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Carbon diffusion behavior in molybdenum at relatively low temperatures

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ABSTRACT

Purpose of this study is to investigate the carbon diffusion behavior in pure molybdenum at relatively low temperatures by means of fracture surface observation. Carbon addition was performed at a temperature of 1273–1373 K with the heating time being changed. Fracture surface of the specimen after carbon addition was examined using SEM and the carbon diffusion distance was estimated from the change of fracture mode as a function of the distance from the surface. Results are summarized as follows. First, the carbon diffusion distance increased approximately linearly with the increase of heating time from 1.2 to 10.8 ks. This relationship does not agree with that obtained at much higher temperatures. From Arrhenius plots of the slope of the straight line and the temperature, activation energy was calculated (155 kJ/mol). Secondly, the carbon diffusion distance estimated in this study was generally larger than that simulated using the data of Rudman, particularly at a longer heating time.

1. Introduction

Our previous study [1] demonstrated that carbon diffusion distance in molybdenum is estimated by fracture surface observation. Grain boundaries of pure molybdenum after recrystallization are intrinsically weak [2] and hence its fracture mode is principally an intergranular-type. However, small addition of carbon strengthens these grain boundaries [2–7] and consequently changes the fracture mode from an intergranular-type to a transgranular-type. Carbon addition was carried out at relatively low temperatures with the heating time being short and constant (1.2 ks). First, we estimated the carbon diffusion distance from the change of fracture mode as a function of the distance from the specimen surface. Then we supposed a parabolic relationship stands up between the carbon diffusion distance and the heating time, and calculated activation energy for carbon diffusion from Arrhenius plots of the carbon diffusion distance and the temperature. The activation energy was 182 kJ/mol and this value approximately agreed with the values by Rudman [8] or Kunze and Reichelt [9]. However the carbon diffusion distance estimated by us was generally much longer than that simulated using diffusion parameters at a relatively high temperature of 1783 K or more [8]. Furthermore, carbon diffusion mechanism was not discussed.

Purpose of this study is to investigate carbon diffusion behavior in molybdenum at relatively low temperatures by means of fracture surface observation. Particularly it is very interesting to determine the change in the carbon diffusion distance with the heating time at a constant temperature. Carbon addition was carried out using the same method as our previous studies [1,10]. Fracture surface was examined using SEM. The change of fracture mode as a function of the distance from the specimen surface was obtained and the carbon diffusion distance was estimated at a given temperature for a given heating time.

2. Experimental procedures

2.1. Specimen preparation

Rectangular specimens of 3 mm wide and 20 mm long were cut out from a commercial powder-metallurgy pure molybdenum sheet of 1 mm thickness. All the specimen surfaces were polished using emery papers of #180–600. Then the specimens were subjected to recrystallization treatment at 1773 K for 3.6 ks in a vacuum of 10^{-4} Pa. Average grain size after recrystallization was about 25 μm.

Carbon addition was carried out with the specimens being immersed in a graphite-filled Ta-container and heated at 1273, 1323 or 1373 K. Heating time changed from 1.2 to 10.8 ks. Three specimens were prepared for each condition. Carbon content in the specimen was analyzed by HORIBA EMIA-810. The specimen was ultrasonically washed in acetone, dried using dryer and then cut into small pieces. Fig. 1 shows the change of carbon content as a function of the heating time. The data point in the figure is just an average value of the 1-mm thickness sheet, though carbon concentration gradient might exist towards the sheet thickness of the specimen. Carbon content before carbon addition was as low as 14 mass ppm. The content increased almost linearly and gradually with the increase of heating time. In addition, the content tended to increase with the increase of temperature.

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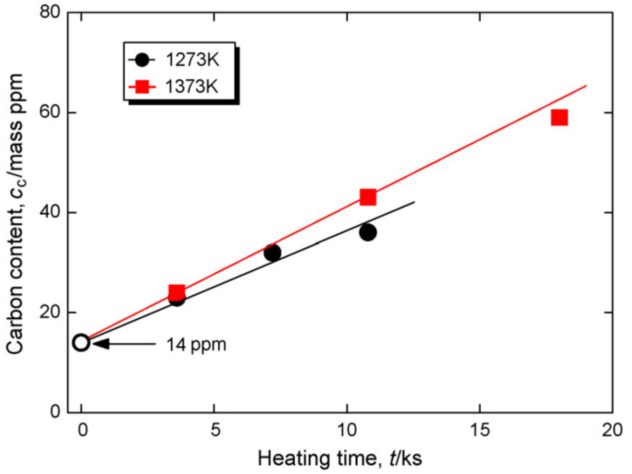

Fig. 1. Change of carbon content as a function of the heating time.

All the specimens after carbon addition were fractured in a brittle manner at liquid nitrogen temperature.

2.2. Fracture surface observation

Fracture surface was examined by HITACHI SEM S-3000H (accelerating voltage: 25 kV). We took photographs from three different sites for each fracture surface. A series of three photographs (magnification of 400) cover whole fracture surface from the surface to the center of the specimen (total distance is about 500 μm). Fracture surface observation demonstrates us the change of fracture mode, an intergranular-type or a transgranular-type or a mixed-type. In this study, a parameter, PIF-value, represents the fracture mode. The PIF-value is defined as the area ratio of the intergranular fracture surface to the total fracture surface. Therefore a high PIF-value suggests that grain boundaries are very weak. For example, the specimen before carbon addition demonstrates a typical intergranular-type fracture mode and the PIF-value is as high as 78% regardless of the distance from the specimen surface. In contrast, the specimen after carbon addition under an appropriate condition demonstrates a typical transgranular-type fracture mode and the PIF-value is as low as 8% regardless of the distance from the specimen surface.

Change of fracture mode as a function of the distance from the specimen surface is obtained as follows. Fig. 2 shows schematic fracture surface observation that covers the whole area from the surface to the center of the specimen. The specimen is after carbon addition at a relatively low temperature for a relatively short heating time. Only the regions near the specimen surface primarily demonstrate a transgranular-type fracture mode and hence the PIF-value is low (about 8%). On the other hand, the regions near the center of the specimen still demonstrate an intergranular-type fracture mode and hence the PIF-value is as high as the value for the specimen before carbon addition (about 78%).

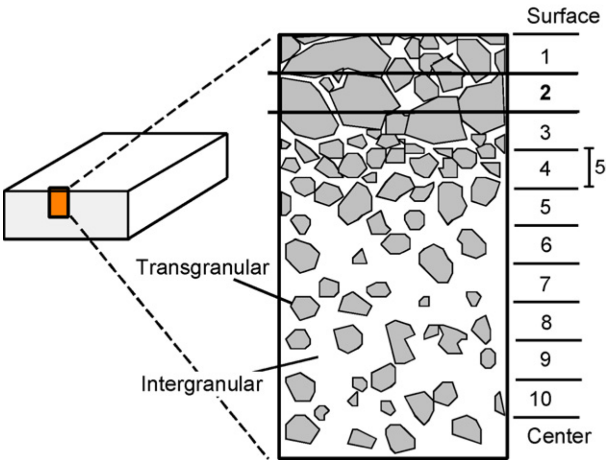

Fig. 2. Schematic fracture surface observation for the specimen after carbon addition.

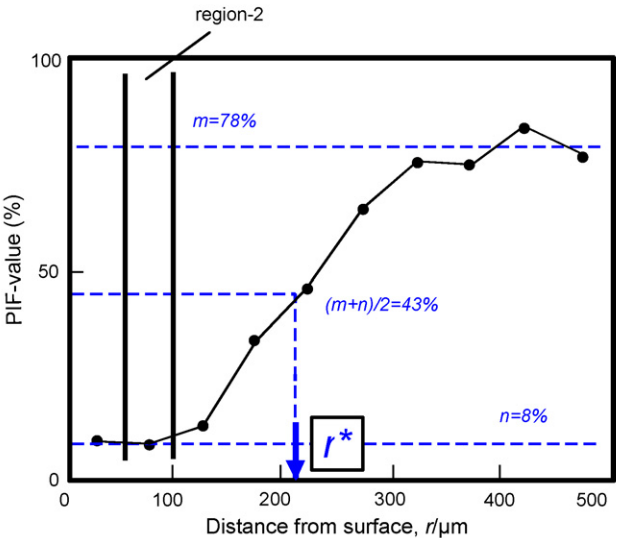

Fig. 3. Schematic change of PIF-value as a function of the distance from the specimen surface and estimation of carbon diffusion distance.

2.3. Estimation of carbon diffusion distance

Change of PIF-value as a function of the distance from the specimen surface is obtainable from Fig. 2. The whole area from the surface to the center of the specimen was divided into ten regions: region-1, region-2, . . ., region-10. Width of each region is about 50 μm. Then the PIF-value was calculated for each region. Fig. 3 shows schematic change of PIF-value as a function of the distance from the specimen surface.

On an assumption that small addition of carbon changes drastically the fracture mode, carbon diffusion distance is estimated as follows. The value, $m = 78\%$, in Fig. 3 is the PIF-value of the specimen before carbon addition in which the grain boundaries are very weak. The value, $n = 8\%$, on the other hand, is the PIF-value of the specimen after carbon addition in which the grain boundaries are sufficiently strengthened. Strictly saying, carbon diffusion distance is the distance at which the fracture mode just changes from a typical intergranular-type to a mixed-type. However, it is difficult to determine such a distance, since the PIF-value as a function of the distance from the surface displays a so-called "S-shape" curve. In our previous study [1], thereby, we defined the carbon diffusion distance as the distance at which the PIF-value is equal to 80% of m (0.80m). In this study, we defined the carbon diffusion distance as the distance at which the PIF-value is equal to a half value of m and n ($(m + n)/2 = 43\%$) considering the followings. First, the value, m (or n) differs from one material to other material. For example, m is 78% in this study, 88% [1] for commercial pure molybdenum, 72% [10] for Mo–1.0%Ti alloy and 96% [11] for sintered molybdenum before carbon addition. On the other hand, n is 8% in this study, 20% [1] for commercial pure molybdenum, 10% [10] for Mo–1.0%Ti alloy and 35% [11] for sintered molybdenum after carbon addition. Secondly, scattering in the data is large in some case. Using the above-mentioned definition, the carbon diffusion distance is estimated as 200 μm in case of Fig. 3.

3. Results

3.1. Change of PIF-value as a function of distance

Fig. 4 (1273 K), Fig. 5 (1323 K) and Fig. 6 (1373 K) show the changes of PIF-value as a function of the distance from the specimen surface after carbon addition. Each data point in the figure is an average of 6–9 values.

Under a condition of low temperature and/or short heating time, only the regions near the surface demonstrated low PIF-values, whilst the other regions still demonstrated PIF-values as high as that of the specimen before carbon addition. As the heating time increased, the transition region showing a mixed-type fracture mode progressed towards the center of the specimen. It is noted that such progress of the transition region became more rapid as the temperature increased. Finally the specimen after carbon addition at 1373 K for 7.2 ks demonstrated low PIF-values of less than 10% regardless of the distance from the surface as shown in Fig. 6.

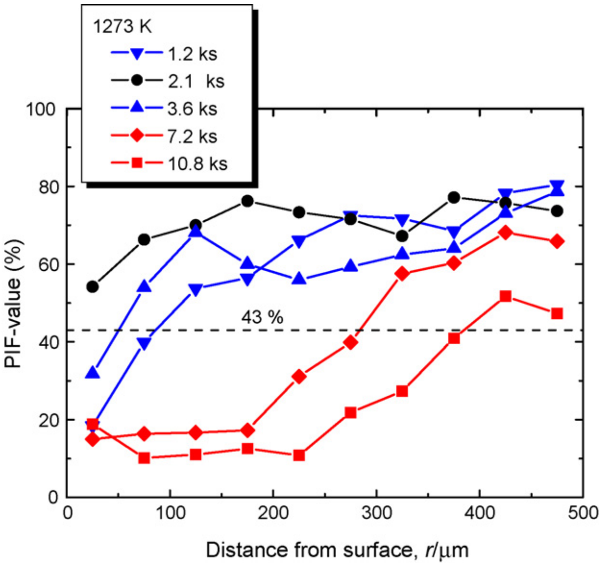

Fig. 4. Change of PIF-value as a function of the distance from the specimen surface after carbon addition at 1273 K.

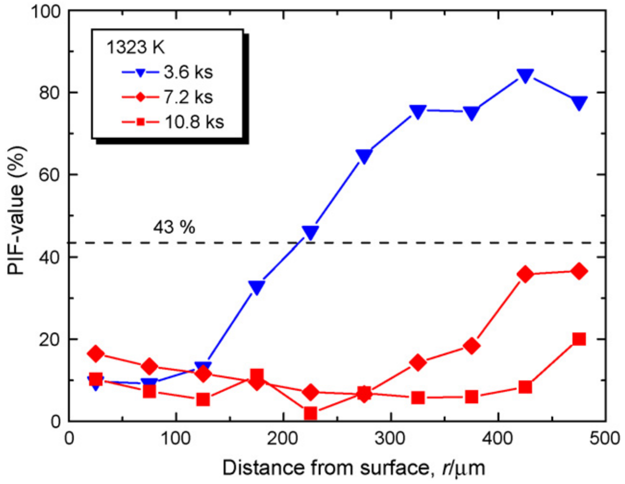

Fig. 5. Change of PIF-value as a function of the distance from the specimen surface after carbon addition at 1323 K.

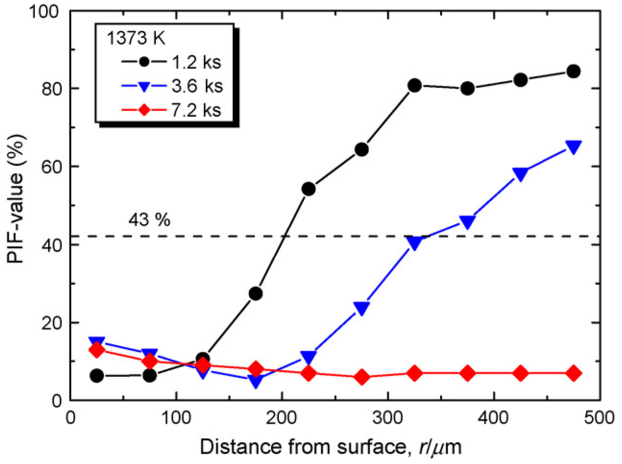

Fig. 6. Change of PIF-value as a function of the distance from the specimen surface after carbon addition at 1373 K.

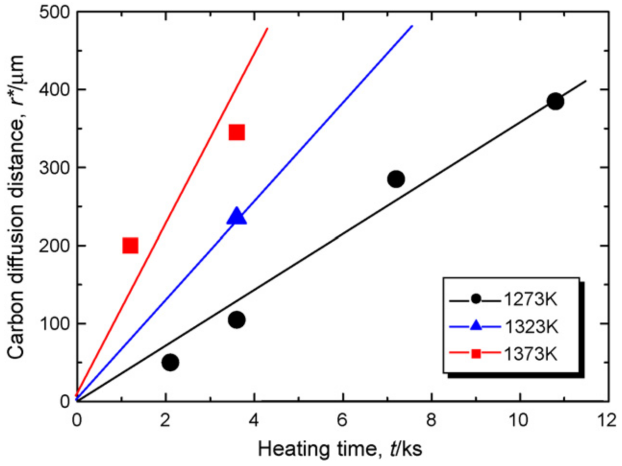

Fig. 7. Plots of the carbon diffusion distance and the heating time.

3.2. Change of carbon diffusion distance with heating time

According to the procedures as mentioned in Section 2.3, the carbon diffusion distance was estimated. In Fig. 7, the carbon diffusion distance is plotted as a function of the heating time in the specimens after carbon addition at a different temperature.

First of all, it is obvious that the carbon diffusion distance increased approximately linearly with the increase of heating time, though available data were quite limited at 1323 and 1373 K. In addition, slope of the straight line tended to increase significantly with the increase of temperature. From these results, the carbon diffusion distance, r^* is given by the following equation.

$$r^* = Kt \tag{1}$$

K is a slope of the straight line and a measure of carbon diffusion rate. K depends on the temperature, T and is given by the following equation.

$$K = K_0 \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

K_0 is a constant and R is a gas constant. The parameter, Q is the activation energy.

3.3. Activation energy

From Eq. (2), plots of the common logarithm of K and the reciprocal of T conduct the activation energy. Fig. 8 shows the Arrhenius plots of K and T.

The data points approximately drop on a straight line, though numbers of available data are limited. From the slope of the straight line, we derived the activation energy of 155 kJ/mol and the constant, $K_0 = 9 \times 10^{-4}$ mm/s. The activation energy obtained by Rudman [8] is 172 kJ/mol in the temperature range between 1783 and 2243 K, whilst the value obtained by Kunze and Reichelt [9] is 164 kJ/mol in the temperature range between 1618 and 2033 K. The value obtained in our previous study [1] is 182 kJ/mol. Previous data are all obtained assuming that a parabolic rule stands up between the carbon diffusion distance and the heating time. However, the activation energy obtained in this study is not comparable with those obtained by Rudman [8] or Kunze and Reichelt [9], since the carbon diffusion mechanism in our case is not made clear at the present.

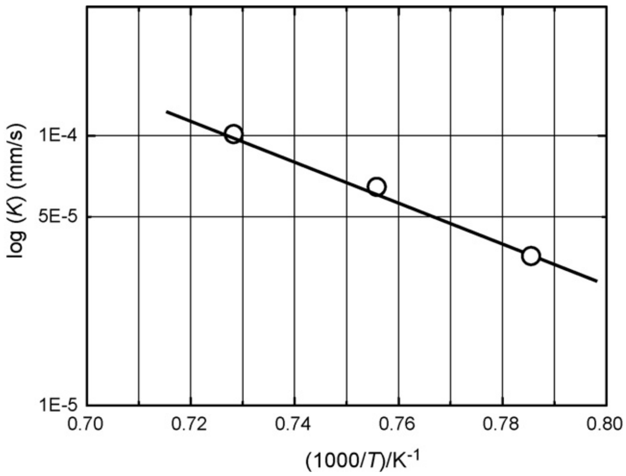

Fig. 8. Arrhenius plots of the slope, *K* and the temperature, *T*.

4. Discussion

First, we have to discuss the utilization of limited numbers of data and the reliability of the conclusion that the carbon diffusion distance increases linearly with the heating time. As shown in Fig. 7, the data points at 1323 or 1373 K are quite limited. This result is attributed to the sensitiveness of the carbon diffusion distance to both the temperature and the time. As shown in Figs. 4–6, the fracture mode changes drastically with the increase of the temperature and the time. Empirically, however, three or four data points are obtainable at a temperature of 1273 K. In Fig. 9, we plot the carbon diffusion distance at 1273 K as a function of the time which were obtained not only in this study but also in our recent studies [11,12]. In sintered molybdenum containing a large number of micro-pores, the carbon diffusion distance increased approximately linearly with the time, though the slope of the straight line was slightly smaller [11]. In pure molybdenum which was carbon added using graphite powders of smaller size than those in this study, the carbon diffusion distance again increased approximately linearly with the time, though the slope of the straight line was slightly larger [12]. In all cases, straight lines are approximately obtainable between the carbon diffusion distance and the time. Therefore, we concluded that the carbon diffusion distance increases linearly with the time from 2.1 to 10.8 ks at such a low temperature of 1273 K. In addition, we concluded that the data points obtained at a temperature near 1273 K should demonstrate a similar relationship to that at 1273 K, and hence drew straight lines even if the data points are limited.

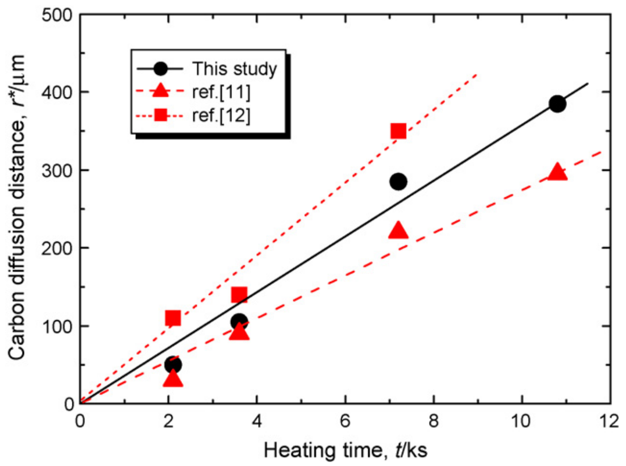

Fig. 9. Plots of the carbon diffusion distance as a function of the heating time at 1273 K in this study and in our recent studies.

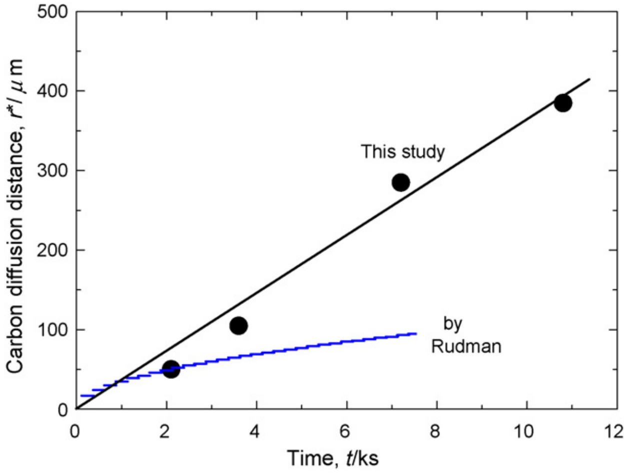

Fig. 10. Comparison of the carbon diffusion distance at 1273 K estimated in this study with that simulated using data of Rudman.

Secondly, we discuss the difference between the result obtained in this study and the results obtained by Rudman [8] or Kunze and Reichelt [9]. The present study suggests that the carbon diffusion mechanism at a relatively low temperature is different from that at a high temperature. Rudman (1783–2243 K) [8] or Kunze and Reichelt (1618–2033 K) [9] supposed that the carbon diffusion distance increases parabolically with the heating time as given by the following equations.

$$(r^*)^2 = 4Dt \tag{3}$$

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \tag{4}$$

D is the diffusivity and is a function of the temperature. D_0 is a constant and *Q* is activation energy. At a high temperature, carbides such as Mo_2C are easy to be formed at the specimen surface. In addition, carbon atoms are likely to diffuse in the bulk metal. In this study, no carbides and no carbide layer were recognized at the specimen surface. At a relatively low temperature, therefore, carbon atoms are likely to be supplied directly from the graphite powders contacting the bulk metal, and that, to diffuse mostly along grain boundary, not in the bulk. It is well known that the activation energy for the grain boundary diffusion is much smaller than the energy for the bulk diffusion. The activation energy calculated in this study is 155 kJ/mol. However, this value cannot be compared with the values by Rudman [8] or Kunze and Reichelt [9], since the carbon diffusion mechanism at a relatively low temperature is still not made clear. In Fig. 10, we compare the carbon diffusion distance at 1273 K estimated in this study with that simulated using data of Rudman [8]. We used $D_0 = 3.4$ and $Q = 172$ kJ/mol to calculate the carbon diffusion distance by Eqs. (3) and (4). In case of shorter heating time (2.1 ks or shorter), difference in the carbon diffusion distance between this study and Rudman [8] is not significant. In case of longer heating time (7.2 ks or longer), on the other hand, difference in the carbon diffusion distance is significantly large.

Thirdly, we discuss the definition to estimate the carbon diffusion distance. In this study, we estimated the carbon diffusion distance as the distance at which the PIF-value is equal to the half value of *m* and *n*. In Fig. 11, we compared the carbon diffusion distance estimated in this study with that estimated using the definition in our previous study [1]. The carbon diffusion distance estimated in this study was generally shorter than that estimated in our previous study. However, the carbon diffusion distance

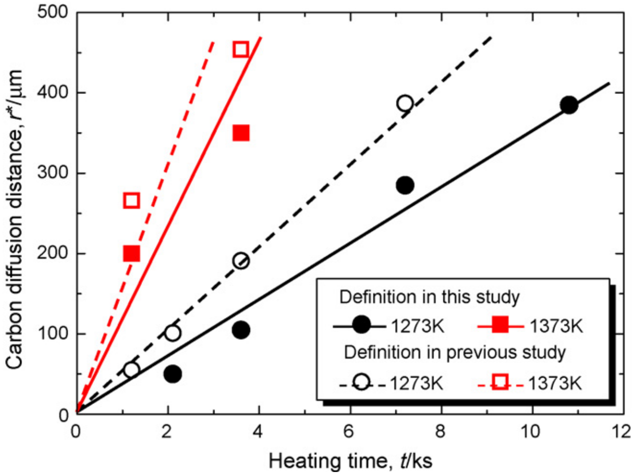

Fig. 11. Comparison of the carbon diffusion distance estimated using a definition in this study with that estimated using a definition in our previous study.

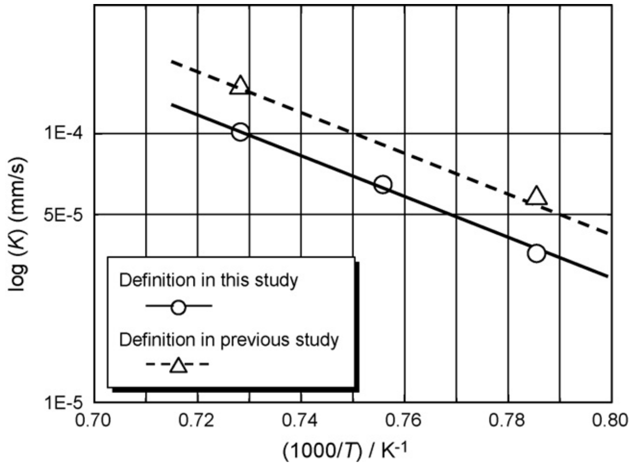

Fig. 12. Comparison of the Arrhenius plots of K and T obtained using a definition in this study with those obtained using a definition in our previous study.

increased approximately linearly with the heating time regardless of the definition. In Fig. 12, we compared the Arrhenius plots of K and T obtained in this study with those obtained using the definition in our previous study. It is obvious that the slopes of two straight lines are almost equivalent, though the constants, K_0 are different. From these results, it is concluded that difference in the definition to estimate the carbon diffusion distance does not essentially influence the conclusions obtained in this study.

5. Summary of results

Results are summarized as follows.

(1) Carbon diffusion distance at a relatively low temperature (1273–1373 K) increases approximately linearly with the increase of heating time from 1.2 to 10.8 ks. This result does not agree with that obtained at much higher temperatures. At a high temperature, a parabolic relationship stands up between the carbon diffusion distance and the time.

(2) Activation energy is calculated (155 kJ/mol) from the Arrhenius plots of the slope of the straight line and the heating temperature.

(3) Carbon diffusion distance estimated in this study is significantly larger than that simulated using the data of Rudman particularly at a longer heating time.

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