the specimen after 9 days. This is thought to be attributed to the escape of H to the outside of the specimen near the surface.

Figure 3(a) and (b) show the cross-sectional tritium distributions in the $\text{Ti}_{40}\text{Cr}_{60}$ specimen three and nine days, respectively, after the H addition. Figure 3(a) and (b) show that H penetrates from the H-added surface to the interior of the specimen and that the penetration distance increases

with increases of diffusion time. However, the H penetration distance in the $\text{Ti}_{40}\text{Cr}_{60}$ specimen is not as deep as that in the $\text{Ti}_{50}\text{Cr}_{50}$ specimen. This suggests that the H diffusion in the $\text{Ti}_{40}\text{Cr}_{60}$ specimen is slower than in the $\text{Ti}_{50}\text{Cr}_{50}$ specimen.

For one-dimensional volume diffusion of a tracer from an infinitesimally thin surface layer into a sufficiently long rod, a solution of Fick's second law is given by^[15]:

$$C_T(X,t) = [M/\sqrt{\pi Dt}] \exp(-X^2/4Dt) \quad (\text{Eq 1})$$

where $C_T(X,t)$ is the concentration at the distance X from the surface after the diffusion time t , D is the diffusion coefficient, and M is the total amount of the tracer before diffusion. Therefore, we can obtain a diffusion coefficient from the gradient of the $\ln C_T$ versus X^2 plots. Figures 2(d) and 3(d) show $\ln C_T$ versus X^2 plots for the $\text{Ti}_{50}\text{Cr}_{50}$ and $\text{Ti}_{40}\text{Cr}_{60}$ specimen, respectively, of the three-day and nine-days diffusion periods. In these figures, the three regions (i.e., the region that is affected by the backward diffusion near the H-added surface, the region of volume diffusion, and the region that is dropped to background) are recognized. We use the region of volume diffusion for the calculation of the H diffusion coefficient. In both Fig. 2(d) and 3(d), the $\ln C_T$ versus X^2 plots show linearity, indicating that Eq 1 holds. From the slopes of the plots, tritium diffusion coefficients are determined. For the $\text{Ti}_{50}\text{Cr}_{50}$ specimen, the mean (\pm SD) tritium diffusion coefficients are $3.3 \pm 0.3 \times 10^{-12}$ and $5.1 \pm 0.3 \times 10^{-12}$ m^2/s , respectively, for three and nine days of diffusion. The mean tritium diffusion coefficients for the $\text{Ti}_{40}\text{Cr}_{60}$ alloy were determined in the same way to be $1.4 \pm 0.1 \times 10^{-12}$ and $1.7 \pm 0.4 \times 10^{-12}$ m^2/s , respectively, for the three and nine days of diffusion. It is found that the diffusion coefficient in the $\text{Ti}_{40}\text{Cr}_{60}$ alloy is smaller than that in the $\text{Ti}_{50}\text{Cr}_{50}$ alloy.

These specimens are two-phase mixtures of a bcc phase and a Laves phase with a C14-type structure, and the amount of Laves phase in the $\text{Ti}_{40}\text{Cr}_{60}$ alloy is larger than that in the $\text{Ti}_{50}\text{Cr}_{50}$ alloy. The present tritium diffusion coefficient in the $\text{Ti}_{40}\text{Cr}_{60}$ alloy is smaller than that in the $\text{Ti}_{50}\text{Cr}_{50}$ alloy which indicates that the tritium diffusion coefficient decreases with increasing amounts of Laves phase. Therefore, we conclude that the H diffusion in the Laves phase is slower than that in the bcc phase.

Finally, we examined an effect of heat treatment on H diffusion. The specimens were heat treated at 1573 K for 8 h and then water-quenched. It is expected by this heat treatment that the ratio of the bcc phase increases and the microstructure develops. The mean tritium diffusion coefficients for the 3 days of diffusion period are determined to be $1.7 \pm 0.4 \times 10^{-12}$ m^2/s for the $\text{Ti}_{50}\text{Cr}_{50}$ alloy and $1.0 \pm 0.1 \times 10^{-12}$ m^2/s for the $\text{Ti}_{40}\text{Cr}_{60}$ alloy. Both values are slightly smaller than those obtained from specimens without heat treatment. Thus, diffusion coefficients are indicated to decrease after heat treatment. This means that the H diffusion coefficients decrease when the specimen has a coarse microstructure. This seems to be attributable to the short-circuiting diffusion of H in the boundary region between the bcc phase and the Laves phase.

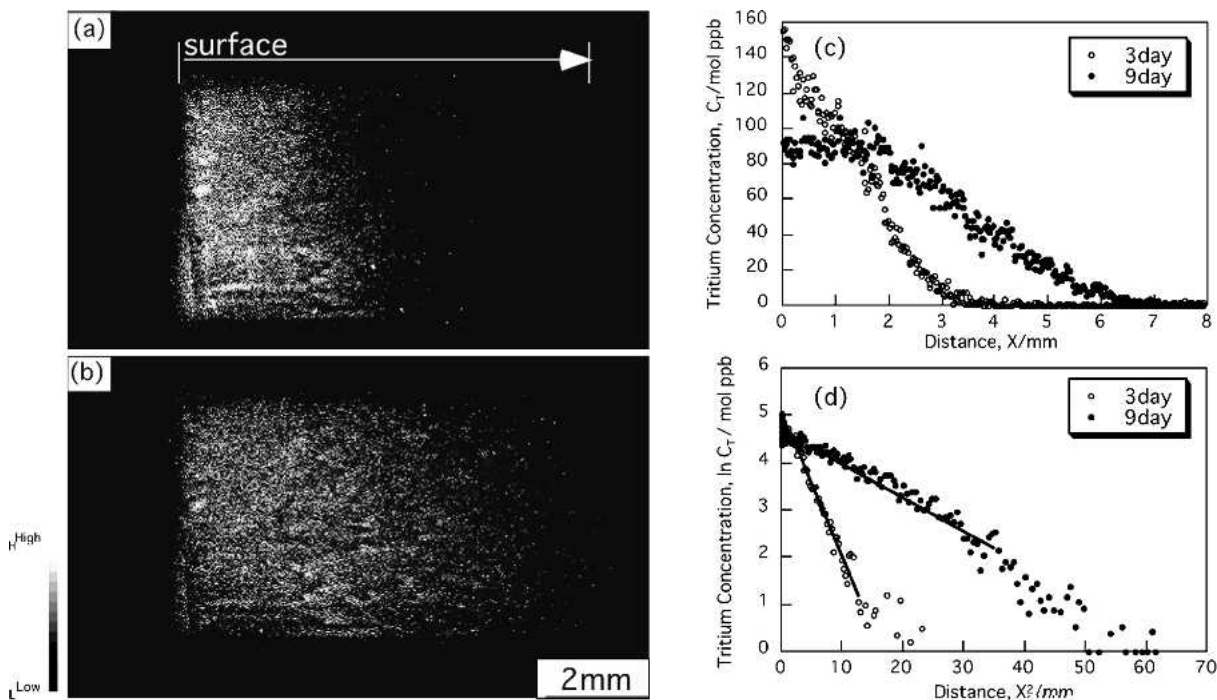


Fig. 2 Tritium radioluminographs of the $Ti_{50}Cr_{50}$ as-cast specimen (a) 3 days and (b) 9 days after the addition of tritium; (c) tritium concentration profiles on the cross sections of (a) and (b); (d) $\ln C_T(X, t)$ versus X^2 plots of (c)

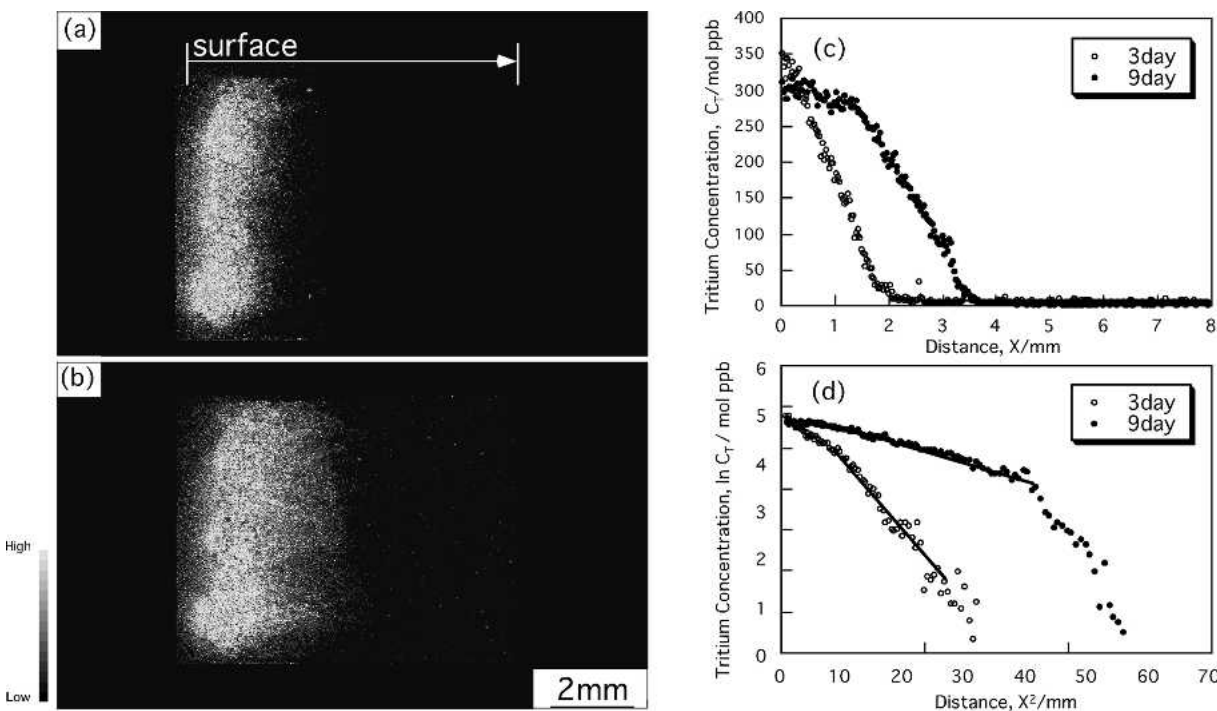


Fig. 3 Tritium radioluminographs of the $Ti_{40}Cr_{60}$ as-cast specimen: (a) 3 days after tritium addition; (b) 9 days after the addition of tritium; (c) tritium concentration profiles on the cross sections of (a) and (b); (d) $\ln C_T(X, t)$ versus X^2 plots of (c)

4. Conclusions

Tritium radioluminography was applied to examine H diffusion in Ti-Cr alloys with two-phase structures of a bcc

phase and a Laves phase. It is shown that tritium radioluminography can be used to determine the tritium diffusion coefficient. From the cross-sectional observation of H distribution, the H concentration profile was measured and the

H diffusion coefficient was obtained. The mean tritium diffusion coefficients that were determined in the $\text{Ti}_{40}\text{Cr}_{60}$ and $\text{Ti}_{50}\text{Cr}_{50}$ alloys after 3 days at ambient temperature were determined to be $3.3 \pm 0.3 \times 10^{-12}$ and $1.4 \pm 0.1 \times 10^{-12}$ m^2/s , respectively, suggesting that the H diffusion in the Laves phase is slower than that in the bcc phase. These diffusion coefficients decreased after heat treatment.

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